PROGRESS
IN PETROLEUM
TECHNOLOGY

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Symposium on Twenty-Five Years of Progress
in Petroleum Technology held by the Division
of Petroleum Chemistry of the American
Chemical Society at the Diamond Jubilee meeting
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chairman, Robert E. Wilson; honorary co-chairmen,
Vladimir N. Ipatieff and William M. Burton

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Scope of the Symposium

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The past twenty-five years roughly match the development of the Division of Petroleum Chemistry, which was formed in 1921. In view of the fine historical summary recently prepared by Egloff and Alexander, there is no need to go into that story in any detail.

From its initial 30 members the division has grown to its present size of more than 2000, and the number of technical men engaged in petroleum research in the United States has increased to more than 10,000. Incidentally, it is hard to understand why any ambitious petroleum chemist fails to belong to the Division of Petroleum Chemistry. The policy of sending out complete preprints gives members a big advantage over other petroleum chemists. There is no substitute for receiving a personal set of these preprints, twice each year.

Oil industry research expenditures are now well over $100,000,000 a year—about 25% of the total amount spent on industrial research in the United States, and about five times the amount spent on petroleum research in 1940. Because of inflation, this fivefold increase in expenditures unfortunately does not mean a fivefold increase in research. However, the research trend is certainly still upward, and it will undoubtedly continue—unless there should arise some unexpected discouraging factor, such as adverse government action toward research expenditures, or dismemberment of the large companies responsible for the principal research effort.

Two Principal Developments

The past quarter-century has seen two outstanding developments in petroleum technology. The first is the great increase in technical knowledge that has arisen from so much research. The petroleum scientists of 25 years ago made good use of the tools they had at hand, but they simply did not possess the extensive thermodynamic information and other fundamental knowledge now available. It was only after physical chemists had compiled data on the behavior of naturally occurring hydrocarbon mixtures—as well as on pure hydrocarbons—that chemical engineers could develop formulas for predicting the performance of fractionation towers and other equipment. Knowledge of the detailed composition of petroleum, so conspicuous by its absence 25 years ago, has also been supplied, mainly by the API cooperative research projects.

Part of the general increase in technology arose from improved techniques in pilot plant operation and interpretation. Studies with small quantities of material provided reliable data for the design of large scale units which could be counted upon to operate successfully. This pilot plant work was greatly facilitated by the parallel development of modern instruments and automatic controls.

The second notable achievement of the past 25 years has been the catalytic revolution. Thermal cracking, the great achievement of the previous 25 years, was a notable advance, but chemists were not exactly surprised to find that hydrocarbons will undergo pyrolysis. Conversions depending on catalysts were less foreseeable. Catalytic cracking has been the most important of these new processes, but such synthetic processes as polymerization, alkylation, isomerization, and hydroforming also represent a series of great new forward steps—particularly as the operating conditions in some instances were severe. Fortunately, engineers had learned to handle, with safety, temperatures and pressures formerly considered too high to be feasible in plant operation.

A rough review indicates that about 60% of the gasoline coming from American refineries consists of new molecules, made in the refinery and not present in the crude oil

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taken in. Outstanding examples are alkylate, polymer gasoline, and cracked gasoline. In the case of alkylate alone, production during World War II reached a level above 15 billion pounds a year, or more than twelve times the present production of ethyl alcohol, both natural and synthetic.

The tremendous volume of such synthetic hydrocarbons used for fuels and lubricants became possible largely as a result of the work of men in attendance at this symposium. These new products represent increased value to the customer per dollar spent, and they also represent increased efficiency in the use of the country's national resources.

The expansion in technology has in turn encouraged research scientists to broaden the scope of their research. Notable advances have been made in such special fields as plastics, polymers, rubber, detergents, and many other synthetic products from petroleum. A number of these items represent broad technological achievements in their own right. Research has also made major contributions to the discovery, production, and transportation of petroleum.

Competitive and Cooperative Work

In the course of the past 25 years the pattern of increasing competition in the petroleum industry has stimulated research. At the same time, through wise use of the cross-licensing arrangements possible under the patent laws, immediate industry-wide use of new developments has become possible. Because licenses can be obtained at reasonable rates, even the small refiners have been able to use the latest methods without prohibitive research expense. In addition, wasteful duplication of research and development has been avoided, and the most recent knowledge has become promptly available to serve as the foundation on which further developments could be built.

Cooperative research has also become increasingly important—notably through the establishment, just 25 years ago, of the API program of fundamental research. Much joint work has also been done with other industries. The automobile industry has joined in various important studies: on the effect of octane number, vapor pressure, and sulfur in fuels, and on the increasingly important subject of additive-containing lubricating oils. The airplane industry and the airplane users—particularly the Armed Forces—have likewise cooperated, and have profited greatly by the results.

Other Fields

Several fields of petroleum research are not covered in this symposium. The most important are exploration and production. Another is research on devices that evaluate oil products and indicate probable performance. Such devices have become important tools in product improvement.

A special field not covered in the symposium is that of insecticides, fungicides, and weed killers. Petroleum products are used to an increasing extent as carriers or principal toxic agents, or both. Modern oil research includes work in greenhouses, gardens, and orchards, as well as with automobiles, locomotives, and industrial machines.

It is safe to say that the next 25 years will see a still greater broadening of the scope of petroleum research, both competitive and cooperative, provided we are not greatly hindered in one way or another by "the dead hand of government."

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The Mechanism of Catalytic Cracking

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The catalytic cracking of four major classes of hydrocarbons is surveyed in terms of gas composition to provide a basic pattern of mode of decomposition. This pattern is correlated with the acid-catalyzed low temperature reverse reactions of olefin polymerization and aromatic alkylation. The Whitmore carbonium ion mechanism is introduced and supported by thermochemical data, and is then applied to provide a common basis for the primary and secondary reactions encountered in catalytic cracking and for acid-catalyzed polymerization and alkylation reactions. Experimental work on the acidity of the cracking catalyst and the nature of carbonium ions is cited. The formation of liquid products in catalytic cracking is reviewed briefly and the properties of the gasoline are correlated with the over-all reaction mechanics.

In little more than half of the 25 years covered by this symposium, catalytic cracking has been developed from its first acceptance to a major industrial process. It has served to increase the amount and octane rating of gasoline and the amounts of valuable C_3 and C_4 gas components obtainable from petroleum feed stocks over those from thermal cracking alone. It is therefore of interest to seek an explanation of the nature of the products obtained in catalytic cracking in terms of the hydrocarbon and catalyst chemistry which has been developed within the past 25 years.

The first object of this paper is to set forth the basic product distributions obtained in the catalytic cracking of the major classes of pure hydrocarbons, which will serve to demonstrate the action of the cracking catalyst. The second object is to assemble these data into patterns having common denominators, to arrive at a consistent mechanism of hydrocarbon cracking which can be specifically related to the chemical nature of the cracking catalyst. The third is to review the experimental data available on the structural energy relationships within and among hydrocarbons to provide real support for the proposed mechanism of catalytic cracking. The proposed mechanism is then utilized to explain a number of important secondary reactions encountered in catalytic cracking operations and to characterize the nature of catalytic gasoline to which both primary and secondary reactions contribute.

The study of the catalytic cracking of pure hydrocarbons as a key to the interpretation of the catalytic cracking of petroleum fractions is predicated on the belief that most of the hydrocarbons present in petroleum can be allocated to relatively few simple classes. This belief is supported particularly by the accumulated results of API Project 6, originally titled "The Separation, Identification, and Determination of the Constituents of Petroleum" (now retitled "Analysis, Purification, and Properties of Hydrocarbons"). For the sake of consistency of experimental conditions, the data reported are those of the

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Shell Development Co. (*5–7*). Full acknowledgment of the work of others reported extensively in the literature is made thankfully, as it was of much assistance.

Accordingly, work has been done on series of *n*-paraffins, isoparaffins, naphthenes, aromatics, and naphthene-aromatics which have been chosen as representative of the major components of petroleum. In addition, olefins, cyclo-olefins, and aromatic olefins have been studied as a means of depicting the important secondary reactions of the copious amounts of unsaturates produced in the majority of catalytic cracking reactions. A silica-zirconia-alumina catalyst was used principally; it resembles closely in cracking properties typical commercial synthetic silica-alumina catalysts.

The cracking of four important classes of petroleum hydrocarbons is surveyed, using the gaseous hydrocarbon products as a basic index of the nature of the cracking process. Table I gives the complete gas analyses. The uniformity of cracking of *n*-paraffins at 500° C. may be seen from the simplified mole percentage gas compositions shown below by carbon number on a hydrogen-free basis.

n-Paraffin	C_1	C_2	C_3	C_4
C_7	5	16	42	37
C_{12}	9	9	42	40
C_{16}	2	6	45	47
C_{24}	5	5	40	50

These gaseous products comprise from 41 to 86 weight % of the total feed reacted. Their striking over-all consistency indicates that a uniform mode of cracking must prevail.

A very similar pattern is given by the cracking of *n*-olefins, which are shown next as mole percentage gas composition. The gaseous product is now 12 to 35 weight % of the total feed reacted for C_{16} and C_8, respectively, and is low because of the low cracking temperature, 400° C. Although rarely present in petroleum, olefins are important primary products of cracking.

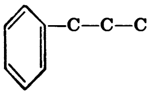
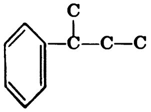
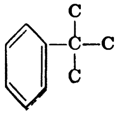
n-Olefin	C_1	C_2	C_3	C_4
C_8	1	2	30	67
C_{16}	5	2	29	64

At 500° C., the gaseous products from cetene and cetane become indistinguishable and the former represents 40 weight % of the feed reacted (see Table II).

The cracking at 500° C. of both monocyclic and bicyclic cyclohexane-type naphthenes, which are important components of petroleum, again displays uniformity in gas compositions, approaching that of the *n*-paraffins. The gaseous products shown here as mole percentage amount to 26 to 52 weight % of the total feed reacted.

Naphthene	C_1	C_2	C_3	C_4
C_9	8	5	35	52
C_{11}	10	7	36	47
C_{12}	4	11	37	48
C_{16}	9	8	36	47

In the case of aromatics, an entirely different gas composition pattern is found. On selecting some of the outstanding examples of this behavior among the alkylbenzenes (*6*), the striking fact emerges that the predominant gas component as mole percentage in each case corresponds exactly in structure to the original alkyl group on the benzene ring.

Aromatic	C_1	C_2	C_3	*n*-C_4	Iso-C_4
	4	4	$\underline{88}$	2	2
	..		7	$\underline{80}$	12
	..				$\underline{86}$

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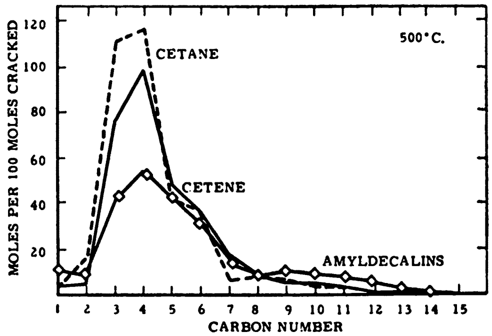

Figure 1. Catalytic Cracking Product Distribution

In all these examples, the total benzene plus the corresponding C_3 or total C_4 gas components amounts to 89% of the feed reacted.

Basic Cracking Patterns

From these simple gas products, which correspond to a very large portion of the reacted feed stock, two basic cracking patterns are postulated; the first is applicable to aliphatics and alicyclics (I) (thus including paraffins, olefins, and naphthenes), the second to substituted aromatics (II). These two basic patterns are best illustrated by Figures 1 and 2, which show the molar distribution of the principal cracked products according to the number of carbon atoms in the fragments, per 100 moles of feed stock cracked, for selected representatives of the four major hydrocarbon classes, all at 500° C. (see Table II for experimental conditions and product analyses).

Table I. Comparative Gas Analyses in Catalytic Cracking

(Mole %; 1 atmosphere; silica-zirconia-alumina catalyst, Universal Oil Products Co. Type B; 1-hour process period)

	Paraffins				Olefins	
	n-Heptane[a]	*n*-Dodecane	*n*-Hexadecane (cetane)	Parowax[b] (ca. *n*-tetracosane)	*n*-Octenes	*n*-Hexadecene (cetene)
	500° C., 13.2 to 14.2 moles per liter per hour				400° C., about 7 moles per liter per hour	
H_2	6.5	6.5	4.9	6.1	1.7	2.2
CH_4	4.3	8.8	1.5	4.9	0.9	4.7
C_2H_4	8.3	5.1	3.4	2.3	0.7	1.4
C_2H_6	6.5	3.2	2.6	2.2	1.3	1.0
C_3H_6	25.8	25.8	32.8	30.5	26.6	23.6
C_3H_8	14.2	13.7	10.3	7.3	2.4	4.9
Iso-C_4H_8	6.4	8.7	10.6	11.9	17.5	11.7
n-C_4H_8	10.6	10.4	15.8	18.4	26.5	22.7
C_4H_{10}	17.4	17.8	18.1	16.4	22.4	27.8
Run No.	C-86	C-103	C-578	C-160	C-174	C-46

	Naphthenes				Aromatics		
	Isopropylcyclohexane	Amylcyclohexanes	Triethylcyclohexanes	Amyl decalins	*n*-Propylbenzene[c]	*sec*-Butyl benzene[d]	*tert*-Butyl benzene[d]
	500° C., about 13 moles per liter per hour				400° and 500° C., 12.3 to 13.7 moles per liter per hour		
H_2	12.0	17.6	14.4	19.3	5.6	4.4	0.6
CH_4	6.9	8.2	3.0	7.3	3.5	0.0	..
C_2H_4	3.7	4.3	6.7	4.2	2.0	0.3	0.2
C_2H_6	0.9	1.7	3.0	2.1	1.7	0.3	1.1[e]
C_3H_6	19.5	19.5	20.7	22.1	76.2	5.4	3.5
C_3H_8	11.1	9.9	10.7	7.2	7.4	1.1	...
Iso-C_4H_8	4.8	4.4	3.8	4.8	1.0	73.4	7.3
n-C_4H_8	8.0	8.3	8.4	9.6	1.0	3.6	76.7
C_4H_{10}	33.1	26.1	29.3	23.4	1.6[f]	11.5[f]	10.6[g]
Run No.	C-146	C-156	C-145	C-144	C-150	C-542	C-540

[a] 550° C.
[b] At 6.8 moles per liter per hour.
[c] 500° C.
[d] 400° C.
[e] C_1–C_3 saturates.
[f] Assume iso/*n* = 3.
[g] Assume iso/*n* = 7

Table II. Catalytic Cracking of Representative Hydrocarbons

(500° C., 1 atmosphere; silica-zirconia-alumina catalyst)

Feed	Cetane	Cetene	Amyl Decalins	Cumene
Process period, min.	60	15	60	60
LHSV	4.0	7.2	3.0	1.9
Moles/liter/hour	13.6	25.0	12.8	13.7
Material balance, wt. % charge, no-loss basis				
Gas	21.0	38.3	18.4	25.0
Liquid below original boiling point	17.9	56.0	51.6	54.4
Remaining liquid	60.0	3.7	28.7	16.4
Coke	1.1	2.0	1.3	4.2[a]
Moles/100 moles cracked				
C_1	4	4	11	3
C_2	16	5	9	2
C_3	112	77	42	79
C_4	116	98	55	2
C_5	43	49	43	100
C_6	38	38	32	
C_7	7	18	18	
C_8	8	9	10	.
C_9	7	7	12	..
C_{10}	4	6	10	..
C_{11}	3	4	9	..
C_{12}	1	4	8	..
C_{13}	1		3	..
C_{14}	1		2	..
C_{15}	..	2	..	..
Total	361	321	264	186
H_2	14	5	28	2
Run No.	C-578	C-1104	C-144	C-131

[a] Carbon only.

To obtain the first clue to the reaction mechanism, two hydrocarbons may be considered: (1) 1-hexadecene (cetene), representing group I, and (2) isopropylbenzene (cumene), representing group II. What common property of the catalyst will explain the cracking patterns of both, in conformity with what is known of the chemical reactions of carbon compounds?

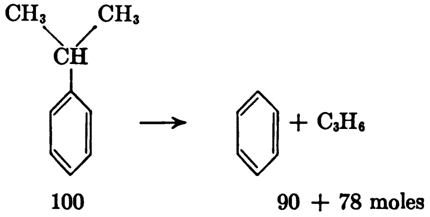

Figure 2. Catalytic Cracking of Cumene

Based on much evidence (both from the literature and these laboratories), it is predicated that the cracking reactions of cetene and cumene are directly related to the well-known low temperature liquid or vapor phase acid-catalyzed reactions of olefin polymerization and the alkylation of aromatics with olefins, respectively. The reciprocal relationship of olefin polymerization and cracking is best demonstrated by the cracking of diisobutenes to give a gaseous product containing 73 mole % isobutene and that of triisobutenes to give a gaseous product containing 81 mole % isobutene. The extension of this reciprocal relationship of polymerization and cracking to straight-chain olefins creates an apparent difficulty, because *n*-olefins polymerize to branched products. However, the same mechanistic rules which predict the structures of such polymers also govern the catalytic cracking of *n*-olefins. In the same sense, aromatic alkylation by olefins using acid catalysts and the cracking of alkyl aromatics have a corresponding reciprocal relationship. To illustrate, the cracking of cumene gave benzene and propylene, the original components, to the extent of about 86 weight % of feed cracked. It is concluded that the correlation between hydrocarbon cracking patterns and acidic catalysts (both proton and "Lewis acid" types) is sufficient to justify further exploration of their relationship.

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The acid-catalyzed reactions of olefin polymerization and aromatic alkylation by olefins have been very well explained by the carbonium ion mechanism developed by Whitmore (*21*). This mechanism provides the basis of the ensuing discussion, which is devoted to the application of such concepts (*7*, *17*) to catalytic cracking systems and to the provision of much added support in terms of recently developed structural energy relationships among hydrocarbons and new experimental evidence.

Study of the primary cracking step of the four major hydrocarbon classes leads to an important generalization, which may be seen from the following type reactions:

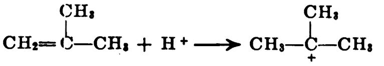
Paraffin ⟶ paraffin + olefin
Olefin ⟶ olefin + olefin
Naphthene ⟶ saturate + olefin or olefin + olefin
Aromatic ⟶ aromatic + olefin

In every case an olefin is one of the products of the primary cracking step. Now by considering each reaction in reverse, a common denominator for all the designated cracking systems can be found in the chemistry of olefins. The answer lies in the character of the olefinic double bond, which comprises the normal valence pair electrons, and in addition two extra or "pi" electrons, which endow the double bond with the ability to attract positively charged groups, especially protons. This ability is expressed quantitatively by the "proton affinity," which is shown below for propylene and isobutylene:

ΔH_{298}, Kg.-Cal./Mole

Propylene $CH_2{=}CH{-}CH_3 + H^+ \longrightarrow CH_3{-}\underset{+}{CH}{-}CH_3$ −181

Isobutylene

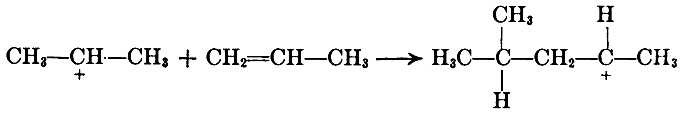


$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3 + H^+ \longrightarrow CH_3{-}\underset{+}{\overset{CH_3}{\overset{|}{C}}}{-}CH_3$

−195

These energy values are calculated from thermochemical tables (*11*) and the ionization potentials of hydrocarbons obtained by Stevenson (*15*) using mass spectrometric methods. The union of an olefin and a proton from an acid catalyst leads to the formation of a positively charged radical, called a "carbonium ion." The two shown above are *sec*-propyl and *tert*-butyl, respectively. [For addition to the other side of the double bond, ΔH_{298} = −151.5 and −146 kg.-cal. per mole, respectively. For comparison, reference is made to the older (*4*) values of Evans and Polanyi, which show differences of −7 and −21 kg.-cal. per mole between the resultant *n*- and *s*-propyl and iso- and *tert*-butyl ions, respectively, against −29.5 and −49 kg.-cal. per mole here. These energy differences control the carbonium ion isomerization reactions discussed below.]

Such an ion may in turn combine with a second olefin:



$$CH_3{-}\underset{+}{CH}{-}CH_3 + CH_2{=}CH{-}CH_3 \longrightarrow H_3C{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\underset{+}{\overset{\overset{H}{|}}{C}}{-}CH_3$$

which is the basic reaction of acid-catalyzed olefin polymerization. By release of a proton, the larger ion becomes the olefin polymer. The heats of addition of the most important carbonium ions to an olefinic double bond may be represented by the following figures, derived from ionization potential data of Stevenson (*14*, *15*) and thermochemical data (*11*) for the reactions alkyl ion (R^+) + ethylene, for two alternative cases:

$$R^+ + H_2C{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2^+ \qquad \text{(Reaction 1)}$$

$$R^+ + H_2C{=}CH_2 \longrightarrow R{-}\underset{+}{CH}{-}CH_3 \qquad \text{(Reaction 2)}$$

Ion, R^+	ΔH_{298}, Kg.-Cal. per Mole				
	CH_3^+	$C_2H_5^+$	*n*-$C_3H_7^+$	*s*-$C_3H_7^+$	*tert*-$C_4H_9^+$
Reaction 1	−58.5	−22	−21	+7	+21.5
Reaction 2	−88	−60.5	−59.5	−31.5	−17
Reaction 3	−93	−58	−57	−29	−13.5

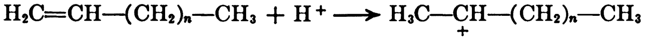
Clearly, Reaction 2 is favored over Reaction 1. In extension of Reaction 2 to higher homologs, Reaction 3 corresponds to the union of the alkyl ion, R^+, with propylene or higher *n*-alpha-olefins ($1\text{-}C_nH_{2n}$), to give the secondary ion, $R—CH_2—\underset{+}{C}H—(CH_2)_{n-3}—CH_3$, with the approximate energy values listed above.

These heats of reaction also apply to the reverse reactions, which represent the cracking of carbonium ions. It is evident that on an energy basis it is much more difficult to obtain methyl or ethyl ions as fragments than to obtain *s*-propyl or *tert*-butyl ions. Furthermore, the release of *s*-propyl ion from an olefin is favored over that of *n*-propyl by about 28 kg.-cal. per mole and the release of *tert*-butyl ion over that of *n*-butyl to an even greater degree—45 kg.-cal. per mole (estimated values, *14*). These structural energy relationships provide the basis for the lack of C_1 and C_2 and the predominance of C_3 and C_4 in the gaseous products of catalytic cracking.

All values derived from mass spectroscopic measurements of ionization potentials are indeed considered to be significant measures of the energy relationships among the ionic reaction intermediates. However, further qualifications are necessary before these values may be applied to the calculation of rates of reaction in a specific catalytic system. These qualifications are yet to be developed.

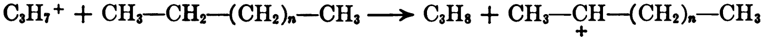
Formation and Reaction of the Carbonium Ion Intermediate

To complete this picture, it is necessary to show how the carbonium ion intermediate is formed in the catalytic cracking of hydrocarbons. For olefins, it is the reaction of proton addition:

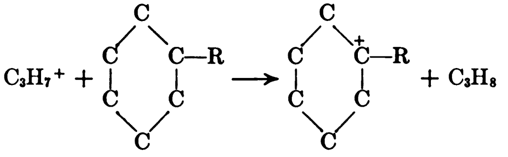


$$H_2C{=}CH—(CH_2)_n—CH_3 + H^+ \longrightarrow H_3C—\underset{+}{C}H—(CH_2)_n—CH_3$$

For paraffins and naphthenes, the important reaction of hydride ion exchange (*2*) is postulated, which is in turn initiated by carbonium ions derived from small amounts of thermally produced olefins in the cracking system.

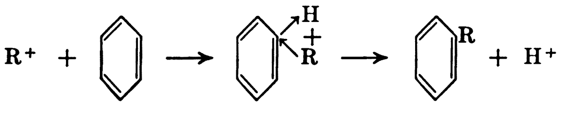


$$C_3H_7^+ + CH_3—CH_2—(CH_2)_n—CH_3 \longrightarrow C_3H_8 + CH_3—\underset{+}{C}H—(CH_2)_n—CH_3$$



Cracking then proceeds by the reverse of olefin polymerization, ultimately producing relatively noncrackable C_3, C_4, and C_5 carbonium ions from the larger carbonium ion intermediates. These small ions revert to olefins by loss of a proton, which is the reverse of the proton addition reactions illustrated previously, or become small paraffins by the hydride ion exchange reaction. The factors governing the size of the accompanying olefinic fragment are discussed later.

Aromatics are in a sense unique in their catalytic cracking reactions. The aromatic ring contains the equivalent of six double bond or pi electrons, which are, however, mutually stabilized by strong resonance energy. We may postulate an association between a carbonium ion and these electrons in a generalized sense:



in which the forward reaction represents the alkylation of an aromatic and the reverse represents the cracking of an aromatic over an acid catalyst. The energies of combination of alkyl carbonium ions and aromatics are not known. Based on experimental results and by analogy with the reaction of carbonium ion and olefin, the same or similar relative energy differences appear to govern the alkylation and cracking of aromatics.

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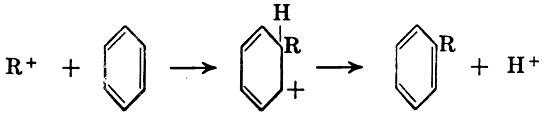
Thus, the ease of cracking alkyl aromatics increases in the order methyl, ethyl, isopropyl, and *tert*-butylbenzene (*6*). This is in exact agreement with the decreasing energies of combination of the corresponding carbonium ions with the ethylenic double bond in ethylene or propylene. Confirmatory evidence for this mechanism has been obtained by Roberts and Good by examining the cracking of alkyl aromatics in which the electron density at the alkyl-aryl bond was changed in a specific manner (*13*).

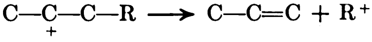
As portrayed above, no aromatic carbonium ion is formed as such. Rather, one positive group is expelled as the other one enters. However, other schemes have been suggested, such as that shown below (*12, 17*), as well as more complicated ones which involve several resonance structures.



In any of these cases, an analogy of the initiatory mechanism to that encountered in olefin cracking is clear; thus, association with a proton, rather than hydride ion removal (as required for paraffins and naphthenes), normally constitutes the first step in the cracking of both aromatics and olefins.

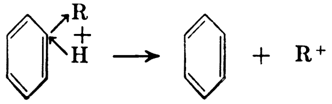
In summary, the two basic types of reaction intermediates and their products are:

For paraffins, olefins, and naphthenes:



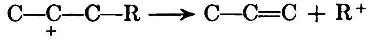
$$\mathrm{C{-}\underset{+}{C}{-}C{-}R \longrightarrow C{-}C{=}C + R^{+}}$$

For aromatics:



In each case, the resultant carbonium ion, R^+, if large, will tend to recrack. In general, the final ion may separate into an olefin and a proton, or especially in the cracking of saturates, may remove a hydride ion from a neutral molecule to form a small paraffin and a new carbonium ion. Therefore, two mechanisms are seen for the propagation of catalytic cracking: (1) proton transfer, wherein a proton is returned to the catalyst or donated to another molecule to regenerate the cycle; and (2) hydride ion exchange, wherein a new carbonium ion is formed by release of a hydride ion to an existing carbonium ion.

All group I hydrocarbons (paraffins, olefins, and naphthenes) crack to give an olefin and a carbonium ion by the generalized mechanism:



$$\mathrm{C{-}\underset{+}{C}{-}C{-}R \longrightarrow C{-}C{=}C + R^{+}}$$

It is noteworthy that the charged carbon atom of the intermediate becomes part of the resultant olefin. The extremely important isomerization reactions of carbonium ions determine the position of the charged atom and therefore both the size and isomeric form of the olefinic fragment in the primary cracking step (see 7, p. 2580, for more detailed explanation). These isomerization reactions are governed by the same energy relationships which enter into the proton-olefin and carbonium ion-olefin combination energies shown above. Thus, whenever possible, primary carbonium ions will rearrange to secondary ions prior to cracking, so that the smallest olefin produced by the simplest possible type of cracking will be propylene, as shown in the example above. Other isomeric, secondary ions will yield larger olefins. If rearrangement to tertiary ions takes place prior to cracking, the smallest olefin will then be isobutylene, by the same principle. The designated mode of cracking at the carbon-carbon bond once removed from the charged carbon atom is the simplest possible mechanism; additionally, the ionic partner,

R^+, may rearrange to a secondary or tertiary ion during the cracking of the "activated complex." In reverse, these same rules successfully predict that branched-chain olefin polymers will be obtained from either straight-chain or branched monomers. With little modification, the structures of paraffin-olefin alkylates from acid catalysts may be predicted in the majority of cases.

The preferential release of C_3 and C_4 as the smallest fragments is a relative matter; ethylene, ethane, and methane can be produced under more drastic experimental conditions, and are produced in small amounts in ordinary catalytic cracking. The conventional process operates under conditions which maximize the desired type of splitting to the more useful gaseous products. To demonstrate the application of theory to practice, the predicted and experimental curves for the cracking of cetane (*7*) are shown in Figure 3.

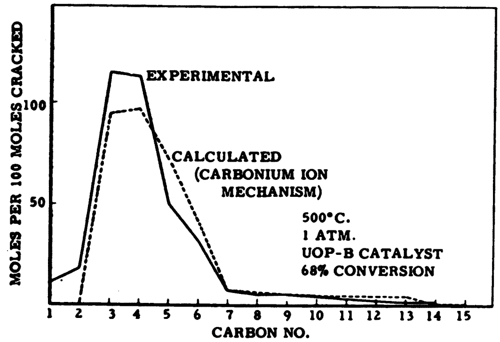


Figure 3. Catalytic Cracking of Cetane

There remains no doubt that the ionic reaction pattern of hydrocarbons is firmly related to the presence of acid catalysts. Recent work at the Shell Development Co. (*1*) and the Houdry Process Corp. (*8*) on the acid-catalyzed hydrogen-deuterium exchange and isomerization reactions of small paraffins has brought forth strong confirmation of the mechanistic pattern already applied to catalytic cracking. Furthermore, the work of Thomas (*17*, *18*), Tamele (*16*), and Milliken, Mills, and Oblad (*9*), among others, has established the conventional cracking catalyst to be an acid catalyst, capable of acting both as a proton donor and as a strongly polar Lewis acid. The valences of silicon, aluminum, and oxygen are so distributed that additional cations, such as protons, are required for electrostatic neutrality. The physical reality of the postulated carbonium ion intermediates is then indeed a question worthy of discussion.

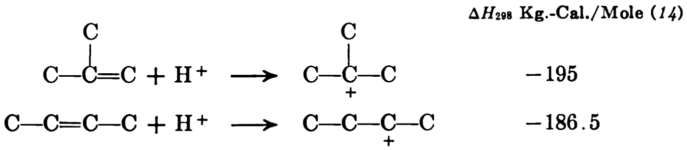
Free alkyl ions are produced under electron impact in the high vacuum of a mass spectrometer. They are the ions recorded by this instrument at the cathode as an "ion current." In the presence of an acid catalyst in a heterogeneous system containing gaseous or liquid hydrocarbons their free existence is difficult to establish, as their negative partners must be close at hand at the surface of the catalyst. At the San Antonio, Tex., Southwest Regional Meeting of the AMERICAN CHEMICAL SOCIETY, December 1950, in a Symposium on Carbonium Ions, Matsen and coworkers (*3*) presented cryoscopic evidence of the existence of carbonium ions formed from 1-octene in sulfuric acid solution. In addition, they indicated that the carbonium ion from 1-octene was detectable by characteristic maximum absorption in the ultraviolet region at 3000 to 3200 A. in acidic media such as sulfuric acid, phosphoric acid, and complexes such as aluminum chloride-*tert*-butyl chloride and boron trifluoride–*n*-propyl chloride.

The reality and the mode of existence of carbonium ions are most interesting topics for further research in the field of hydrocarbon chemistry.

Applications

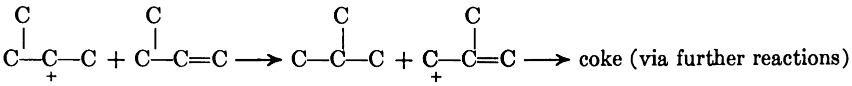
From the general principles of carbonium ion systems, a host of applications may be made to important reactions of the catalytic cracking system. Some of these follow:

Preferential Saturation of Isobutylene vs. n-Butylenes



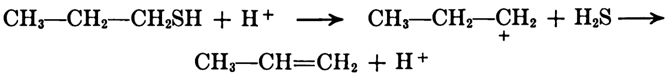
$$\begin{array}{lr} & \Delta H_{298}\text{ Kg.-Cal./Mole }(14)\\ C-\overset{\overset{C}{|}}{C}=C + H^+ \longrightarrow C-\underset{+}{\overset{\overset{C}{|}}{C}}-C & -195\\ C-C=C-C+H^+ \longrightarrow C-C-\underset{+}{C}-C & -186.5\end{array}$$

Self-Saturation of Olefins



$$C-\underset{+}{\overset{\overset{C}{|}}{C}}-C + C-\overset{\overset{C}{|}}{C}=C \longrightarrow C-\overset{\overset{C}{|}}{C}-C + \underset{+}{C}-\overset{\overset{C}{|}}{C}=C \longrightarrow \text{coke (via further reactions)}$$

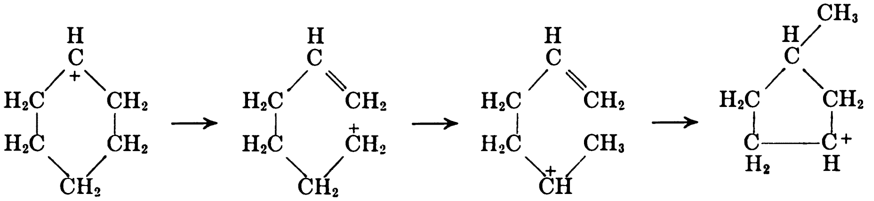
Desulfurization of Mercaptans (Thiols)



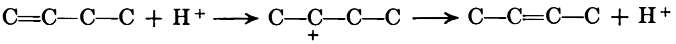
$$CH_3-CH_2-CH_2SH + H^+ \longrightarrow CH_3-CH_2-\underset{+}{CH_2} + H_2S \longrightarrow$$

$$CH_3-CH=CH_2 + H^+$$

Isomerization of Naphthenes

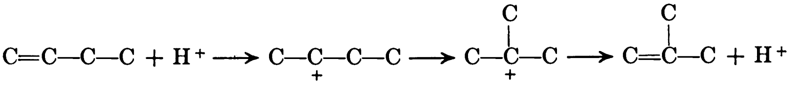


Double Bond Shift of Olefins



$$C=C-C-C + H^+ \longrightarrow C-\underset{+}{C}-C-C \longrightarrow C-C=C-C + H^+$$

Isomerization of Olefins



$$C=C-C-C+H^+ \longrightarrow C-\underset{+}{C}-C-C \longrightarrow C-\underset{+}{\overset{\overset{C}{|}}{C}}-C \longrightarrow C=\overset{\overset{C}{|}}{C}-C + H^+$$

Despite much recent progress, the energetic relationships and specific mechanistic steps involved in these reactions require more detailed experimental examination to provide explanation of all the observed facts and to enable more reliable prediction of new reactions. Likewise, the specific interaction between cracking catalyst and hydrocarbon, which also has been the subject of recent work (*8*, *9*), is a promising field for mechanistic studies.

Liquid Products

The liquid products of catalytic cracking (obtained in accordance with the described principles) have been omitted from consideration thus far, except in the case of the alkyl aromatics. To the refiner, the liquid obtained is of prime importance, both as gasoline and heavier intermediate oils.

Paraffins produce mostly C_5 and C_6 liquid product, principally olefins and paraffins. Based on feed reacted, n-C_{12} gave 49, n-C_{16} gave 44, and n-C_{24} gave 57 weight % liquid product (*20*), under conditions given in Table I.

Monocyclic naphthenes give relatively more cracked liquid than paraffins, primarily because of the partial retention of rings after the cracking of side chains and because of some dehydrogenation to aromatics. Based on feed reacted, C_{11} gave 59, C_{12} gave 68, and C_{15} gave 73 weight % liquid product (*20*), under conditions as in Table I.

Bicyclic aromatics and naphthenes are important components of cracking feed stocks. The former, after cracking in the side chains to gasoline and gas, will remain as smaller bicyclic aromatics in the cracked gas oil. The latter will be converted to naphthenes and aromatics distributed in both the gasoline and gas oil, together with aliphatic gas and gasoline components.

Olefins are usually absent from petroleum feed stocks, but they occupy a position of great importance in determining the character of the gasoline. In general, the catalytic cracking of any hydrocarbon gives at least one olefinic fragment. Such olefins are both rapidly transformed and considerably equilibrated thermodynamically by a number of the ionic reactions illustrated, including double bond shift, skeletal isomerization, polymerization, and cracking (*19*). For this reason, the gasolines produced in the catalytic cracking of a wide variety of petroleum feed stocks have notable similarities in composition, physical properties, and engine performance. This is in contrast to the gasolines obtained by thermal cracking; the absence of a catalyst capable of promoting the transformations of olefins makes many of the properties of thermal gasolines much more dependent upon the composition of the feed stock and the exact conditions of cracking.

The general relationship of the cracking of pure paraffins, naphthenes, and aromatics to that of petroleum fractions was given recently by Voge, Good, and Greensfelder (*20*) at the Third World Petroleum Congress. In general, it was demonstrated that gasoline yields are capable of reasonably close prediction from hydrocarbon-type analysis of the feed stock. The presence of aromatic nitrogen bases, which specifically poison the catalyst as shown by Mills, Boedeker, and Oblad (*10*), makes these predictions inapplicable unless the nitrogen compounds are extracted; their data also provide new evidence of the acidic nature of the cracking catalyst.

Summary

Fundamental studies of catalytic cracking have led to the conclusion that the chief characteristics of the products may be traced to the primary cracking of the hydrocarbons in the feed stock and to the secondary reactions of the olefins produced; both correspond to the ionic reaction mechanisms of hydrocarbons in the presence of acidic catalysts. The chemistry of both the hydrocarbons and catalysts dealt with here has advanced rapidly in the last decade. Nevertheless, much further exploration is required with respect to the nature of the catalyst and the properties of the hydrocarbons undergoing reaction. A promising field lies ahead for future research.

Acknowledgment

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Catalytic Cracking in Fixed- and Moving-Bed Processes

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The application of cracking catalysts to the production of high octane motor gasoline from petroleum distillates was initially investigated by Eugene J. Houdry. The results of those studies led to the development of the fixed-bed process and later to the Thermofor, Houdriflow, and modified Thermofor air lift moving-bed processes. Effects of operating variables and characteristics and performance of catalysts upon yields and quality of products have been fully investigated. The important process and engineering phases of fixed- and moving-bed processes and information on the cracking reaction, properties of catalytic products, and characteristics of catalysts are presented in this paper.

The application of catalysis to the production of motor fuel by cracking of less volatile petroleum oils was first investigated in France by Eugene J. Houdry in the period 1927 to 1930. The results from these investigations clearly established the superiority of catalytically cracked gasoline over that made by the thermal processes; the economic possibilities were also indicated.

It had been previously recognized that certain activated clays, of the type used for decolorization, catalyzed to some degree the decomposition of heavy oils into products of lower boiling range. Concurrently with the production of lighter hydrocarbons, products of condensation were formed and retained on the catalyst in the form of a coke deposit. This deposit impaired the catalyst activity and gave decreased yields of the lower boiling range product. Early in the course of his studies, Houdry discovered that a high level of catalyst activity could be maintained if the catalyst was regenerated frequently by burning the coke deposit at controlled temperatures before its concentration on the catalyst had attained a level that would substantially impair the cracking reaction. As a result, a process was conceived in which oil in the vapor phase was passed through a bed of catalyst until the catalyst deposit had reached a predetermined amount. The oil charge was then discontinued, and the catalyst deposit was burned by circulation of oxygen-bearing gas. These two operations succeeded each other in relatively rapid alternation.

By maintaining high catalyst activity in this manner, a motor fuel high in antiknock quality and low in sulfur and gum-forming components could be produced, irrespective of the character of the oil charged. Ultimate gasoline yields were comparable to or better than those realized by the thermal processes. The total recovery of liquid products was relatively high and the residual liquid in the boiling range above motor gasoline was a clean, low boiling fuel irrespective of the boiling range of the charge stock. When heavy distillates were processed, this last phenomenon meant an actual upgrading of a large

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portion of the charge stock in addition to the production of high quality gasoline. All these factors had an important bearing on the better utilization of petroleum crudes and, therefore, on the economy of the refining industry.

Late in 1930, Houdry was brought to the United States by the Vacuum Oil Co., subsequently the Socony-Vacuum Oil Co. His activities were transferred to the Sun Oil Co. in 1933, at which time the Houdry Process Corp. was organized. Socony rejoined the development in 1935.

With the financial and technical help of those two oil companies, extensive development work on the catalytic cracking process was carried out on a laboratory and semiplant scale. This included the study of catalysts and the process variables, as well as the development of new engineering concepts which led to the first commercial application of this process in 1936.

The first commercial plant was a Houdry fixed-bed three-case unit charging light gas oil at a capacity of 2000 barrels per day. A large commercial plant charging heavy oil with a capacity of 10,000 barrels per day was completed in 1937. At the start of World War II, sixteen full scale Houdry fixed-bed units were operating or under construction. Altogether 29 fixed-bed units having a charging capacity of 375,000 barrels per day were erected.

A number of process limitations and a relatively high initial investment cost, which were inherent in the fixed-bed process, added impetus to the development of the moving-bed process. Thermofor catalytic cracking was a result of this development. During the late war years and immediately thereafter, 34 catalytic cracking units of the Thermofor design having a capacity of 375,000 barrels per day were built. The catalyst in the Thermofor units flows in a continuous stream alternately through a reactor and a regenerator. Mechanical elevators are used to move the catalyst from the bottom of one vessel to the top of the other.

Investment cost and capacity limitations of the elevators, together with other engineering and process features, led to the development in the past 4 years of the latest concept in moving-bed catalytic cracking. This new development, utilizing the original catalytic cracking principles, employs pneumatic lifts to transport the catalyst between process vessels. Both the Houdriflow catalytic cracking process (*5*), licensed by the Houdry Process Corp., and the basically similar Thermofor air lift process, licensed by the Socony-Vacuum Oil Co., are of this type.

Cracking Reaction

The cracking reaction in all catalytic cracking processes is affected by the following factors (*2*): catalyst type and inherent activity; charge stock characteristics and midboiling point; space rate, usually measured in terms of liquid oil volume per volume of catalyst per hour; ratio of catalyst to oil, the amount of catalyst in the reaction zone per unit of oil reacted, which in the fixed-bed process becomes the ratio of reciprocal space rate to time on stream, and in the moving-bed process is the ratio of catalyst rate to oil rate; temperature; and oil partial pressure.

In present catalytic cracking processes the production of gasoline is accompanied by the formation of substantial amounts of coke, as well as the production of hydrogen and light hydrocarbons. As the control of the combustion of coke was the main problem facing the commercial development, the effects of variables are conveniently expressed in terms of coke formation in the following discussion.

Effect of Catalyst Activity. In the preliminary investigations of cracking catalysts, it was found that each type of catalyst had a so-called inherent activity which could be adjusted during the process of manufacture. The activity index (A.I.) is the yield of gasoline produced from a specific charging stock under standard conditions of pressure, temperature, space rate, and time on stream (*1*). The activity of a catalyst is correlated with its chemical properties (*13*) and, for a given type of catalyst, it is somewhat related to its physical properties. The inherent activity will decrease in operation, owing mostly to exposure to certain vapors such as steam. Catalyst activity is an independent variable. Replacing activity by other operating variables to maintain

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constant conversion results in lower gasoline yield. Figure 1 shows the yield of gasoline as a function of the coke yield for catalysts of different activity index (*1*).

Effect of Charge Stock Characteristics and Mid-Boiling Point. The chemical composition of the charge stock has a substantial effect on the yield of gasoline at a given coke production. As a rule, the higher the naphthene concentration in the charge the higher is the yield of gasoline.

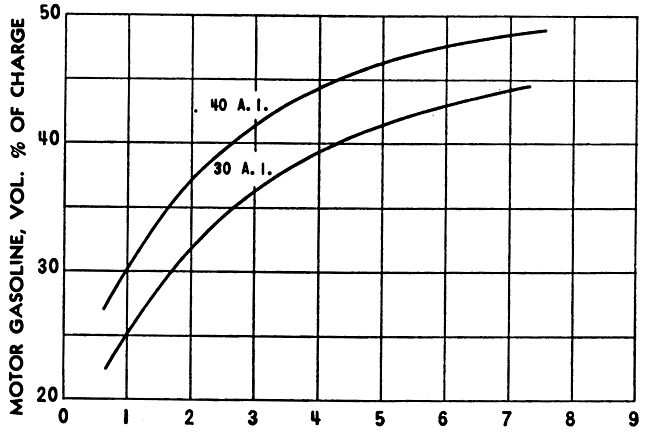

Figure 1. Effect of Catalyst Activity on Gasoline Yield

Once-through cracking light East Texas gas oil

Figures 2 and 3 show the product distribution versus coke yield for a gas oil from mixed-base crude, and yields of gasoline versus coke for different types of charge stock.

The effect of the mid-boiling point on product distribution at constant temperature and coke yield is shown in Figure 4. An increase in mid-boiling point favors the production of unsaturates in the gasoline (*3*) and the lighter products.

Stocks of higher mid-boiling point are more readily decomposed and necessitate the use of milder conditions for a given rate of coke production. This is attained in the fixed-bed units by the use of lower oil partial pressures and catalyst activities, and in the moving-bed units by higher space rates.

Effect of Space Rate and Ratio of Catalyst to Oil. Space rate, *R*, affects coke formation as an exponential function of the form

$$\text{Coke (weight \% of charge)} = K\,(R)^x$$

where *K* is a constant. Ratio of catalyst to oil affects coke formation as an exponential function of the form

$$\text{Coke (weight \% of charge)} = K_1\left(\frac{C}{O}\right)^y$$

The exponents vary somewhat with charge stocks. For East Texas light gas oil the values of x and y are -0.4 and 0.6, respectively. When other conditions are constant, any combination of these two variables which results in a given yield of coke will also result in given yields of gasoline, gas, and residual gas oil (*20*). Therefore, space rate and ratio of catalyst to oil are interchangeable variables.

Effect of Temperature. Figure 5 illustrates the effect of temperature on product distribution. An increase in temperature decreases yields of gasoline and increases gas yields. In addition, the yield of butylenes in the C_4 cut increases with increased temperature and the octane number of the gasoline produced is higher.

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Effect of Pressure. Pressure is an independent variable. An increase in pressure favors the production of coke. It also favors production of gasolines of low olefin content, which is necessary in the production of aviation gasoline.

Effect of Recycle Operation. Catalytically cracked gas oils are as a rule not so favorable charge stocks as the virgin materials. The ratio of hydrogen to carbon in the cracked gas oil is less than in the virgin charge. As the extent of cracking increases, the gas oil product becomes more refractory and aromatic. If a small heavy fraction is removed from the cycle oil, the production of gasoline from a given amount of virgin feed can be increased at constant coke yield by recycling the catalytic gas oil. The extent of recycling is limited by economic considerations.

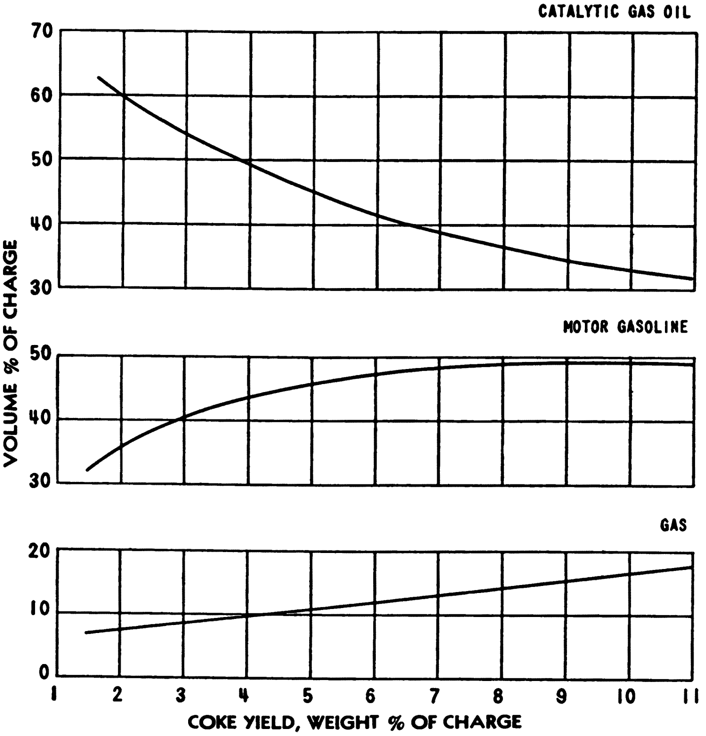

Figure 2. Product Distribution vs. Coke Yield

Once-through cracking gas oil distillate from mixed-base crude

Figure 6 illustrates the comparison between once-through and recycle cracking in fixed-bed operation. An illustration of moving-bed recycling is also shown. These two curves are not to be compared, as both charge stock and catalyst differ in the two examples.

For practical use, combination charts (*12*, *20*) have been prepared which show the effect of the above process variables on product distribution and also the interrelationships of the yields of the various products.

Although the reaction in fixed- and moving-bed units is essentially the same, some deviations in results occur. These are due to the following facts:

In the fixed-bed unit, commercial reactor design results in a wide variation of temperature during the oil cycle.

In the fixed-bed unit, the character of the catalyst varies during the cycle time, owing to the variation of temperature mentioned above and to the progressive accumulation of coke. In the moving-bed unit, the oil is always exposed to catalyst of the same average coke concentration.

Properties of Catalytic Products

Catalytic cracking enjoys the distinction of being capable of producing gasoline of high quality from almost any crude oil. Generally, the F-1 or Research octane rating of a 10-pound RVP catalytic unleaded gasoline is in the range of 86 to 92 octane number. The F-2 or ASTM motor octane number falls in the range of 78 to 82. Catalytic gasolines show an excellent response to tetraethyllead. Catalytic gasolines are generally low in gum-forming constituents and in corrosive sulfur compounds, so that the requirements for chemical treating are minimized.

An important feature of catalytic gasolines is the uniformly good octane throughout the boiling range of the gasoline (*4*). The reason for the good octanes obtained with catalytic gasolines is substantiated by chemical analysis. The front end of the catalytic gasoline is predominantly isoparaffins, which contribute markedly to the high octane performance obtained. Table I shows the composition of the hexane cuts from catalytic, thermal, and straight-run gasolines (*3*). Typical gasolines have been analyzed for paraffin, olefin, naphthene, and aromatic contents in narrow boiling cuts as illustrated in Figure 7. The large concentration of higher boiling aromatics accounts for the good octanes shown by catalytic gasolines of high end point. This fact allows much latitude in cutting gasoline end point best to fit the refiner's interest without affecting gasoline quality as measured by octane number.

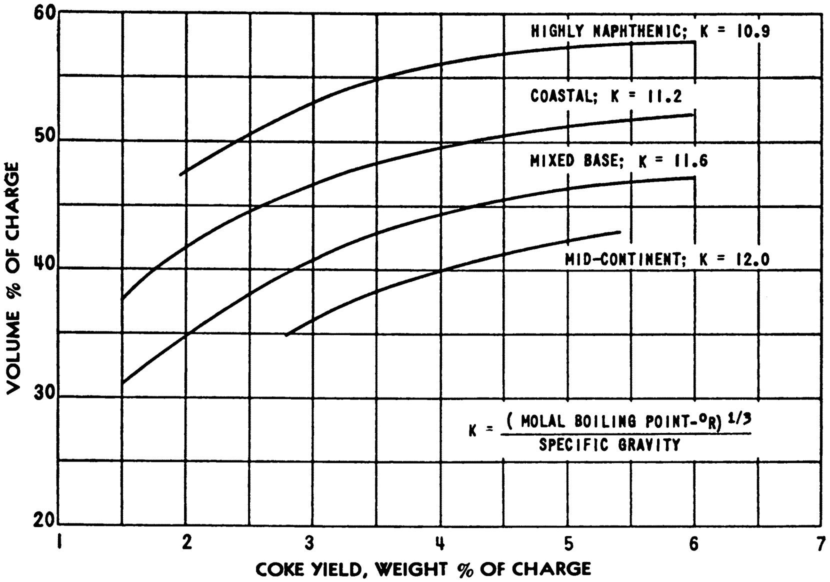

Figure 3. Effect of Type of Charge on Gasoline Yield

Once-through cracking of distillate gas oils

With naphthenic charge stocks, the higher boiling fraction of the gasoline may show even higher octane than the average gasoline octane because of the high aromatic content in this boiling range. Overlap between end point of the gasoline and initial boiling point of the virgin charge stock will cause a loss in octane number because of the inclusion of low octane uncracked naphtha in the higher boiling fraction of the gasoline product. The virgin heavy naphtha, which is much more refractory than the gas oil, is substantially unaffected by passing over the cracking catalyst at normal cracking conditions.

The final test of a good gasoline is the road performance. At low engine speed, gasolines respond in accordance with F-1 or Research octane numbers; at higher engine speeds, the gasoline performance follows the F-2 or motor octane number. A single example of one of many tests comparing catalytic, straight-run, and thermal gasolines is

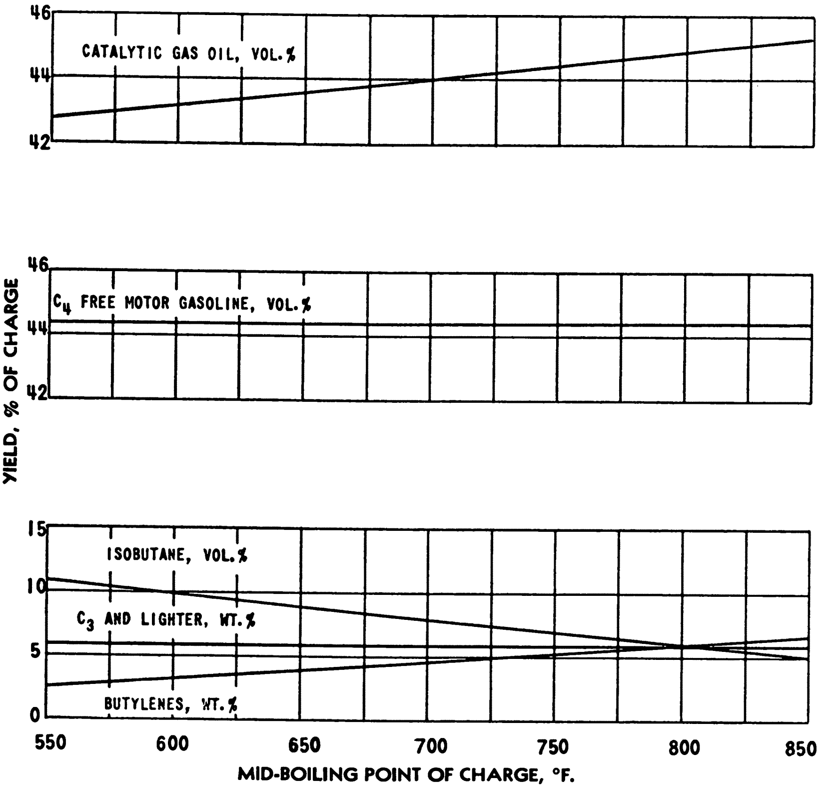

Figure 4. Product Distribution vs. Mid-Boiling Point of Charge

Constant temperature, constant coke yield, 5 weight % of charge

shown in Figure 8 (*4*). The catalytic fuel shows road test octane ratings above the maximum required in this particular test. The availability of high octane catalytic gasoline has permitted automotive engineers to develop higher compression engines to put more power and economy into today's cars.

The lighter hydrocarbons and fixed gas from the catalytic cracking reactions are principally in the C_3 to C_4 boiling range. The hydrogen production is about 0.1 weight % of the charge, and the total methane, ethane, and ethylene gas amounts to between 1 and 2 weight % of the charge at 50% conversion.

Distribution between saturated and unsaturated hydrocarbons in the C_3 and C_4 cuts is affected by a number of variables, including temperature, oil partial pressure, boiling range and type of charge stock, and type of catalyst. High cracking temperature, higher boiling range charge, and low oil partial pressure all favor unsaturation. Natural clay catalyst will give more unsaturation and less isobutane than synthetic silica-alumina catalysts, other factors being equal.

Table I. Composition of Hexane Cut of Houdry Catalytic, Thermal, and Straight-Run Gasolines

(Per cent by volume)

Paraffins from C_6 cut	Houdry Catalytic Gasoline	Thermal Gasoline	East Texas Straight-Run Gasoline
n-Hexane	9	63	51
2-Methylpentane	48	18	32
3-Methylpentane	27	16	16
2,3-Dimethylbutane	13	3	1
2,2-Dimethylbutane	3	...	..
Total isoparaffins	91	37	49

Butanes produced are predominantly isobutane (2-methylpropane), the proportion ranging from 80 to 90 % of the total C_4 saturates.

The cracked liquid products boiling above gasoline have been utilized in Diesel, distillate, and residual fuels, in addition to catalytic recycling and thermal cracking for additional gasoline yield (*4, 6, 7, 15, 21*).

The catalytic Diesel fuel has a lower cetane number than the corresponding component of the virgin charge because of the changes in chemical composition effected in the cracking operation. However, in mild cracking conditions, the drop may amount to only a few numbers in Diesel index.

Nos. 1 and 2 distillate fuels cut from catalytic gas oils are lower in both gravity and aniline point than corresponding virgin stock fuels. But the catalytic fuels have been used satisfactorily in atomizing pressure-type oil burners.

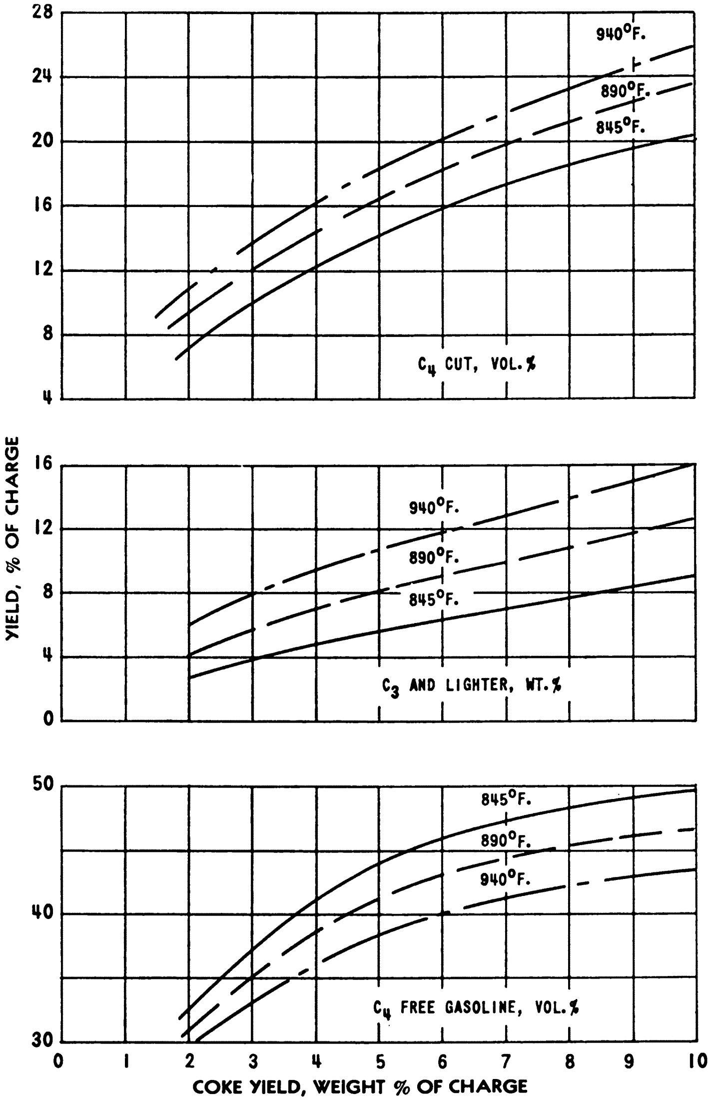

Figure 5. Effect of Temperature on Product Distribution

Fixed-bed operation

Catalytic Aviation Gasoline

Prior to the development of the catalytic cracking process, aviation gasoline was produced by adding tetraethyllead to blends of commercial iso-octane (2,2,4-trimethylpentane) and selected straight-run petroleum fractions.

The commercial development of catalytic cracking made available additional supplies of blending stocks having the necessary requirements of volatility, stability, and antiknock value. At the same time, by-product isobutane and butylenes provided charging stocks for the newly developed alkylation processes.

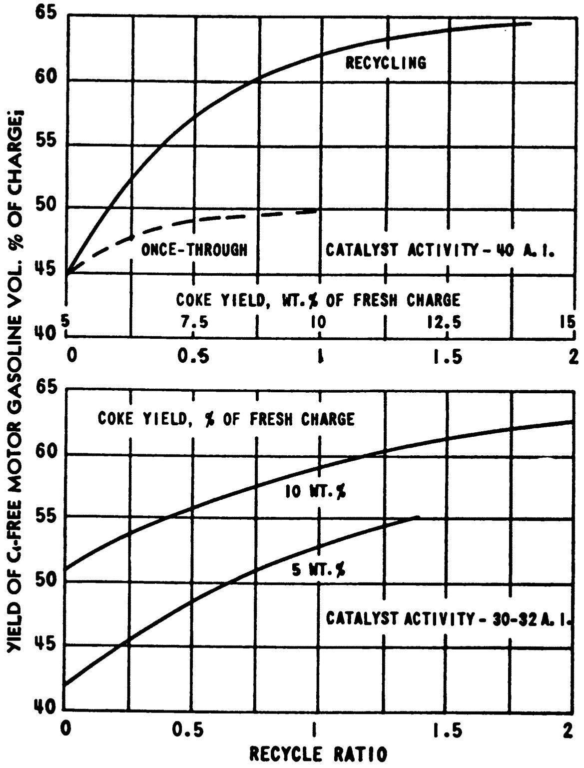

Figure 6. Recycling in Fixed- and Moving-Bed Processes

Upper. Fixed-bed operation
Lower. Moving-bed operation

At the outbreak of World War II a synthetic-type cracking catalyst (*22*) was made available and the quality of the gasoline produced was further improved. The production of this aviation fuel added greatly to the over-all output of finished aviation gasoline (*18*). Even so, the availability of the components of commercial iso-octanes and alkylates was limiting.

As far back as 1938, it had been proved commercially that repassing or treating the primary aviation gasoline over the cracking catalyst resulted in a product of lower olefin content, higher aromatic content, and improved response to tetraethyllead, decreasing sharply the proportion of alkylate necessary in the blend.

This process was fully utilized in commercial units early in 1942 and played an important part in satisfying the ever-increasing requirements of our Armed Forces. Usually, a debutanized motor gasoline was charged to the treating unit at relatively severe conditions to crack the heavier fractions and increase the yield and quality of aviation base stock. Typical results are given in Table II.

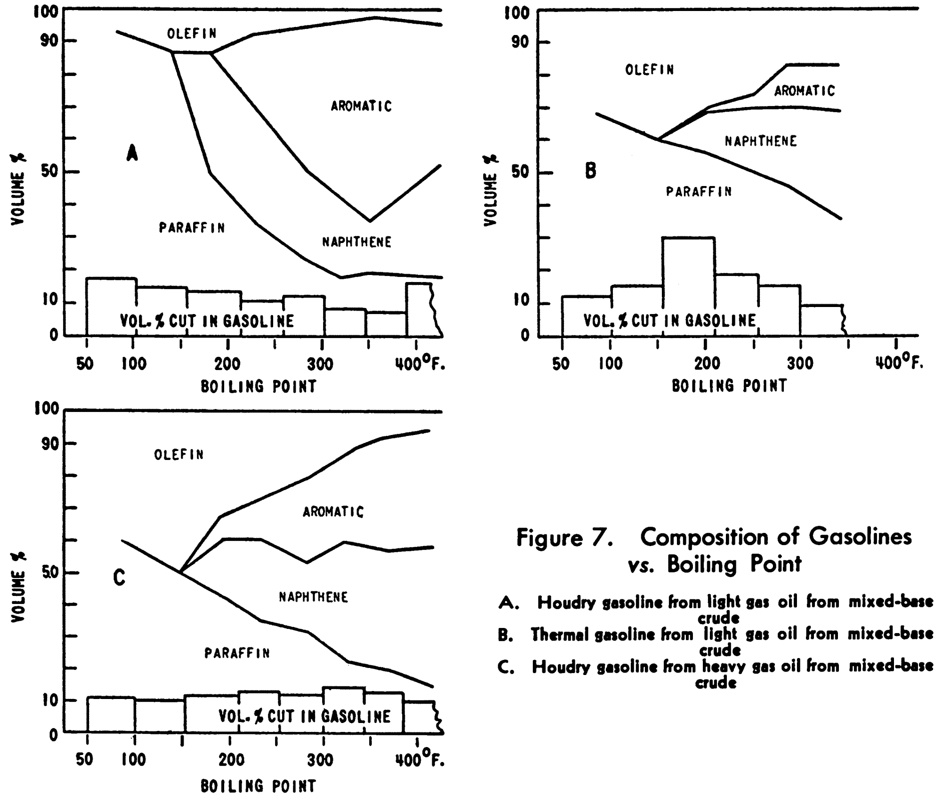

Figure 7. Composition of Gasolines vs. Boiling Point

A. Houdry gasoline from light gas oil from mixed-base crude
B. Thermal gasoline from light gas oil from mixed-base crude
C. Houdry gasoline from heavy gas oil from mixed-base crude

Catalyst

Types and Properties. The properties of the catalysts used with the Houdry fixed-bed process, and with all true catalytic cracking processes, comprise the major factor not only in promoting the desired reactions, but also in the design and economy of construction and operation of the plant.

The cracking process requires that the catalyst take part in two alternating reactions: (1) the decomposition of heavy to predominantly lighter hydrocarbon products, which is an endothermic reaction; and (2) the exothermic oxidation of the nonvolatile hydrocarbons retained on the catalyst during the cracking operation. This complete cycle of operations demands of the catalyst unusual chemical and physical properties, so that it not only promotes the desired reactions when first applied, but also remains effective for a long time.

The requirement of chemical stability will be appreciated when it is considered that the catalyst is exposed during the cracking step to hydrocarbon vapors, sulfur and nitrogen compounds, and water vapor. During the regeneration step it is exposed to sulfur dioxide, carbon monoxide, carbon dioxide, water vapor, and possibly nitrogen compounds in addition to air.

Table II. Aviation Gasoline from Catalytic Cracking and Treating

	Gasoline from Light Gas Oil		Gasoline from Heavy Gas Oil	
	Before treating	After treating	Before treating	After treating
Chemical analysis, vol. %				
Paraffins	57.7	55.3	40.7	54.2
Olefins	8.1	3.3	29.6	2.7
Naphthenes	15.5	8.1	11.3	8.1
Aromatics	18.7	33.3	18.4	35.0
F-3 octane rating (4 ml. TEL)	94	98	91	98
7-lb. RVP alkylate in blend required for 100 octane rating, vol. %	46	22	56	22

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Physical stability is required of the catalyst in view of high temperatures reached during the regeneration step and because it is subjected to considerable mechanical strain from external sources, such as temperature fluctuations and impact loading.

The earliest catalyst developed for commercial use was produced from naturally occurring bentonitic-type clays. Such clays are carefully selected and further refined and activated by chemical means to bring out their latent cracking characteristics. A typical analysis of this type of commercial catalyst follows:

	Wt. %		Wt. %
SiO_2	67.1	MgO	3.8
Al_2O_3	15.6	CuO	0.001
Total alkali as Na_2O	0.5	NiO	0.001
Fe_2O_3	2.0	Ignition loss	8.8
CaO	1.8		

The inherent variability of the raw mineral, particularly with respect to minor constituents which in certain cases were known to have major effects on the cracking reaction, led to the development by the Houdry Process Corp. of a synthetic silica-alumina catalyst of controlled chemical composition and more stable catalytic properties. Full scale manufacture of synthetic catalyst was started in 1939.

The superiority of synthetic catalyst over the natural clay type for the production of aviation gasoline from a yield and octane standpoint is shown in the following comparisons:

	One-Pass Aviation Gasoline				Two-Pass Aviation Gasoline	
Charge stock	Naphtha from coastal crude		Gas oil from mixed-base crude		Gas oil from California crude	
Catalyst	Synthetic	Clay	Synthetic	Clay	Synthetic	Clay
Yield, vol. %	38	34	34	32	37	32
Octane, AFD-1C + 4 ml. TEL	96.2	93.9	95.2	93.5	98.9	94.9

The synthetic catalyst also yields an aviation fuel of considerably lower olefin content which, in effect, reduces gum-forming tendencies and improves storage stability.

For use in commercial plants, the natural-type catalyst is produced as pellets approximately 4 mm. in diameter and length. The synthetic-type catalyst finds general

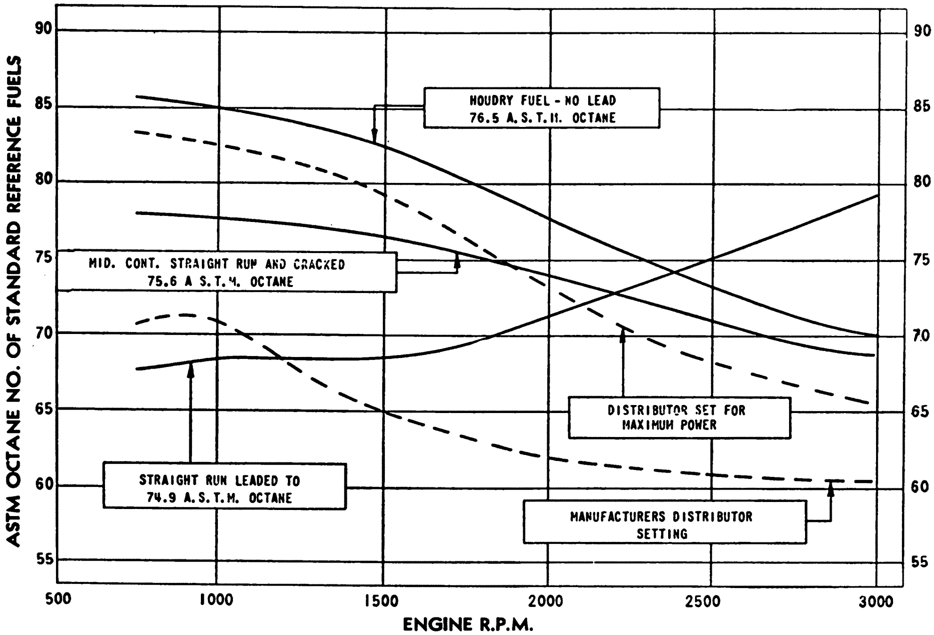

Figure 8. Road Octane Performance of Motor Fuels

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application also in the pellet form; however, the "bead" form developed by the Socony-Vacuum Oil Co., primarily for use with the Thermofor process, is also utilized in fixed-bed units. This catalyst gives essentially the same product distribution as synthetic pelleted catalyst. The bead form was developed primarily to give the catalyst greater physical strength. The size of the individual particles of catalyst for use with the fixed-bed process has been based on the results of extensive studies with respect to pressure drop through a bed of catalyst and satisfactory design of the internal elements of the reactor.

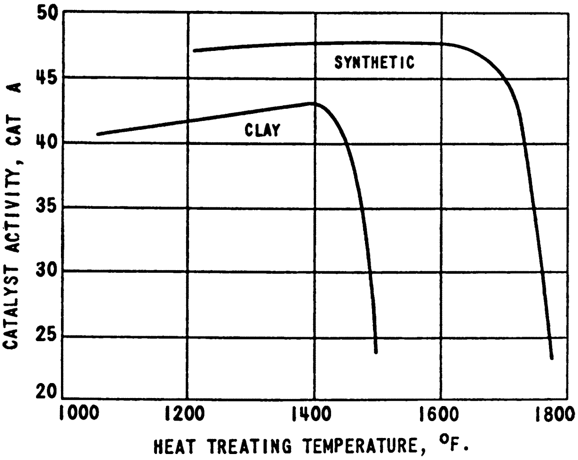

Figure 9. Thermal Stability of Natural Clay and Synthetic Types of Catalyst

Condition for carrying out the regeneration of the catalyst is of particular importance. The primary variables in the regeneration of cracking catalysts are type of catalyst, instantaneous carbon content, combustion temperature, and oxygen partial pressure (*8*). The burning rate indicates second-order dependency on carbon content at carbon concentrations less than 2 weight % on catalyst and first-order dependency on oxygen partial pressure. The specific reaction rates indicate that the effect of temperature follows the Arrhenius equation. For clay cracking catalysts the energy of activation is 26,600 calories per gram mole.

The maximum temperature that can be used for regeneration is limited by the thermal stability of the catalyst. Figure 9 shows the temperature stability of natural and synthetic catalysts in bone-dry air. In commercial units these catalysts are regenerated at substantially lower temperature because the presence of steam reduces the thermal stability limit. The steam is produced from the combustion of the hydrogen in the coke deposit on the catalyst.

A number of other catalysts of both synthetic and natural clay types have been developed. Some of these catalysts have shown improvement in product distribution, but none have given appreciable octane benefit. For this reason, they have not been used commercially in fixed- or moving-bed units.

Aging. Cracking catalysts do not maintain their initial activity with use, and this phenomenon becomes an integral function in evaluating the economics of catalytic cracking. The design of commercial plants incorporates the requisite flexibility for maintaining a high level of conversion to favorable products over an acceptable service life of the catalyst. Commercial experience with widely varying operations has placed the economic life of the catalyst in fixed-bed units within the range of 12 to 24 months. This range is dictated purely by specific refinery situations.

The term "catalyst activity" is frequently applied rather loosely. Actually, it is a measure of the degree to which a catalyst responds to a given set of carefully controlled testing conditions, preferably performed in bench scale equipment. One such standard test, known as CAT-A (*1*), makes use of the fixed-bed cracking principle. With the CAT-A test 38 to 42 and 45 to 48 activity index are the present maximum activities of natural clay and synthetic commercial catalysts, respectively. However, catalyst activity measured by a standard test is not necessarily synonymous with the ability of the catalyst to function satisfactorily in a specific application. For instance, the catalysts produced for the Houdry fixed-bed process are of carefully controlled initial activities which vary considerably with the boiling range of the charge stock to be processed. Naphthas and light gas oils can use effectively a synthetic-type catalyst of 45 to 48 activity index, whereas a heavy gas oil of the order of 750° F. mid-boiling point is best handled, within the limits of practical plant conditions, with catalysts of 34 to 36 activity index. The following table illustrates the points in question:

Basis, 16-month catalyst service life

	Case 1	Case 2
Charge stock		
Type	Light gas oil	Heavy gas oil
Mid-boiling point, ° F.	540	750
Catalyst activity (basis, CAT-A test)		
Initial	45	36
Terminal	30	23
% variation	33	36
Gasoline yield, vol. %		
Initial	45	43
Terminal	39	37
% variation	13	14

Thus, the rates of activity decline are substantially constant for these two cases, and the gasoline production is similar with both operations. This is true even though the initial activity of the catalyst employed for cracking the heavy gas oil falls toward the terminal activity of the catalyst applied to the light gas oil cracking operation.

In the moving-bed process high-activity catalyst is continuously added to the system to replace attrition losses and, in certain cases, to maintain a desirable average activity.

The conditions contributing to aging of catalysts or decline of catalytic activity are varied and a number of causes have been identified. These factors can be grouped into two general classifications—those causing normal aging and those contributing to abnormal aging. The essential differences between the two types of aging become apparent from a consideration of the following data obtained with natural clay catalyst:

	Gasoline, Vol. %	Gas, Wt. %	Coke, Wt. %	Ratio	
				Gasoline-gas	Gasoline-coke
Normal aging					
At start of aging period	42.0	4.8	4.2	8.8	10.0
At finish of aging period	33.0	4.1	3.1	8.1	10.6
Abnormal aging					
At start of aging period	39.4	7.0	3.7	5.6	10.7
At finish of aging period	25.1	8.9	6.2	2.8	4.0

Normal aging is attributable to water vapor in contact with the catalyst during any phase of the operating cycle. The loss in gasoline yield (at constant operating conditions) is always accompanied by a decrease in gas and coke, so that the gasoline-gas and gasoline-coke ratios remain substantially constant. Abnormal aging, on the other hand, causes the gasoline-gas and gasoline-coke ratios to decline as indicated by the data shown.

Both the natural clay and the synthetic types of catalyst undergo normal aging. Abnormal aging, due to sulfur compounds, has been found only with natural clay catalyst; the synthetic types are stable under similar conditions. Natural clay catalysts can be protected against abnormal aging from sulfur compounds by hydrating with steam after regeneration. Certain types of iron-free clays and bentonitic clays treated to remove iron do not show sulfur deactivation.

All catalysts will show abnormal aging if the charge stock contains even minute quantities of heavy metals such as copper, nickel, and vanadium (*14*).

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Fixed-Bed Cracking Process

General Concept. The development of the fixed-bed process was based upon the idea of using a static bed of catalyst and maintaining a continuous flow of hydrocarbon vapor by the use of multiple reactors (*17*). Each reactor was submitted to a cycle of operations consisting of:

Flow of oil vapors through the bed
Discontinuance of vapor flow and removal of residual vapors by combined effect of a steam sweep and vacuum produced by steam ejectors
Removal of nonvolatile hydrocarbons deposited on the catalyst by combustion in a stream of air
Discontinuance of air flow and removal of oxygen-containing gases

The number of reactors depended upon the relation between the duration of the hydrocarbon flow and the time required for the subsequent operations of the cycle. In the ultimate commercial realization, the use of three reactors resulted in continuous flow of oil and air.

Commercial Development of Fixed-Bed Process. From the above process considerations it became obvious that the capacity of a commercial unit, and its economic value, were closely related to its ability to burn coke. Indeed, most of the design problems associated with catalytic cracking have been centered around the question of catalyst regeneration. To obtain the most favorable economic return from a 10,000-barrel-per-day unit, it was designed to burn approximately 6000 pounds per hour of coke. This coke yield represents approximately 5% by weight of the charge.

The first conception of reactor design developed on a semicommercial scale was the use of flue gas recirculation, at controlled oxygen contents, to burn the coke and remove the heat of combustion. Oil vapors and air were alternately introduced in the catalyst mass at a multiplicity of points, through perforated tubular elements. Internal heat exchange was provided between the catalyst mass and the incoming fluids. By this arrangement operation on a short-time cycle provided isothermal cracking conditions. During the regeneration period the use of relatively cool flue gas at a fairly high (5%) oxygen content was possible.

The next development was the use of internal cooling by intermittent water circulation during the regeneration period. The heat was removed by radiation and flue gas convection from the walls of perforated pipes to water-cooled tubular coils installed inside these pipes. Thus, direct contact with the catalyst was avoided, which precluded cooling parts of the catalyst to temperatures at which combustion would stop. Most of the heat of combustion was recovered as steam. This was the basis of the design of the first commercial unit installed and operated in 1936.

The extensive study of the combustion characteristics of the coke led to the next development, which was the use of air under pressure for regeneration. A turbocompressor (*9*, *19*) developed by a European manufacturer and comprising an air compressor driven by a gas turbine was used. Because the process pressure drop was relatively low and the air was heated by part of the heat of combustion, enough power was available at the turbine to supply the power requirements of the compressor. This development marks the first commercial application of gas turbines in the United States.

Certain mechanical failures related to the use of water for temperature control were eliminated by the use of a molten salt (*10*), an eutectic mixture of potassium nitrate and sodium nitrite, which has a low melting point (284° F.), high specific heat (0.38), and low viscosity. This salt has practically no vapor pressure and is thermally stable and noncorrosive to carbon steel in the operating range considered. It is pumped through tubular elements to absorb the heat liberated during the regeneration period and is then used to supply a portion of the heat required by the oil during the processing step. The excess heat liberated in the combustion step is absorbed in a boiler of special design, and is recovered as high pressure steam.

These developments resulted in the design of the fixed-bed unit, practically as they stand now. Mechanical difficulties encountered on most units in removal of catalyst during catalyst changes have been eliminated to a large extent by changes in design of the reactor internals (*11*). These mechanical engineering features of the operating fixed-bed units have been described in the current literature.

It is gratifying to the technicians of the Houdry Process Corp., Socony-Vacuum Oil Co., and Sun Oil Co. that a number of these engineering features developed in connection with the first commercial applications of fixed-bed catalytic cracking have proved of considerable interest to other industries where they are currently used.

Moving-Bed Cracking Process

Low Ratio of Catalyst to Oil. Although a Houdry fixed-bed catalytic cracking unit as a whole operated continuously, each of the reactor cases which constituted the unit operated intermittently. Each case served as both cracking reactor and catalyst regenerator. It was therefore necessary that the equipment be designed to withstand the most severe conditions incident to each function. This was extremely costly when sulfur-containing stocks were to be run, because all the internals had to be alloy-protected. Furthermore, because the cracking reaction is markedly endothermic and regeneration is highly exothermic, a "flywheel"—the circulating molten salt system—had to be provided for proper temperature control. The operating complexities and high investment cost incurred by this type of operation pointed to the desirability of separating the cracking and regeneration steps into separate vessels. This was accomplished through application of the moving-bed technique (*16*).

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In essence, the moving-bed system, as first typified by the Thermofor catalytic cracking process, consists of a reaction vessel in which the cracking takes place, and a kiln in which spent catalyst is regenerated. Continuous movement of catalyst between these vessels is provided by mechanical bucket elevators. The process takes its name from the Thermofor kiln, which was originally developed for the regeneration of treating clay. As applied to catalytic cracking, the Thermofor kiln is a rectangular vertical vessel, through which catalyst flows from top to bottom. Regeneration is accomplished in a series of semi-independent burning zones stacked within the vessel. Each zone is provided with a set of air distribution channels, from which air flows both up and down. Flue gas is collected in common headers between zones. Temperature control is obtained through the use of multiple banks of steam generating cooling coils at each zone. The kiln operates at essentially atmospheric pressure, using air supplied by a low pressure centrifugal blower. Provision is made for preheating the combustion air for start-up and, under certain conditions, during on-stream periods. Catalyst temperatures are controlled to 1100° to 1150° F. maximum by the distribution of the air and the number of cooling coils used at each level.

The Thermofor reactor is a cylindrical vessel designed to operate at a pressure of 6 to 12 pounds per square inch gage. Hot regenerated catalyst is fed to the top of the reactor through a vertical pressure seal leg, and gravitates through the reactor as a compact bed approximately at catalyst bulk density. Facilities for purging spent catalyst of residual hydrocarbons are provided in the reactor before the catalyst is returned to the kiln for regeneration.

The first Thermofor reactors were designed for true countercurrent contacting, and were thus limited to vapor-phase charge. Feed preparation consisted of flashing reduced crude with 3 to 4 weight % steam at a temperature of 760° to 890° F. and pressure of 10 to 12 pounds per square inch gage. Because the octane number of the catalytic gasoline is a function principally of the average reactor temperature, the tar separator overhead was superheated in some units to about 950° F. to add heat to the reactor. The trend toward the inclusion of heavier crude fractions in catalytic cracking feed and the necessity for obtaining even higher octane numbers led to the change to concurrent flow reactors. In order to be able to charge heavier stocks, it was necessary to develop a feed device which would give good distribution of liquid over the major part of the catalyst. This was accomplished through the use of a special nozzle which discharged the liquid onto a curtain of catalyst falling around it. With the application of the liquid feed nozzle, the flexibility of the Thermofor catalytic cracking unit so far as charge stock is concerned was considerably increased. With the mechanical difficulties eliminated, the range of usable charge stock became limited by the heat balance of the unit, the coke yield from heavy stock, and the possibility of catalyst deactivation. This latter factor arises because the heavier fractions of many crudes contained trace amounts of metals such as copper and vanadium, even very small quantities of which act as true poisons for cracking catalysts and cause permanent deactivation. Therefore, charge stocks are distillate fractions which are cut to eliminate these heavy metals.

The processing of high-sulfur stocks is worth at least a brief mention. From strictly a processing standpoint it was found that synthetic silica-alumina catalysts were satisfactory for processing high-sulfur stocks without any special precautions other than proper corrosion protection for the reactor and associated oil-handling equipment. Natural clay catalyst, however, suffered deactivation which resulted in effectively lowered activity and correspondingly poor product distribution. The problem of adapting clay catalyst to high-sulfur stocks was solved through the relatively simple expedient of prehydrating the regenerated catalyst before it came in contact with the oil vapor. Selective adsorption of steam has the effect of protecting the catalyst from the action of the sulfur compounds. The sensitivity of clay catalyst to sulfur poisoning has been attributed to traces of iron present in the catalyst, which in combination with the sulfur produces uneconomically high yields of coke and gas. Specially treated clays and certain naturally occurring iron-free clays are resistant to sulfur poisoning without any special hydration.

The adoption of the moving-bed Thermofor process overcame many of the limitations which had been encountered with the Houdry fixed-bed process. Investment cost was markedly reduced, particularly for processing sulfur-containing stocks, and general processing was simplified. However, there was still considerable room for improvement. Largely because of the cost of mechanical elevators, Thermofor units were limited to a weight ratio of catalyst to oil in the range of 1.5 to 2.5. In this range the weight of coke deposited per pound of catalyst at normal conversion levels is so much that the heat of combustion will result in excessive catalyst temperature unless considerable heat is removed by cooling coils in the kiln. At the same time, in order to maintain the desired average cracking temperature, the charge to the unit must be heated to relatively high temperatures. It was recognized that a great improvement could be effected if more of the heat liberated during regeneration could be transferred directly to the reactor. An increase in the quantity of catalyst circulated for a given oil charge rate would accomplish this desirable change. An increase in ratio of catalyst to oil would present no problems in processing, as conversion could be set at any desired level by compensating adjustment in space rate. For a given oil throughput this requires only a change in the volume of catalyst maintained in the reactor. These considerations have led to the commercialization of the present Houdriflow and Thermofor air lift units.

High Ratio of Catalyst to Oil. In order to secure the desired high catalyst circulation rates, a pneumatic lift for catalyst transportation was developed. With this system it was entirely feasible to increase ratios of catalyst to oil to the range of 4 to 7 and correspondingly to increase the space rate from approximately 1 in Thermofor units to as high as 3 or 4. The higher catalyst circulation rate resulted in a marked decrease in feed preheat requirement, a general improvement in heat balance between the reactor and the kiln, and better oxygen utilization in regeneration. Many mechanical simplifications were also made possible. The most striking of these appeared in the design of the kiln. With the higher circulation rates, at normal coke makes, a much greater part of the heat of regeneration can be absorbed by the catalyst without reaching a temperature which would cause thermal deactivation. Therefore, cooling capacity in the kiln could be very greatly reduced. The over-all effect of this increased heat adsorption was to simplify the kiln to the point where it consists of one or two burning zones in contrast to the 7 to 10 commonly used in the Thermofor kiln.

The kilns built for Houdriflow units, the first employing the gas lift principle, are cylindrical vessels 12 to 20 feet in diameter and contain one or two split-flow or counterflow burning zones. These regenerators are operated at pressures of from 3 to 10 pounds per square inch gage. The increase in pressure effects a further saving in burning volume, as

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it corresponds to an increase in the oxygen partial pressure. The reactors employed in the high catalyst circulation units differ from those used in the Thermofor unit principally in that the bed depth is considerably reduced in order to obtain the necessary high space rate. A major physical change in the Houdriflow units was a rearrangement of the vessels to superimpose the reactor above the kiln. In the later units the kiln and reactor were built in one self-supporting shell and the reaction and regenerating sections were connected by a short seal or run-down leg, depending on the pressure of operation. With the two main process vessels superimposed, it was necessary to use only one pneumatic lift, fed at the bottom with hot regenerated catalyst from the kiln and discharging to a disengager which fed the reactor top seal leg.

The availability of large quantities of heat in the reactor further increased the flexibility with respect to charge stock boiling range. The mechanics of handling nonvaporizable stocks were improved through the development of a feed nozzle which could handle mixed-phase charge. The mixed-phase charge technique eliminated the need for a tar separator in some cases and for a recycle feed heater, so that the feed preparation section was also considerably simplified.

The pneumatic lift, in addition to being able to handle large quantities of catalyst, is very flexible with respect to catalyst circulation. Therefore, in a gas lift unit it is entirely practical to adjust catalyst circulation rate as required by other processing considerations.

The gas lift unit represents a further improvement over the Thermofor in the elimination of complex internals in the kiln and the mechanical catalyst elevators. These mechanical simplifications in combination with the greatly improved unit heat balance effected an appreciable reduction in investment cost and in unit operating cost. The elimination of so many mechanical components of the unit further resulted in a saving in maintenance, which at the very least would correspond to the reduction in investment.

Although catalyst consumption is somewhat higher in moving-bed than in fixed-bed units, the consumption of catalyst in the units with high ratio of catalyst to oil has been proved commercially to be at least as good as or better than that obtained in low ratio units per unit of catalyst circulated. The pneumatic lift for transporting relatively large quantities of catalyst at high temperatures has been proved commercially.

Conclusions

Catalytic cracking as a commercial process is only 15 years old. The Houdry fixed-bed process, which started a revolution in petroleum refining in 1936, has already given way in new construction to the moving-bed process, where recent improvements have been made by operating at higher ratios of catalyst to oil. These developments, first commercialized in the Houdriflow process and later by the modified Thermofor air lift units, have resulted in substantial savings in investment, utility, and maintenance costs, accomplished by simplification of the kiln and reactor design, general improvement of heat balance between reactor and kiln, and simplified feed preparation. In spite of outstanding mechanical and processing improvements proportionately fewer advances have been made in the development of cracking catalysts. Some new catalysts have given somewhat better product distribution from distillate stocks but at some sacrifice in octane number of the catalytic gasoline. The prospects for improvements in the moving-bed catalytic cracking process appear to be in the direction of improved catalysts which provide increased yields of gasoline for a given yield of coke and have higher regeneration rates and greater chemical and physical stability.

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Fluid Catalytic Cracking Process

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Catalytic cracking is an outgrowth of the oil industry's quest for more efficient utilization of the heavier petroleum fractions present in crude oil. Fluid catalytic cracking is but one of the processes that have resulted from the extensive technical effort to develop efficient and improved means for carrying out this cracking reaction. The Fluid process, however, is of particular interest not only because of its leading position in refinery applications, but also because it represents the first widespread application of a new chemical engineering unit operation, the Fluid solids technique. This paper reviews the development of the process and describes its more pertinent process and engineering features.

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Development

In catalytic cracking, oil is passed over a catalyst to obtain the desired conversion. This is accompanied by deposition of a cokelike deposit on the catalyst, which can be removed by burning with air. The first catalytic cracking plants used fixed catalyst beds, the shortcomings of which were evident from the first work done in this field. The substantial deposits of coke formed during the reaction necessitated frequent regeneration and resulted in a discontinuous process in so far as the catalyst was concerned. From a mechanical standpoint, this discontinuity meant more equipment and consequently greater cost. From a process standpoint, flexibility in operations was severely limited; in addition, attainment of accurate and uniform temperature control during the cracking or regeneration cycles was difficult even with complicated and ingenious mechanical design of the reaction vessels. The large quantities of heat liberated during regeneration of the catalyst could not be transferred efficiently to the cracking section, where a substantial heat input was required to heat and to vaporize the oil and to satisfy the heat of reaction.

Experimental work was accordingly begun on cracking systems using powdered catalyst fed continuously with the oil. The initial work, carried out in small coil-type reactors, indicated promise. Investigations were therefore initiated to obtain knowledge on the physical phenomena involved in the flow of this system of mixed-phase gas and

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powdered solids. This work resulted in the fundamentally important discovery that the degree of slippage between a rising gas stream and fine solids suspended in that gas was great enough, under certain conditions, to establish a dense phase of solids, and thus the concept of the Fluid bed was established. The degree of slippage so obtained was considerably greater than that expected, based on knowledge existing at that time. The high concentration of catalyst so obtained afforded a major economic advantage in providing small reactor volume and low pressure drop through the catalyst flow system. The similarity in appearance of the Fluid solid bed to a boiling liquid led to the idea of using an aerated standpipe for raising pressure on a powdered solid when transfer of the material was required. This standpipe represented a major development, in that it provided a simple means for circulating the catalyst, eliminating need for complicated mechanical devices such as pumps or lock hoppers.

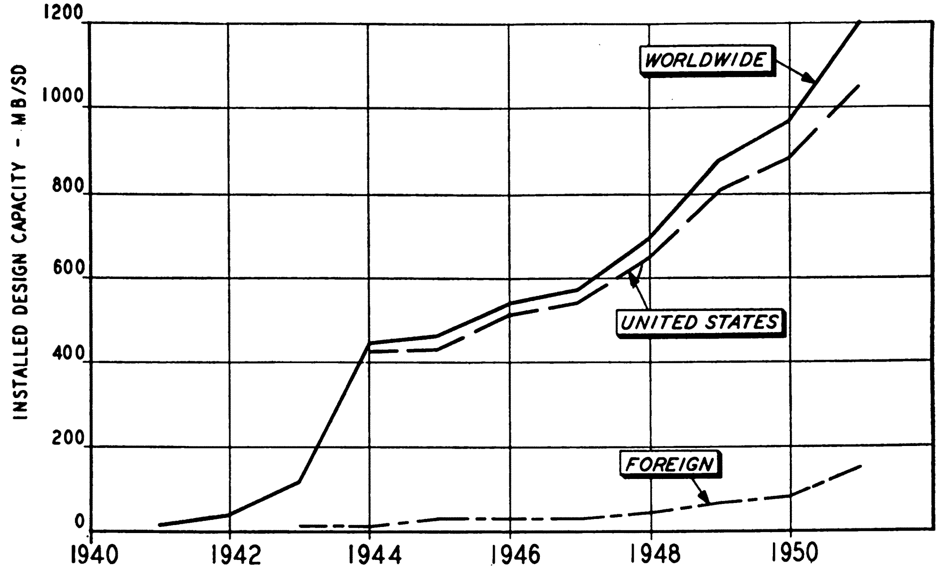

Figure 1. Growth of Fluid Catalytic Cracking Process

Engineering studies based on this evidence clearly pointed out the possibility of a radically new and improved process. A semicommercial scale pilot plant, which was being used to investigate the use of powdered solids for catalytic cracking, was accordingly rebuilt to incorporate Fluid beds and standpipes; successful operations were immediately achieved. Three 13,000-barrel-per-day plants using this technique were immediately installed, even as major improvements in the process were rendering the installations somewhat out of date. Although the major emphasis in the development was of a process nature, numerous problems of a mechanical type arose and were solved: design of suitable valves to control catalyst flow, an adequate system for recovery of solids, control of erosion, and instrumentation of a gas-solids system.

The Fluid catalytic cracking process passed to a commercial phase in the extremely short period of 3 years, largely because of intensive effort. The advent of World War II further accelerated its commercial application, particularly because its inherently flexible nature made it well suited to supply the major share of the raw material needed for the production of synthetic rubber and 100 octane aviation gasoline. The widespread use of the Fluid process is evident in Figure 1, which shows the Fluid process capacity installed during the past 10 years. Installed design capacity at the end of 1951 will be approximately 1,200,000 barrels per day; more than 700,000 barrels per stream day represent postwar installations. Actual plant throughputs are appreciably higher than the design ratings given, and are estimated to be 1,600,000 barrels per stream day at present. The Fluid catalyst cracking process currently accounts for well over half of all installed catalytic cracking capacity.

Process Description

A Fluid catalytic cracking plant is composed of three sections: cracking, regeneration, and fractionation. The cracking reaction takes place continuously in one reactor, the spent catalyst being removed continuously for regeneration in a separate vessel, from which it is returned to the cracking vessel. Continuity of flow of catalyst as well as of oil is thus accomplished, and the characteristic features of fixed-bed designs involving the intermittent shifting of reactors through cracking, purging, and regeneration cycles are eliminated.

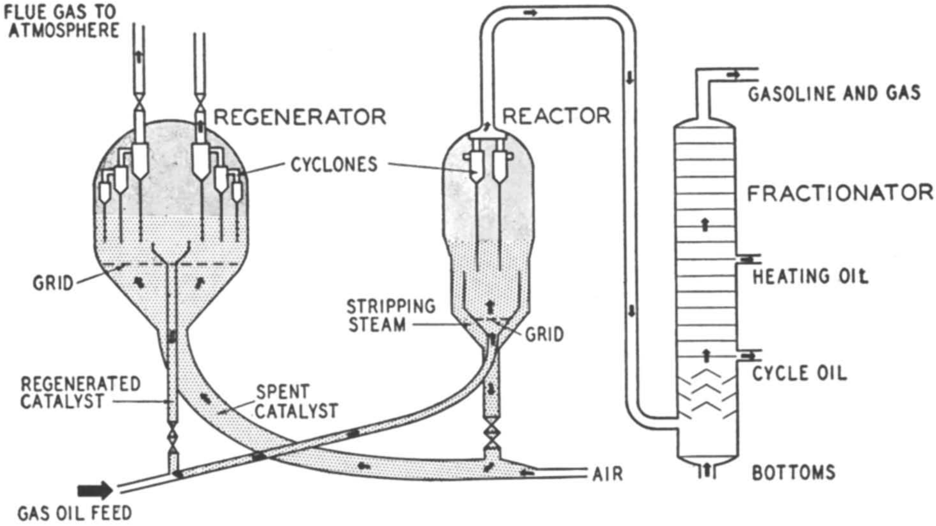

Figure 2. Fluid Catalytic Cracking Process

The flow through a typical plant representative of the latest installed postwar design (Figure 2) is as follows:

Regenerated catalyst is withdrawn from the regenerator and flows by gravity down a standpipe, wherein a sufficiently high pressure head is built up on the catalyst to allow its injection into the fresh liquid oil stream. The resulting mixture of oil and catalyst flows into the reaction vessel, in which gas velocity is intentionally low, so that a high concentration of catalyst will result. The cracking that takes place results in carbon deposition on the catalyst, requiring regeneration of the catalyst. The cracked product oil vapors are withdrawn from the top of the reactor after passing through cyclone separators to free them of any entrained catalyst particles, while the spent catalyst is withdrawn from the bottom of the reactor and is injected into a stream of undiluted air which carries the catalyst into the regeneration vessel. The products of combustion resulting from the regeneration of the catalyst leave the top of this vessel and pass through a series of cyclones where the bulk of the entrained catalyst is recovered. The regenerated catalyst is withdrawn from the bottom of the vessel to complete its cycle.

The Fluid plant as described represents an improved design over the original 13,000-barrel-per-day plants, which have been called Model I designs, and the 31 Model II plants installed during World War II. These early designs have been described in detail in numerous papers. The distinguishing feature of the Model I design was that all of the catalyst circulated passed overhead from the Fluid beds and through an extensive external cyclone recovery system. Catalyst circulation rate was also limited, requiring extensive feed preheat and vaporization equipment as well as coolers to remove regeneration heat.

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The Model II plants were of a greatly improved design, incorporating two basic major developments—the "downflow" or "bottom withdrawal" Fluid bed and the direct liquid injection of oil feed into the reaction zone. The downflow development permitted withdrawal of catalyst for circulation from the bottom of the bed.

The first development resulted in a major reduction in plant investment and maintenance costs and increased the operating flexibility substantially, because cracking intensity could be varied simply by changing the catalyst level in the Fluid bed. Investment savings were brought about by the fact that the downflow bed materially reduced the problem of catalyst recovery and permitted major simplifications in plant layout. Liquid injection permitted all available heat liberated from the combustion of coke to be utilized in the cracking section, thereby eliminating the somewhat paradoxical need for both oil preheaters and regenerated catalyst coolers in the same plant. The inherent ability of the Fluid solids technique to circulate vast quantities of catalyst made it practical to transfer the heat of regeneration and thus made possible this "heat balance" feature of the Model II plants.

Additional developments incorporated in the plant shown in Figure 2, referred to in some quarters as a Model III design, included further simplifications in the catalyst recovery system and in equipment layout. Experience obtained in the operation of the earlier designs indicated that the use of several stages of cyclones in series without a Cottrell precipitator would give satisfactory catalyst recovery and improve plant serviceability. Commercial operations of the new design have amply confirmed this. A modified plant layout with the reactor and regeneration vessels at the same elevation, together with application of engineering knowledge gained from commercial operations, resulted in other substantial investment reductions. Still other layouts involving superimposing the reactor vessel on the regenerator have resulted in substantial economies in small plants. A number of these plants, sponsored and designed by the Universal Oil Products Co., have been constructed in the past few years.

Process Features

From a process standpoint, the chief characteristic of the Fluid catalyst cracking process is flexibility. Cracking operations can be readily carried out on a wide variety of feed stocks and over a wide range of temperatures, conversion levels, and catalysts. Each of these factors affects results profoundly, making the Fluid process adaptable to widely different refinery product yield and quality requirements. Table I shows the Fluid process applied in a "conventional" refinery situation first to improve gasoline yield and octane number at the expense of the fuel oil, and then to reduce fuel oil yields further to produce either additional gasoline or middle distillates by cracking the heavy crude fractions obtainable by vacuum distillation, deasphalting, or coking.

Feed Stocks. The Fluid process is capable of processing almost any petroleum fraction ranging from a naphtha to a reduced crude. Market requirements, however,

Table I. Refinery Applications of Fluid Catalytic Cracking in Processing Typical U. S. Crude

Situation	A	B	C	D	E	F
Gas oil preparation	Atmospheric Distillation		Vacuum Distillation	Vacuum Distillation and Deasphalting	Vacuum Distillation and Coking	
Cracking	Thermal	Fluid Catalytic Cracking[a]				
Other processes	Thermal Reforming, Nonselective Polymerization, Visbreaking[b]					
Product yields						
Motor gasoline, vol. %	38	46	50	52	53	80
Heating oil, vol. %	36	28	30	31	36	0
Fuel oil, vol. %	24	19	14	11	0	0
Coke, wt. %	..	..	..	..	2	2
Motor gasoline						
F-1 clear	74	83	86	87	87	90
F-1 + 1.6 ml. TEL/gallon	84	90	92	93	93	95
F-2 clear	69	76	78	79	79	81
F-2 + 1.6 ml. TEL/gallon	78	82	83	84	84	86

[a] Cracking gas oil above heating oil except in column F.
[b] Employed in cases B and C only.

make it generally advantageous to process the medium or high boiling gas oil fractions. Typical results obtained from Fluid cracking gas oil stocks of various boiling ranges are summarized in Table II. These stocks have been cracked with no difficulty in both pilot and commercial scale operations. The higher boiling oils are less refractory and thus require considerably less catalyst to carry out the reaction. These higher boiling stocks are desirable raw materials, because they yield more gasoline and less gas and butane than the lower boiling stocks.

Table II. Effect of Feed Stock Boiling Range in Fluid Catalytic Cracking Using Silica-Alumina Catalyst

West Texas	Light Gas Oil	Heavy Gas Oil	Vacuum Gas Oil
Feed stock			
Gravity, °API	33.4	24.2	20.5
20% T.B.P., ° F.	494	690	712
50% T.B.P., ° F.	536	781	900
80% T.B.P., ° F.	587	917	1200
Conradson carbon, wt. %	0.06	0.28	2.6
Operating conditions			
Temperature, ° F.	975	975	981
Conversion, vol. %	60.5	63.2	60.0
Product distribution			
C_3 and lighter, wt. %	13.4	10.3	8.8
Butanes, vol. %	9.3	4.6	2.6
Butylenes, vol. %	7.5	11.3	8.2
Gasoline, 10 lb. RVP, vol. %	37.2	47.2	49.2
620° F. e.p. gas oil, vol. %	37.5	18.0	17.5
Heavy gas oil, vol. %	2.0	18.8	22.5
Carbon, wt. %	3.5	3.9	5.2
10-lb. RVP gasoline			
F-1 clear	99.8	97.8	94.6
F-1 + 1.5 ml. TEL/gallon	100+	99.1	96.5
F-2 clear	85.8	84.0	80.7

Fluid cracking of reduced crude has been demonstrated in both pilot and commercial plants. Typical results obtained from the 100-barrel-per-day Fluid pilot plant operating on a 50% West Texas reduced crude and using natural catalyst are shown in Table III. They reflect operations on a catalyst which has already been seriously degraded by contaminants present in the reduced crude. Although the results obtained are reasonably attractive, this operation has been utilized commercially only in isolated cases, as most refineries dispose of residual fuel fractions in other ways. The undesirable nature of the contaminating and high carbon-producing materials found in reduced crudes has led to the development of other methods for obtaining and recovering the deeper crude fractions for subsequent cracking. In the postwar years, considerable refinery equipment has been installed to make these stocks available at the expense of fuel oil by deep vacuum flashing, propane deasphalting, coking, or thermal visbreaking.

A wide variety of miscellaneous refinery streams have also been profitably processed:

Table III. Fluid Catalytic Cracking of Reduced Crude Using Activated Natural Clay Catalyst

	West Texas
Feed stock	
Gravity, ° API	25.7
20% T.B.P., ° F.	575
50% T.B.P., ° F.	770
80% T.B.P., ° F.	1030
Conradson carbon, wt. %	3.3
Ash, lb./M bbl.	48.3
Operating conditions	
Temperature, ° F.	975
Conversion, vol. %	50.0
Catalyst activity, D + L	18.0
Product distribution	
C_3 and lighter, wt. %	6.1
Excess butane, vol. %	4.0
Gasoline, 10 lb. RVP, vol. %	40.6
620° F. e.p. gas oil, vol. %	31.0
Heavy gas oil, vol. %	19.0
Carbon, wt. %	7.3
10-lb. RVP gasoline	
F-1 clear	94.6
ASTM, % at 158° F.	23.5
ASTM, % at 212° F	44.0

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thermal and catalytic cycle stocks, phenol plant extract, sulfur dioxide plant extract, petrolatum, slop, and separator oils.

Virgin or cracked naphthas can also be processed in Fluid cracking operations. First-pass catalytic naphtha was catalytically recracked to some extent during the war to improve the quality of the aviation gasoline fraction; Table IV summarizes the improvement in gasoline quality obtained by such processing of a naphtha derived from high temperature first-pass operations, and compares this gasoline quality with that obtained by single-stage, low temperature operations for production of aviation-base stock. Low temperature single-pass cracking was never carried out extensively because the demand for butylenes for alkylation raw material made high temperature Fluid operations more attractive. The Fluid cracking process for improving virgin naphthas, however, is not widely used commercially, because processes such as thermal reforming or hydroforming are more attractive.

Table IV. Aviation Gasoline Quality from Fluid Catalytic Cracking Using Silica-Alumina Catalyst

Operation	Two-Stage		Single-Stage	
Charge stock	1st pass gas oil	2nd pass naphtha	Paraffinic gas oil	Naphthenic gas oil
Reactor temperature	High	Moderate	Low	Low
Gasoline inspections				
Gravity, ° API	60.2	56.6	67.7	57.6
Reid vapor pressure	7.0	7.0	7.0	7.0
Aniline point, ° F.	66	64	122	85
Bromine No., cg./g.	63	13	20	10
Acid heat, ° F.	135	27	39	24
ASTM distillation				
I.b.p.	121	108	114	114
10%	141	139	141	140
50%	190	210	189	203
90%	292	293	274	273
F.b.p.	338	324	316	300
Antiknock quality				
F-2 clear	80.5	83.1	77.9	81.6
F-3 + 4 ml. TEL/gallon	90.6	97.0	93.3	96.0

Operating Conditions. The two most important operating variables affecting yields and product quality are conversion and temperature levels; conversion is probably the more important. Conversion is an index of the extent to which the feed stock is cracked. When a gas oil feed stock is cracked, conversion is conventionally defined as the per cent of the gas oil that is converted to material boiling below 400° F. In normal plant operations, conversion level is usually controlled by varying the space velocity and by changing the level of the Fluid reactor bed, although catalyst circulation and cracking temperature are sometimes used as controls.

Table V. Effect of Conversion Level[a] in Fluid Catalytic Cracking Using Silica-Alumina Catalyst

Operation	Once-Through Cracking				Recycle
Conversion, vol. %	35	50	65	75	75
Temperature, ° F.	950	950	950	950	950
Product distribution					
C_3 and lighter, wt. %	3.6	5.9	9.5	12.9	10.1
Butanes, vol. %	1.9	4.2	8.7	12.6	7.2
Butylenes, vol. %	3.7	6.4	8.1	7.8	7.2
C_5, 400° F., vol. %	29.6	38.6	43.0	43.0	52.6
620° F. e.p. gas oil, vol. %	35.0	31.0	24.2	18.4	17.0
Heavy gas oil, vol. %	30.0	19.0	10.8	6.6	8.0
Carbon, wt. %	2.1	3.1	6.0	9.8	8.4
Gasoline quality					
F-1 clear	95.5	96.2	96.9	97.5	96.5
F-1 + 2 ml. TEL/gallon	99.2	99.8	100.4	100.6	100.0
F-2 clear	80.3	81.7	83.0	84.1	81.9

[a] Feed stock, 26.8° API; T.B.P. 20% at 529° F., 50% at 735° F., 80% at 908° F.

When conversion levels are increased, the yields of gas, butanes, gasoline, and carbon also increase, and gasoline octane number and volatility improve. For single-pass operations on normal gas oil feed stocks, operations in the 50 to 60% conversion range have been generally found economic. Single-pass conversion operations above this range result in appreciably poorer cracking selectivity and in significantly increased investments, particularly for facilities for regeneration and recovery of light ends. However, recycle operations involving recracking of the cycle gas oil streams to partial or complete destruction can be carried out to obtain conversion levels in the 70 to 90% range without excessive degradation of gasoline to gas and coke. The manner in which product yields and quality vary with conversion level is illustrated in Table V.

Cracking temperatures between 875° and 975° F. are generally maintained in most commercial operations, although lower or higher temperatures can be used if desired. With typical gas oils, higher yields of gasoline are produced at the lower temperatures; higher cracking temperatures result in higher butylene yields, lower coke formation, and a higher octane number gasoline product. Table VI illustrates the effect of temperature on yields and quality of products.

Table VI. Effect of Cracking Temperature in Fluid Catalytic Cracking Using Silica-Alumina Catalyst

Temperature, ° F.	850	900	950	1000
Conversion, vol. %	55.0	55.0	55.0	55.0
Product distribution				
C_3 and lighter, wt. %	4.4	5.5	6.9	8.5
Butanes, vol. %	6.6	6.0	5.4	4.5
Butylenes, vol. %	3.9	5.3	7.2	9.5
C_5, 400° F., vol. %	43.3	42.1	40.6	39.0
Gas oil, vol. %	45.0	45.0	45.0	45.0
Carbon, wt. %	5.8	4.7	3.8	3.2
Gasoline quality				
F-1 clear	93.8	95.2	96.5	97.5
F-1 + 2 ml. TEL/gallon	98.1	98.9	99.9	100.5
F-2 clear	82.0	82.1	82.1	82.5

Catalyst Types. Three types of catalyst have been used in commercial Fluid operations to date—synthetic silica-alumina, activated natural clays, and synthetic silica-magnesia. The choice of catalyst depends on the product yield and quality requirements in the individual situation. Comparative yield data from the three catalysts (Table VII) indicate that the catalyst giving the higher gasoline yields simultaneously produces a gasoline of lower octane number. The natural clay catalyst gives results intermediate to the two synthetics; silica-alumina gives the highest octane number and silica-magnesia gives the highest gasoline yield.

Table VII. Effect of Catalyst Types in Fluid Catalytic Cracking of Gas Oils[a]

	Catalyst		
	Silica-alumina	Activated natural clay	Silica-magnesia
Operating conditions			
Conversion, vol. %	60	60	60
Temperature, ° F.	975	975	975
C/O ratio, wt.	9-12	7-10	6-10
Product distribution			
C_3 and lighter, wt. %	9.0	8.7	6.2
Butanes, vol. %	7.0	4.8	3.6
Butylenes, vol. %	9.0	9.2	6.4
Gasoline, 10 lb. RVP, vol. %	45.5	47.8	56.2
Gas oil, vol. %	40.0	40.0	40.0
Carbon, wt. %	2.9	3.1	2.9
10-lb. RVP gasoline			
F-1 clear	95.0	93.6	91.5
F-2 clear	81.6	79.8	79.2
ASTM, % at 158° F.	32.0	27.5	25.0
ASTM, % at 212° F.	54.0	52.0	46.0
ASTM, % at 257° F.	65.5	64.5	61.0

[a] Feed stock, 29.4° API, ASTM 50% at 701° F.

Most of the commercial Fluid plants have found it economical to continue operations on the silica-alumina catalyst which was used exclusively during the war to maximize raw material production for aviation gasoline and synthetic rubber. The lower cost of the natural clays, however, coupled with the different product distribution, has influenced a number of plants to switch to the use of this material. As the choice of catalyst is almost entirely an economic one varying with the refinery situation, the use of these three, as well as other catalysts that may be developed, can be expected to continue.

New Design Developments

The major design changes made in plants that have been installed to date have been described briefly. Many other individual improvements have also been made, but their combined impact on existing plants and in design of new units is not generally recognized.

Several Model II plants, for example, have been revamped gradually over a period of years at a very low cost; the capacity of a typical plant has been increased from its designed rate of 15,000 barrels per day to 50,000 barrels per day, by modifying operating conditions to permit substantial increases in regeneration capacity, by improving carbon-conversion relationships through spent catalyst stripper development, and by making various other process and mechanical improvements. The success of these measures in increasing stream-day capacity is attested to by the fact that over-all serviceability of the plants simultaneously improved, the on-stream time increasing from an average of 88% up to 93% in the plants operated by affiliates of the Standard Oil Co. (New Jersey).

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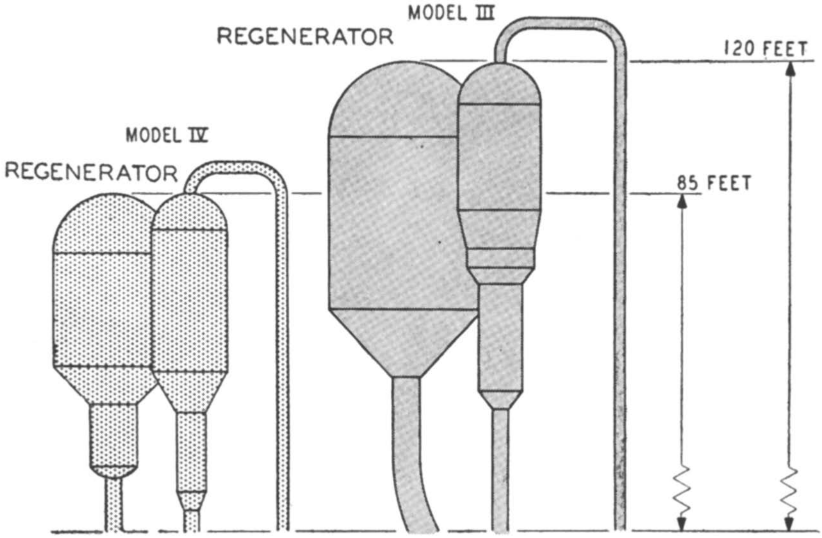

Figure 3. Schematic Comparison of Model III and IV Fluid Units

The experience obtained from increasing the capacity and improving the operation of existing Fluid catalytic units is being utilized in the designs now being offered by various engineering companies. Utilization of this experience together with new design features has markedly reduced the investment per unit of capacity of Fluid units and will reduce operating costs. One of the new designs, the Model IV, is based on improvements worked out and demonstrated on a large pilot plant scale by the Standard Oil Development Co. Figure 3 gives elevation views of a plant of the Model IV design and a plant of the same capacity representative of earlier, widely used designs. The saving in investment due to this simplified design is estimated at about 25%. Several plants of Model IV design are being processed through engineering and construction stages.

Another interesting design development that has been incorporated in several units now undergoing mechanical design or construction involves the integration of the Fluid cracking plant with crude distillation, from naphtha reforming and light ends processing. This combination unit offers a reduction in refinery handling losses, lower personnel requirements, and substantial economies in fuel, steam, and cooling water requirements. The combination units can be designed advantageously in size from 2000 to 60,000 barrels per day of crude, but are particularly suited for the small refiner. Engineering studies indicate that in the Gulf Coast area such a design results in an investment saving of 30 to 40% over a conventional refinery. Studies have also shown that a 10,000-barrel-per-day refinery using this development could manufacture products as economically as a 50,000-barrel-per-day refinery having a conventional processing sequence.

Future Outlook

Since the original development of the Fluid cracking process, a large number of improvements, mainly engineering in character, have greatly decreased investment and operating costs. Such improvements should continue, but they may be at a lower rate than in the past. Further possibilities exist for integrating Fluid cracking units into refinery operations as a whole, to give substantial savings in investment and over-all operations. Because catalysts play an important role in the catalytic cracking process further and new developments in this field may be expected.

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Intermittent and Fluid Catalytic Reforming of Naphthas

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Hydroforming was the first catalytic naphtha-reforming process to be employed commercially. Eight plants built before and during World War II synthesized nitration grade toluene and aviation gasoline components. Operation is now for motor gasoline and/or aromatics. Continued research and development work have resulted in a fluid hydroforming process offering lower investment and operating costs and improved product distribution. As it is a regenerative process, it is truly continuous and can operate on cracked or virgin naphthas of any boiling range and crude source regardless of sulfur content. Another attribute lies in the very high octane numbers that are attainable.

Twenty-five years ago low quality straight-run naphtha obtained by simple distillation from crude was used directly as motor gasoline. Not long thereafter thermal processing in the form of high-pressure high-temperature reforming was used, and in the middle thirties, other forms of thermal or pyrolytic naphtha upgrading such as naphtha reversion, polyforming, and pyrolysis were introduced.

In 1939 the first catalytic naphtha upgrading process—hydroforming—became a commercial reality, marking a distinct departure from the previous methods, which employed a combination of heat and pressure to effect the desired reaction. Numerous other catalytic processes including catalytic cracking, isomerization, alkylation, and catalytic polymerization were also launched in the late thirties. The principal reaction in hydroforming, which is essentially a dehydrogenation process normally using a molybdena-alumina catalyst, is the synthesis of aromatics. Hydroforming is conducted in the presence of hydrogen, which is derived from the process itself. The large amount of dehydrogenation taking place is the source of the recycled hydrogen. The endothermic heat of reaction, which must be supplied, is almost a direct function of the hydrogen produced. The heat of reaction can be reduced, if desired, by introduction of olefins—e.g., a thermally cracked naphtha—or by operation at high pressure.

Another dehydrogenation process was introduced before 1944 for converting methylcyclohexane to toluene over a tungsten–nickel sulfide catalyst. Substantially higher hydrogen partial pressures are employed in this process than in hydroforming.

Conventional hydroforming is carried out at temperatures of 850° to 1000° F. and pressures of 150 to 300 pounds per square inch gage. Recycle gas rates normally range between 2000 and 4000 cubic feet per barrel of naphtha. Reaction periods of 2 to 12 hours are normally employed in the fixed-bed units.

The commercial feasibility of hydroforming was demonstrated prior to and during World War II by the construction and successful operation of eight plants, seven of which were designed and built for premium grade motor gasoline and/or toluene and one for

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Table I. Laboratory Results of Thermal Reforming 248/396° F. East Texas Virgin Heavy Naphtha at 1000 Pounds per Square Inch

(Reaction pressure 1000 pounds per square inch gage)

Run No.		A	B	C	D	E	F	G	H
Maximum lead temp., ° F.		985	1000	1000	1015	1015	1030	1030	1045
Soaking volume factor		2.97	2.76	4.01	5.26	5.24	6.22	7.14	9.68
Coil volume above 900° F., cu. ft./bbl. naphtha/day		0.0218	0.0201	0.0199	0.0190	0.0190	0.0248	0.0194	0.0216
Basis 100% C_4 recovery									
Net yields, wt. % basis feed									
Gas									
$H_2 + CH_4$		1.4	1.9	2.4	3.1	2.8	3.5	4.2	5.5
C_2H_4		0.4	0.5	0.6	0.7	0.6	0.6	0.7	0.6
C_2H_6		2.1	2.3	3.0	4.0	3.4	3.9	4.6	5.6
C_3H_6		1.9	2.1	2.4	2.7	2.8	3.0	3.7	3.2
C_3H_8		3.1	3.2	4.0	4.2	5.4	5.5	6.6	6.7
Total		8.9	10.0	12.4	14.7	15.0	16.5	19.8	21.6
Gasoline (400° F. e.p.		87.8	86.4	83.1	79.3	79.3	76.6	73.3	70.6
Tar		3.3	3.6	4.5	6.0	5.7	6.9	6.9	7.8
Net yields, vol. % basis feed									
Gasoline (400° F. e.p.)		89.2	87.3	84.8	80.3	80.9	78.2	74.9	72.1
Tar		2.7	2.9	3.6	4.7	4.5	5.4	5.3	6.0
Gasoline inspections									
Gravity, °API		55.6	52.2	53.9	52.5	53.8	54.1	54.2	54.1
Reid vapor pressure, lb./sq. inch		9.0	6.9	10.2	9.8	11.6	12.2	13.2	13.4
Aniline point, ° F.		99	94	84	78	78	70	62	58
Octane No., CFRM clear		70.2	70.8	74.4	76.1	76.4	77.8	79.5	80.1
Tar inspections									
Gravity, °API		18.4	16.6	12.7	11.3	11.5	10.3	8.5	8.0
Basis reforming plus catalytic polymerization of propylene and butylene									
100% C_4 gasoline	Feed								
Yield, vol. % basis feed	..	90.8	89.7	86.3	82.4	82.6	80.0	77.1	74.1
Gravity, °API	50.3	53.2	53.1	52.4	51.8	52.0	51.8	51.4	51.8
Reid vapor pressure, lb./sq. inch	..	4.6	5.0	5.7	6.3	6.2	6.6	7.2	7.9
Octane No., CFRM	42.3	69.6	70.7	73.5	76.2	75.8	77.3	79.3	80.3
10-lb. RVP gasoline									
Yield, vol. % basis feed	..	98.4	96.6	92.3	87.4	87.7	84.6	80.7	76.9
Extraneous butanes, vol. % basis feed	..	7.6	7.0	6.0	5.1	5.2	4.6	3.7	2.8
Gravity, °API	..	57.0	55.9	55.7	53.9	54.3	54.1	53.2	53.3
Octane No., CFRM	..	71.9	72.8	75.2	77.6	77.2	78.5	80.2	81.0

desulfurization of cracked naphtha from a heavy, very sour crude. During World War II it was necessary to operate largely on a narrow-cut feed stock, preferably a C_7 heart cut or a C_7-C_8 narrow boiling fraction, to produce toluene and aviation gasoline blending agents. In this type of operation, one of these plants alone produced more than one half the toluene that went into TNT for the U. S. Armed Forces (*6*).

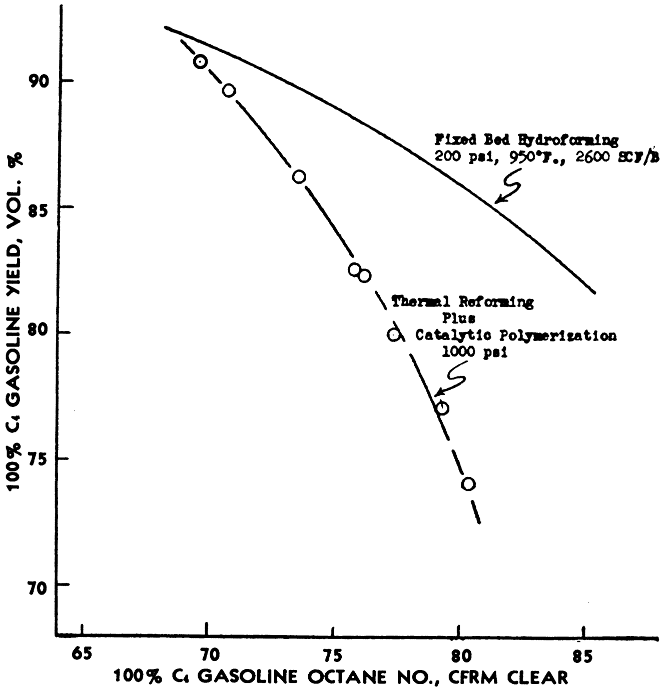


Figure 1. Thermal Reforming vs. Hydroforming of East Texas Virgin Heavy Naphtha

100% C_4 gasoline yield vs. CFRM octane, pilot plant data

Since 1946, hydroformer operation has been shifted largely to the production of automotive gasoline or benzene and aromatic solvents. These types of operation have been described in the literature in recent years (*3*, *5*, *7*).

Considerable development work has been and is now being carried out by many organizations to improve or replace the original catalyst as well as the component parts of the hydroforming unit itself. This paper describes a new and improved hydroforming process, which permits continuous operation through the use of a powdered or "fluid" catalyst. The new process is compared with thermal reforming and with the intermittent or "cyclic" fixed-bed process employed in the commercial plants mentioned above.

Thermal Reforming

The most widely used noncatalytic method of naphtha processing is thermal reforming. Propylene and butylenes from this operation are subsequently catalytically polymerized primarily for the production of high octane gasoline. Some typical laboratory results on single-pass thermal reforming of 248° to 396° F. East Texas virgin heavy naphtha at 1000 pounds per square inch are presented as Table I. The additional gasoline that would be produced by catalytic polymerization of the propylene and butylenes is also shown, and these results are compared with conventional fixed-bed hydroforming in Figure 1. It can be seen that yield advantage for hydroforming increases from 2 volume % at 72 CFRM (cooperative fuel research motor No.) octane to 12 volume % at 80

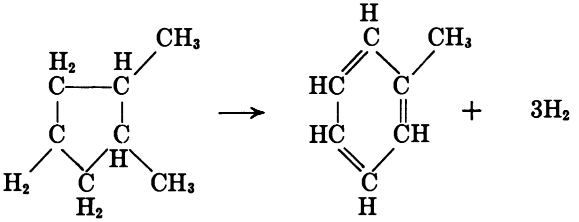
CFRM octane. Examples of other yield comparisons, employing mid-continent and West Texas heavy naphthas, are shown in Table II. The comparison using the mid-continent naphtha is based on processing the naphtha by thermal or catalytic means to such an octane level that the gasoline will rate 80 octane (CFRM) after addition of 1.5 ml. of tetraethyllead per gallon and butanes to bring the vapor pressure to 10 pounds RVP (Reid vapor pressure); in other words, the "base octane" is the rating on a sample containing lead. The yield differential in this case is seen to be almost 19 volume % in favor of hydroforming. The comparison using West Texas naphtha is at 85 octane (CFRM) after addition of 1.5 ml. of lead per gallon. At this octane level the yield differential is nearly 20 volume %.

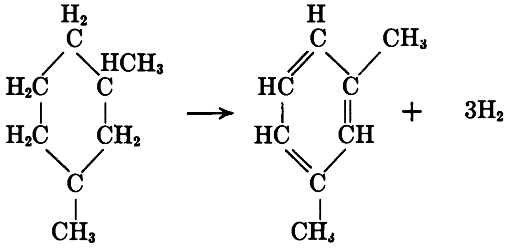
Because of its yield advantage, hydroforming invariably showed substantially higher net operating credits before depreciation in any economic comparison of the two processes, even in areas of high fuel value. However, the higher investment cost for hydroforming (the investment ratio for the two processes was on the order of 1.7 to 1) generally resulted in longer "pay-out" times for the process, even in areas of low fuel value. A period of 3 to 7 years was required to overcome this investment cost differential, depending upon the location. In cases where high octane or high aromatics yields were desired, the hydroforming process was capable of operating at a level which was inoperable for the combination of thermal reforming plus catalytic polymerization.

Hydroforming Reaction

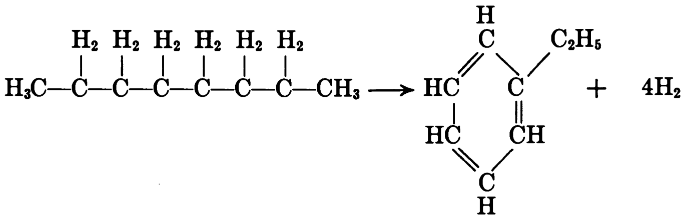
The various reactions involved in hydroforming of petroleum naphthas have been ably investigated and reported (*2–7*) during the past 10 years. Consequently, the principal ones are only briefly reviewed at this time. These are:

Dehydrogenation of naphthenes containing C_5 and C_6 ring compounds. Examples of these reactions are shown below:





Dehydrocyclization of paraffins and olefins to aromatics:



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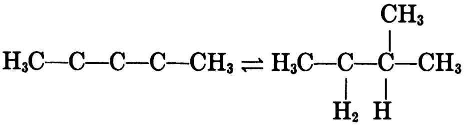
Cracking in the presence of hydrogen to form saturated hydrocarbons:

$$n\text{-}C_{11}H_{24} + H_2 \longrightarrow C_3H_8 + n\text{-}C_8H_{18}$$

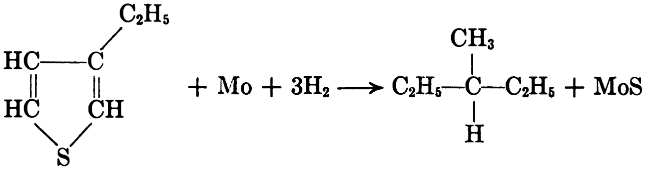
Isomerization of paraffins:



$$H_3C{-}C{-}C{-}C{-}CH_3 \rightleftharpoons H_3C{-}\underset{H_2}{C}{-}\underset{H}{\overset{CH_3}{C}}{-}CH_3$$

The pentane fractions produced in the hydroforming process will normally contain approximately 60% isopentanes.

Desulfurization:



Thiophene-type sulfur is found in cracked naphthas and is not removed in most gasoline-treating processes, except with very high losses in liquid yield.

The extent to which the various reactions occur is a function of operating conditions, feed stock, and condition of catalyst.

The Catalyst

In the middle thirties the reactions of naphtha and certain compounds known to be present in naphtha were being studied in university and industrial laboratories. One of the problems was to find a catalyst that was capable of synthesizing an aromatic from a paraffin. It was reasoned that the hydrogenation-dehydrogenation oxide-type catalysts such as molybdenum oxide and chromium might possess suitable activity at temperatures well below those employed in thermal reforming.

Table II. Yield Comparison of Conventional Fixed-Bed Hydroforming with Thermal Reforming Plus Catalytic Polymerization

Feed stock	Mid-continent Heavy Naphtha, 52° API		West Texas Heavy Naphtha, 49.5° API	
Process	Hydroforming	Thermal reforming plus catalytic polymerization	Hydroforming	Thermal reforming plus catalytic polymerization
Yield-quality data				
Finished gasoline, vol. %	97.6	78.8	95.4	75.7
RVP, lb./sq. inch	10		10	
CFRM octane (clear)	70	74.1	77.0	79.6
Base octane, CFRM	80		85	
Ml. TEL/gal. to base octane	1.5		1.5	
Fuel oil, vol. %	1.3	3.3	1.6	4.6
Fuel gas (FOE), vol. %[a]	7.7	16.2	7.3	16.8
Extraneous butanes required, vol. %	7.0	..	5.9	..
Excess butanes, vol. %	..	..	..	1.7

[a] FOE denotes "fuel oil equivalent" and is calculated on heating value basis.

Initially tests were conducted in glass equipment at atmospheric pressure. It was discovered that a more durable catalyst could be made if the Group VI metal oxide were deposited on an alumina support. The best support found for this reaction was alumina, and the first commercial catalyst was made by impregnating a material very similar to "activated alumina" with a molybdenum salt solution, followed by drying and calcining at a temperature above 1000° F. Interestingly enough, the supported chromia catalyst which showed a marked superiority over the supported molybdena catalyst at atmospheric pressure for dehydrocyclization of *n*-heptane was markedly inferior to the latter catalyst under substantial hydrogen partial pressure (hydroforming conditions); consequently, the molybdena-alumina catalyst was used for hydroforming. When this catalyst was put in a commercial unit its life was disappointingly short, and the selectivity declined—e.g., the yield of a given octane number gasoline was lower. The deterioration of the catalyst was also accomplished by agglomeration, resulting in gas channeling through the beds. In less than 3 months it was necessary to discard the catalyst. Presumably the activity declined because of some combination of high temperature and steam partial pressure during catalyst revivification.

Laboratory investigation revealed that sodium, which was present in the support to the extent of several tenths of 1%, had a profound effect on stability and activity of the molybdena-alumina catalyst. Over a period of time it was possible to alter the procedure for preparing the support on successive occasions until the catalyst contained much less than 0.1% sodium oxide. The reduction in sodium content of the support was immediately reflected in improved catalyst life. Ultimately the life was extended to 9 to 12 months before replacement. Various forms of alumina have been used as a support, including alumina gel and a stabilized alumina gel. Molybdena-alumina catalyst has been employed exclusively in the eight commercial plants previously referred to. Today the majority of refiners who operate hydroformers are using molybdena on alumina gel as a catalyst. The molybdic oxide content of the catalyst is somewhat below 10%. Although similar to the original catalyst as far as chemical composition is concerned, it possesses superior activity and life.

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Feed Stock

The role that the feed stock plays in the hydroforming process is of considerable significance. In general, the more naphthenic stocks, especially those in which cyclohexane homologs predominate, will give the best yield-octane relationships and the highest aromatic yields. The various reactions do not all occur at the same rate—for example, C_6 ring naphthene dehydrogenation proceeds very rapidly, whereas the conversion of paraffins to aromatics is very much slower. Likewise, the side reactions with C_6 ring naphthenes are almost negligible; such is not the case with paraffins.

Besides feed source, feed boiling range and molecular weight are also important, with C_7, C_8, C_9, and C_{10} compounds responding most favorably. The C_8-C_9 fraction will tend to give a high yield of gasoline and hydrogen and low carbon formation. Material boiling higher than gasoline tends to be less selective.

Hydroforming Unit

The conventional "fixed-bed" hydroforming unit for motor gasoline production has been described in detail (*5*). A typical unit is equipped with four reactors filled with granular or pelleted catalyst; two reactors are always in series on reaction and two are in the process of prepurging, regeneration, and afterpurging. The reactors are switched from reaction through purging and regeneration steps and back to reaction by an electrical cycle-controller. In the majority of units the reactants are "reheated" between the two reactors in series.

The necessity for regeneration arises from the fact that catalyst activity declines with time on reaction, owing to small deposits of carbonaceous material and sulfur compounds on the catalyst. This deposit, of course, varies with feed stock, catalyst, and process conditions. The regeneration is carried out by oxidizing the deposits on the catalyst with a stream of air diluted to 2 to 3% oxygen with recycled flue gas.

The reaction products are recovered and fractionated in a two- or a four-tower fractionating and absorbing system, depending on whether or not hydrogen enrichment is employed. Hydrogen enrichment is accomplished by passing the hydrogen-containing gas, which separates from the liquid product at operating pressure and 80° to 100° F., countercurrent to a stream of oil in an absorption tower. The oil removes the heavier ends (hydrocarbons) from the gas stream, thereby enriching the gas leaving the top of the adsorber prior to recycling. This method of operation was desirable to incorporate into

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the design when it was planned eventually to run on a heavy naphtha with a relatively high ratio of C_5 to C_6 ring naphthenes for the production of high octane gasoline. The products of the recovery system are:

A stabilized 400° F. end-point gasoline

A hydrogen-rich gas which may be substantially free of hydrocarbons heavier than propane

A highly aromatic product boiling above 400° F. (the yield of which depends on the feed stock boiling range and on the process conditions)

Commercial Hydroforming Data

An example of the performance of a commercial unit on a 265/328° F. feed stock to produce motor gasoline is presented in Table III. The plant produced 101.2 to 105.6 volume % of 94.4 to 97.2 leaded research octane, 10-pound RVP gasoline (including 11.5 to 12.4 volume % extraneous butanes).

Table III. Hydroformer Data on Motor Gasoline Operation of Baytown Plant

Run No.		1	2	3
Catalyst		Kellogg Low Soda (MoO_3 on Activated Alumina)		
Operating conditions				
Temperature, ° F.		865	882	902
Pressure, lb./sq. inch gage		250		
Feed rate, bbl./day		14800	24290	24090
Space velocity, vol./hour/vol.		0.6	1.0	1.0
Recycle gas rate, standard cu. ft./bbl. feed		3390	2900	2740
% H_2 in recycle gas		76	84.5	77.4
Yields, basis feed				
Butanes, vol. %		1.0	0.9	2.0
C_5 and heavier product, vol. %		92.0	93.2	89.4
100% C_4 gasoline, vol. %		93.0	94.1	91.4
Dry gas (C_3 and lighter), wt. %		4.9	4.1	6.7
Coke, wt. %		0.17	0.17	0.33
10-lb. RVP gasoline, vol. %		103.5	105.6	101.2
Quality data	Feed	C_5 and heavier product		
Gravity, °API	49.4	44.9	45.7	44.7
ASTM distillation				
I.b.p., ° F.	265	152	170	153
5%	272	237	246	236
10%	275	255	260	252
50%	288	288	288	287
90%	311	322	322	321
95%	320	337	336	337
E.p.	328	382	380	396
Octane Nos.				
CFRR clear	53.0	85.5	81.5	86.4
CFRR + 1.5 ml. TEL/gal.	66.0	92.0	89.1	92.6
CFRR + 3.0 ml. TEL/gal.	71.5	94.9	91.8	95.0
CFRM clear	51.5	74.4	71.7	75.4
CFRM + 1.5 ml. TEL/gal.	..	82.8	81.1	83.1
CFRM + 3.0 ml. TEL/gal.	..	84.4	82.9	84.9
Reid vapor pressure, lb./sq. inch	..	2.3	1.8	1.9
Bromine no.	..	2.2	2.3	3.0
Toluene, vol. % basis feed	0.2	1.6	1.5	1.8
Xylenes, vol. % basis feed	13.0	22.6	20.9	21.8
Heavier aromatics, vol. % basis feed	7.1	19.4	18.2	19.1
10-lb. RVP gasoline				
Octane No., CFRR + 3 ml. TEL/gal.	..	97.1	94.4	97.2
Extraneous butanes, vol. % basis feed	..	11.5	12.4	11.8
Tail gas, million standard cu. ft./day	..	10.0	15.2	18.7
% H_2	..	76.0	84.5	77.4
% C_1	..	18.1	6.3	11.0
% C_2	..	1.5	3.6	5.2
% C_3	..	1.7	1.8	3.3
% C_4	..	0.4	0.7	1.2

Another fixed-bed hydroformer is operating for production of aromatic blending components for aviation gasoline (115/145 grade). These data are summarized in Table IV. The toluene and C_8 aromatic concentrates, and in some cases the light hydroformate also, can be blended with alkylates and isopentane to meet all specifications for 115/145 grade aviation gasoline. If it were desirable to operate for higher liquid recovery, the quality or quantity of aviation blending agents would be reduced.

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Table IV. Aviation Gasoline Operation

(S.O. of Indiana plant hydroformer)

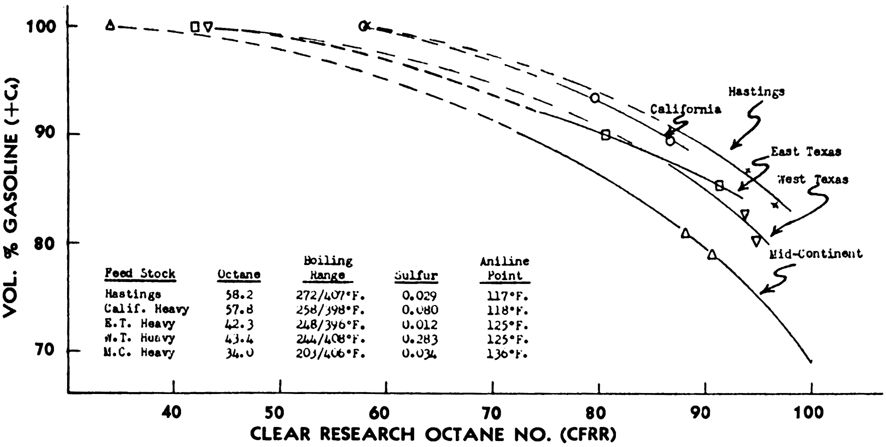
Operation No.	1	2
Catalyst	MoO$_3$ on alumina gel	
Feed inspections	Mid-continent plus West Texas	
Gravity, °API	57.9	57.5
ASTM distillation		
I.b.p., ° F.	191	200
10%	200	207
50%	224	225
90%	262	264
E.p.	296	296
Dimethylcyclopentanes, vol. %	8.8	7.6
Ethylcyclopentane + methylcyclohexane, vol. %	7.5	7.5
Benzene, vol. %	2.5	2.7
Toluene, vol. %	4.8	5.1
Xylenes and ethylbenzene, vol. %	3.3	4.6
Octane No., CFRR clear	58.4	57
Operating conditions		
Temperatures, ° F.		
Naphtha transfer line	1024	1024
Recycle gas transfer line	1050	1050
Reheat outlet	1026	1026
Primary reactor	935	935
Secondary reactor	965	970
Pressure, lb./sq. inch gage	250	250
Feed rate, bbl./day	9530	9750
Space velocity, vol./hour/vol.	0.52	0.53
Recycle gas rate, standard cu. ft./bbl. feed	2750	3000
% H_2	..	78
Reaction period, hours	4.5	4.5
Yields, basis feed		
100% C_4 gasoline, vol. %	75.0	74.3
Butanes, vol. %	7.5	5.8
Polymer, vol. %	3.7	3.7
Light hydroformate, vol. %	34.3	32.1
Toluene concentrate, vol. %	18.6	17.5
Xylene concentrate, vol. %	14.6	18.9
Dry gas (C_3 and lighter), wt. %	17.1	17.6
Coke, wt. %	1.2	1.3
Hydrogen produced, standard cu. ft./bbl. feed	525	560
Quality, 100% C_4 hydroformate		
Benzene, vol. %	10.4	9.5
Toluene, vol. %	23.0	22.8
C_8 aromatics, vol. %	15.8	14.7
Octane No., CFRR clear	95.3	96.7
Aviation octane no.	+4.6 ml. TEL/gal.	+ 4.4 ml. TEL/gal.
F-4 blending index		
Light hydroformate	114	105
Toluene concentrate	219	202
Xylene concentrate	211	209
F-3 blending octane		
Light hydroformate	96.8	93.7
Toluene concentrate	99.6	97.2
Xylene concentrate	97.2	103

Pilot Plant Data

Conventional Fixed-Bed Hydroforming. Pilot plant results on Hastings, California, East Texas, West Texas, and mid-continent heavy naphthas for the fixed-bed process are summarized in Table V; the feed stock inspections are presented as Table VI. Yield-octane curves based on these data are on Figure 2, where the wide variation from naphthas of different compositions is apparent. The following tabulation shows the relative yields at two octane levels:

Feed Stock	Octane No. of Product, CFRR 85 Vol. % gasoline (C_4-400)	 95
Hastings, 272/407° F., 58.2 CFRR	91.6	85.6
California, 258/398° F., 57.8 CFRR	90.6	..
East Texas, 248/396° F., 42.3 CFRR	88.2	82.7
West Texas, 244/408° F., 43.4 CFRR	88.2	80.4
Mid-continent, 203/406° F., 34.0 CFRR	83.2	75.0

Desulfurization. The removal of sulfur compounds from both virgin and cracked naphthas has long taxed the ingenuity of petroleum technologists. At the present time, a number of processes are available for reducing sulfur content and altering the structure of certain classes of sulfur compounds. The change in octane number of the gasoline is invariably slight; however, the responsiveness to tetraethyllead is oftentimes improved. Ordinarily, the extent of desulfurization depends on the type and amount of sulfur compounds in the feed stock, far better percentage sulfur removal being obtained when low-sulfur virgin naphthas are processed. Cracked stocks with appreciable amounts of relatively stable sulfur compounds, particularly of the thiophene type, are attacked but little by the methods generally employed.



Feed Stock	Octane	Boiling Range	Sulfur	Aniline Point
Hastings	58.2	272/407°F.	0.029	117°F.
Calif. Heavy	57.8	258/398°F.	0.080	118°F.
E.T. Heavy	42.3	248/396°F.	0.012	125°F.
W.T. Heavy	43.4	244/408°F.	0.283	125°F.
M.C. Heavy	34.0	203/406°F.	0.034	136°F.

Figure 2. Conventional Fixed-Bed Hydroforming of Various Virgin Naphthas

Kellogg MoO_3 on activated alumina catalyst
100% C_4 gasoline yield *vs.* CFRR octane, pilot plant data

An interesting type of operation which was conducted on a pilot plant was a combination of hydroforming and desulfurizing, employing a dehexanized California thermally cracked naphtha containing 2.2% sulfur. The sulfur compounds were largely of the ring type and consequently very resistant to most desulfurization processes. The pertinent data are presented as Table VII. The process could be operated with or without an extraneous supply of hydrogen-containing gas. An example of an operation at conditions resulting in hydrogen consumption is shown in the experiment conducted at 150 pounds per square inch. The yield of gasoline was greater or the desulfurization better than in tests at 75 to 100 pounds operating on the hydrogen production side. Without the use of extraneous hydrogen, correlation of the data indicated that 85.8 volume % 100% C_4 gasoline (or 89.3 volume % total 100% C_4 recovery liquid) of 75 CFRM octane would be produced. This gasoline would be low in Reid vapor pressure (thus permitting addition of appreciable extraneous butanes) and would contain on the order of 30% olefins, which would raise the research octane above that normally obtained with hydroformates.

Whether the sulfur is eliminated as a metal sulfide, as shown in the section entitled "Hydroforming Reaction" and burned off during regeneration of the catalyst, or is eliminated directly as hydrogen sulfide is a function of the pressure and catalyst holding time. At high pressure the bulk of the sulfur is eliminated as hydrogen sulfide.

Fluid Catalyst Hydroforming Process

Apparatus. It was believed that fluid hydroforming might be a considerable improvement over the fixed-bed process. The following incentives existed for development of fluid hydroforming:

The investment and operating costs would probably be greatly reduced.

The operation could be conducted at steady state conditions with periodic addition of fresh catalyst and removal of spent catalyst without a shutdown.

The catalyst life would probably be longer, because of better temperature control during regeneration.

The complicated time cycle control system could be eliminated.

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Table V. Typical Pilot Plant Data for Conventional Fixed-Bed Hydroforming of Various Virgin Heavy Naphthas

Experiment No.	1	2	3	4	5	6	7	8	9	10
Feed stock	Hastings		California		East Texas		West Texas		Mid-continent	
Catalyst	Kellogg MoO_3 on Activated Alumina									
Operating conditions										
Pressure, lb./sq. inch gage	200	200	200	200	200	200	200	200	200	200
Temperature, ° F.	975	975	930	930	945	930	945	940	960	955
Recycle gas rate, standard cu. ft./bbl.	2510	2610	2625	2700	2500	2890	2750	2660	2640	2640
Hydrogen in recycle, vol. %	69	67	(66)	(61)	68	70	51	45	62	58
Space velocity, vol./hour/vol.	1.07	0.76	1.00	0.50	1.04	0.51	0.50	0.50	0.70	0.64
Reaction period, hours	6	6	20	20	4	6	6	6	6	6
Yields on feed										
Gasoline (100% C_4), wt. %	87.4	84.2	93.7	89.8	90.6	86.9	83.9	81.9	82.3	80.9
Dry gas (C_4-free), wt. %	8.9	10.6	4.2	6.9	7.8	10.6	11.4	13.3	12.2	15.6
Carbon, wt. %	0.4	0.8	0.3	0.7	0.1	0.2	1.7	1.8	1.1	1.2
Gasoline (100% C_4), vol. %	86.6	83.4	93.4	89.3	89.9	85.2	82.6	80.1	80.8	78.7
Total liquid (100% C_4), vol. %	89.2	86.4	94.8	91.3	91.1	87.0	84.7	82.2	84.2	80.5
Butanes, vol. %	..	..	..	..	..	..	..	..	5.3	6.0
Hydrogen produced, standard cu. ft./bbl.	604	598	260	350	563	676	597	652	520	600
Dry gas produced, standard cu. ft./bbl.	..	..	..	..	838	1030	..	..	941	1145
Mole % H_2	..	..	..	..	67.2	65.6	..	..	55.5	52.1
Mole % CH_4	..	..	..	..	15.8	17.2	..	..	19.3	22.4
Mole % C_2	..	..	..	..	12.3	6.6	..	..	13.9	14.7
Mole % C_3	..	..	..	..	4.7	10.6	..	..	11.3	10.8
Corrected gasoline inspections, 100% C_4 gasoline										
Gravity, °API	42.4	42.7	46.5	46.0	48.7	46.4	46.4	45.8	47.9	47.7
Reid vapor pressure, lb./sq. inch	5.1	6.2	2.9	4.7	4.3	6.5	6.7	6.1	6.9	7.3
ASTM (D + L) at 158° F., vol. %	..	..	..	..	6.5	9.0	..	..	9.6	11.5
ASTM end point, ° F.	399	404	396	397	391	396	403	402	400	400
Octane No.										
CFRM clear	83.2	84.9	72.8	78.0	73.6	81.3	83.0	83.8	78.5	80.4
CFRR clear	94	96.5	79.7	86.8	80.7	91.4	93.8	94.8	88.2	90.7
CFRR + 3 ml. Pb[a]	101	103	92.5	96.5	93	99.3	100.8	101.5	97.4	98.9

[a] Values obtained by correlation of lead susceptibility data.

In PROGRESS IN PETROLEUM TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1951.

Table VI. Feed Stocks Used in Pilot Plant Tests

	Fixed-Bed Hydroforming				
Description	Hastings	California	East Texas	West Texas	Mid-continent
Gravity, °API	44.0	47.0	50.3	50.0	50.1
ASTM distillation					
I.b.p., ° F.	272	258	248	244	203
5%	286	273	270	264	265
10%	300	278	278	270	280
20%	310	285	288	278	301
30%	320	291	294	284	316
40%	328	297	302	296	326
50%	336	305	310	304	338
60%	344	313	317	316	349
70%	353	323	327	330	358
80%	363	336	338	348	369
90%	378	356	356	368	382
95%	390	375	376	390	392
E.p.	407	398	396	408	406
% Recovery	98.0	98.5	98.0	98.0	98.5
Residue	1.0	0.9	1.2	0.5	1.0
Loss	1.0	0.6	0.8	1.5	0.5
Octane No., CFRR	58.2	57.8	42.3	43.4	34.0
Reid vapor pressure, lb./sq. inch	...	0.2	...	0.2	0.5
Aniline point, ° F.	117	118	125	125	136
Aromatics, vol. % (ASTM)	18	14	14	18	12
Olefins, mole %	0.3	1.5	0	2	0.7
Sulfur, wt. %	0.029	0.08	0.01	0.283	0.034

The multiple reactor system could probably be eliminated. The reactor would not have to be designed for regeneration as well as reaction.

The reaction could be operated isothermally, a type of operation which was demonstrated to be superior from a selectivity standpoint in fixed-bed studies.

Regeneration technique could be greatly simplified.

Regeneration would be easier to control and cheaper to carry out.

Utilization of catalyst would be more efficient. Channeling has sometimes been experienced in fixed-bed plants, resulting in ineffectiveness of a portion of the catalyst bed. Trouble due to channeling has sometimes been experienced during regeneration.

A flow sheet for a 3-barrel-per-day fluid hydroformer is shown as Figure 3.

Flow through Reaction System. The feed naphtha was pumped from the oil feed tank, *T*-1, on scale to the preheater, *B*-2, and thence to the bottom of the reactor, *D*-1, which was 45 feet long.

The reactor effluent passed through porous stainless steel filters at the top of *D*-1 to a water-cooled condenser and then to the high pressure separator, *F*-4. The liquid from the high pressure separator was removed through a level control valve at the bottom of *F*-4 to a low-pressure receiver, *F*-7, which was surrounded by ice water.

The flash gas from the top of *F*-7 passed through a wet-test meter to a sample tap and was vented to the atmosphere. Condensed liquid product was collected through a valve at the bottom of *F*-7, weighed, and analyzed.

High pressure separator gas from the top of *F*-4 passed through the unit pressure control valve, to the suction of the gas compressor, *J*-3. Compressed recycle gas was piped from the fourth stage of the compressor to knock-out drums; a small portion went to bleed and blowback rotameters for *D*-1, and the major portion went to a flow control valve, *FRC*-1, and orifice, through *B*-2, and back to the bottom of the reactor. A portion of this stream was also drawn off ahead of the flow control valve through a wet-test meter for catalyst charging from catalyst charge drum *F*-2 to catalyst storage vessel, *F*-1, or for transfer of catalyst from *F*-1 to the top of *D*-1, or for pressuring spent catalyst drum, *F*-3, to aid in transfer of spent catalyst from this point to the regenerator.

Flow through Regeneration System. Air was drawn in through a filter to the suction of air compressor *J*-2. The desired air for regeneration passed from a knockout drum to a wet-test meter and subsequently to a control valve, *FRRC*-1. This flow control valve was arranged to control the air rate in a given ratio to the recycle flue gas—or nitrogen—stream to the regenerator. Air from *FRRC*-1 then passed through an orifice to preheater *B*-1 and to the bottom of the regenerator.

Regenerator flue gas left the top of regenerator through porous stainless steel filters to pressure control valve *PRC*-6, to an orifice, and a sample tap. From this point the flue gas could be vented, as shown on the flow sheet for nitrogen-air once-through operation, or recycled to the regenerator through a scrubber, knock-out drums, and compressor (none of which is shown on the flow sheet).

Nitrogen was used for once-through operation. It was obtained from a plant storage tank and passed to a plant pressure regulator and flow control valve, *PIC*-1, to an orifice. It then passed through or around preheater *B*-1, to a check valve. From this point it was routed either to the bottom of the regenerator or through the catalyst transfer line from the bottom of the regenerator to the top of the *F*-1. When flue gas recycling was employed, it passed through *PIC*-1 and traveled the same paths as described for the nitrogen.

Using the fluid hydroforming pilot plant, the catalyst has also been regenerated with undiluted air by charging air to a mixture of carbonized and uncarbonized catalyst.

The pilot plant employed intermittent rather than continuous catalyst transfer, because of the difficulties involved on this scale in circulating the small flows of catalyst required.

At regular intervals (usually every 4 hours) a portion of the spent carbonized catalyst was withdrawn from reactor *D*-1 to catalyst drum *F*-3. The catalyst drum was then pressured with gas and a carrier gas flowed through the transfer line from the bottom of the catalyst drum to the top of the regenerator, *D*-2. When the valve below the catalyst drum was opened, the catalyst flowed up through the transfer line into *D*-2. An equivalent amount of regenerated catalyst was then transferred in a similar manner from the regenerated catalyst storage vessel, *F*-1, bottom to the top of reactor *D*-1 via a transfer line to replace the "spent" carbonized catalyst which was withdrawn. When the regenerator catalyst level reached a predetermined point by virtue of the periodic transfers of "spent" catalyst into it, the regeneration step was carried out. Then the regenerated catalyst was transferred by means of gas pressure and carrier gases to the storage vessel, *F*-1.

Fluid Hydroforming for Motor Gasoline

A large volume of data has been compiled from the fluid hydroforming pilot plant just described. These data show definite improvement over fixed-bed hydroforming from a yield standpoint. A yield comparison has been made graphically on Figure 4 for operation on mid-continent heavy naphtha. Detailed data for this comparison are presented

Table VII. Combination Hydroforming-Desulfurization of High-Sulfur Dehexanized California Cracked Naphtha (217/426° F.)

Run No.		1	2	3	From correlation of 20 tests
Operating conditions					
Pressure, lb./sq. inch gage		75	150	100	100
Temperature, ° F.		980	950	945	940
Gas rate, standard cu. ft./bbl.		2600	4700	5000	5000
% Hydrogen in gas		54	51[a]	51[a]	Equil.
Naphtha space velocity, vol./hour/vol.		1.58	0.81	0.40	0.8
Reaction period, hours		2.1	2.1	2.1	1.0
Yields, basis feed					
100% C_4 gasoline, vol. %		87.7	91.7	85.7	85.8
Butanes, vol. %		2.1	2.2	4.3	(4)
Polymer, vol. %		4.0	3.2	3.5	(3.5)
Dry gas (C_3 and lighter), wt. %		4.7	4.7	7.5	(7)
Carbon, wt. %		2.4	1.1	2.8	2.8
Sulfur, wt. %[b]		0.9	2.1	2.1	2.2
Hydrogen produced, standard cu. ft./bbl.		180	−60	145	187
Dry gas produced, standard cu. ft./bbl.		355	145	440	
Gasoline inspections					
100% C_4 recovery gasoline					
Gravity, °API		47.1	50.9	49.8	
Reid vapor pressure, lb./sq. inch		3.3	3.8	6.0	(4.5)
Octane No., CFRM clear		76.0	75.6	77.7	75
Debutanized gasoline	Feed				
Gravity, °API	46.0	46.2	49.9	47.8	
Reid vapor pressure, lb./sq. inch	0.6	1.5	2.1	2.6	
Aniline point, ° F.	89	66	76	57	
Olefins, mole %	(50)	(53)	24	26	(30)
Sulfur, wt. %	2.2	1.49	0.07	0.10	0.08
Octane No., CFRM clear	69.4	75.6	75.2	77.1	
Polymer gravity		11.9	12.4	10.1	

[a] Gas fed once-through (51% H_2).
[b] Eliminated as H_2S.

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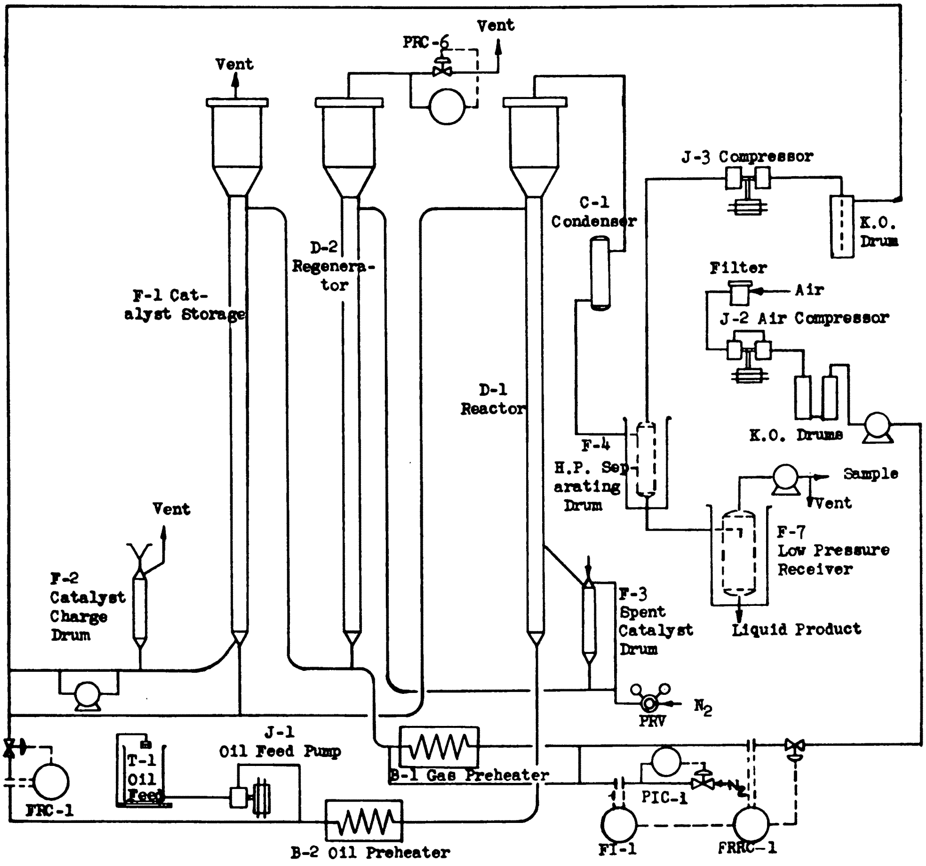

Figure 3. Flow Diagram of Fluid Hydroformer Pilot Plant

in Table VIII for the fluid catalyst pilot plant; the fixed-bed pilot plant data were taken from a published paper (*5*) and converted from CFRM to CFRR (cooperative fuel research, research No.) octane numbers. It can be seen that fluid hydroforming gave 2.0 to 2.5 volume % higher gasoline yields (including butanes) at a given octane than the conventional process. The comparative feed naphtha inspections were as follows:

Process	Fixed-Bed	Fluid-Bed
Gravity, °API	50.1	52.7
ASTM distillation		
I.b.p., ° F.	203	208
5%	265	242
10%	280	254
50%	338	311
90%	382	379
95%	392	398
E.p.	406	425
Aniline point, ° F.	136	137
Octane No., CFRR clear	34	36

The fluid hydroforming process can be made to produce a liquid product containing very little material boiling above 400° F. by operating with a feed stock possessing an end point somewhat below 400° F. Examples of yields from a 204/373° F. mid-continent heavy naphtha are given in Table IX. Inspections of the feed stock appear as the first column of this table. The yields of gasoline from these operations—where the liquid is substantially all 400 end point gasoline—are superior to those plotted for higher end-point feed stocks in Figure 4. Excellent "octane appreciation," which is the differential

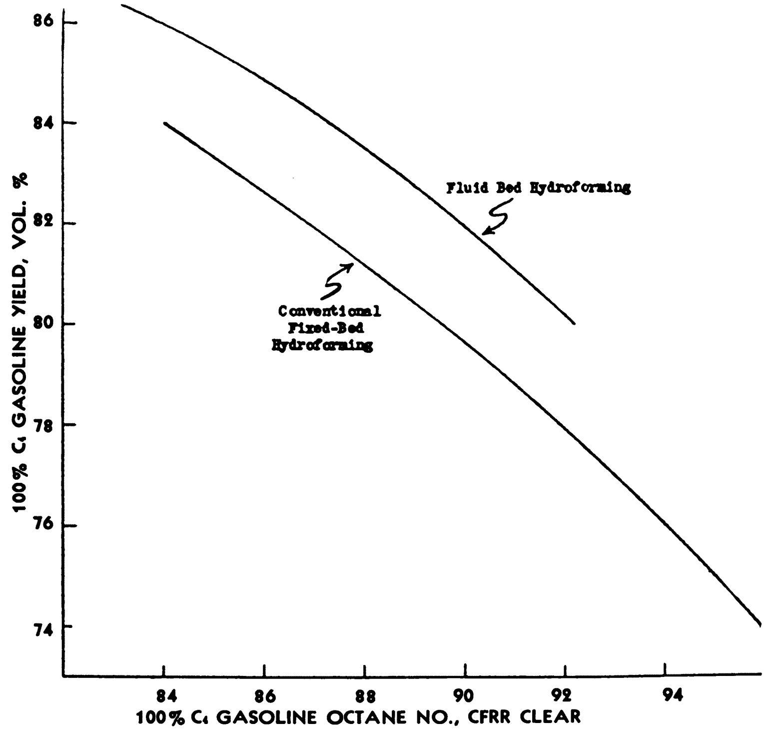

Figure 4. Fluid vs. Conventional Fixed-Bed Hydroforming of Mid-continent Heavy Naphtha

100% C_4 gasoline yield vs. CFRR octane, pilot plant data

between CFRR and CFRM clear octanes and lead response are obtained on these hydroformates. Over the octane range of gasoline currently marketed, the Reid vapor pressures are sufficiently low to permit addition of appreciable butanes to make a finished 10-pound Reid vapor pressure motor gasoline.

Figure 5 illustrates graphically the relationship between 10-pound Reid vapor pressure gasoline yield and leaded research octane number (CFRR + 3 ml. of tetraethyllead per gallon) for this series of experiments. At 500 pounds per square inch a yield of 83 volume % of 100 leaded research octane was obtained, while at 250 pounds per square inch this yield was increased to 88 volume % of 100 leaded research octane gasoline.

Pilot plant data for fluid catalyst hydroforming of East Texas heavy naphtha are summarized in Table X, and are compared with fixed-bed hydroforming pilot plant data in Figure 6. Comparative data on the East Texas naphthas employed in the pilot plant comparison of Figure 6 are shown in the following tabulation:

Process	Fixed-Bed	Fluid Bed
Gravity, °API	50.3	48.7
ASTM distillation		
I.b.p., ° F.	248	236
5%	270	260
10%	278	267
50%	310	308
90%	356	375
95%	376	400
E.p.	396	430
Aniline point, ° F.	125	116
Octane No., CFRR clear	42.3	44.9

A yield advantage on the order of 2 volume % is again shown for the fluid catalyst process. The yields of 10-pound Reid vapor pressure gasoline when blending with extra-

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neous butanes for vapor pressure were 92.4 to 94.7 volume % and the leaded research octanes (CFRR + 3 ml. of tetraethyllead per gallon) were 98.7 to 98.9. Carbon yields from the 236/430° F. East Texas heavy naphtha at this octane level were 0.2 to 0.27 weight %. With any particular feed stock, carbon formation is primarily a function of hydrogen partial pressure.

Fluid Hydroforming for Aviation Gasoline

The fluid catalyst pilot plant has also been operated for the production of high aromatics yields to produce aromatic blending components for 115/145 grade aviation gasoline. A 200° to 300° F. (true boiling point) fraction from a mixed crude source was used as the feed stock. Inspections of this fraction are tabulated below:

Gravity, °API	56.1
ASTM distillation	
I.b.p., ° F.	214
5%	224
10%	226
50%	240
90%	273
95%	281
E.p.	291
Aniline point, ° F	118
Octane No.	
CFRM clear	55.3
CFRR clear	58.1
Sulfur, wt. %	0.027

The process data are summarized in Table XI. The operation was conducted at a pressure of 250 pounds per square inch and a temperature of 934° F. The dependentanized liquid product was fractionated into three cuts called preaviation, aviation, and postaviation blending agents. The yields of these three products were 22.8, 33.5, and 12.6 volume %, respectively. The aviation blending agent had an F-3 blending octane number (1-C) of 100 and an F-4 blending index number (3-C) of 216. The clear research oc-

Table VIII. Typical Pilot Plant Data on Fluid Catalyst Hydroforming

(Kellogg MoO_3 on Al_2O_3 gel catalyst, mid-continent heavy naphtha)

Experiment No.	1	2	3	4
Feed stock	208/425° F. Mid-continent Naphtha			
Operating conditions				
Pressure, lb./sq. inch gage	500	500	500	500
Temperature, ° F.	911	920	927	938
Yields on feed				
Gasoline (100% C_4), wt. %	86.7	83.2	82.6	79.9
Dry gas (C_4-free), wt. %	10.6	13.9	14.7	17.0
Carbon, wt. %	0.05	0.38	0.41	0.30
Gasoline (100% C_4), vol. %	87.3	83.5	82.5	79.9
Total liquid (100% C_4), vol. %	89.3	85.3	84.2	82.0
Butanes, vol. %	5.3	6.7	7.1	8.4
Gasoline (10-lb. RVP), vol. %	91.4	85.4	83.6	80.0
Total liquid (10-lb. RVP), vol. %	93.4	87.2	85.3	82.1
Extra butanes for 10-lb. RVP, vol. %	4.1	1.9	1.1	0.1
Hydrogen produced, standard cu. ft./bbl.	415	315	360	408
Dry gas (C_4-free), standard cu. ft./bbl.	786	801	875	1008
Mole % H_2	52.9	39.3	41.2	40.5
Mole % CH_4	21.8	24.7	25.5	25.4
Mole % C_2	13.8	19.5	18.4	19.0
Mole % C_3	11.5	16.5	14.9	15.1
Corrected gasoline inspections,				
100% C_4 gasoline				
Gravity, °API	53.2	51.8	51.8	51.8
Reid vapor pressure, lb./sq. inch	7.2	8.7	9.2	9.9
ASTM (D + L) at 158° F., vol. %	10.2	14.4	14.7	18.2
ASTM end point, ° F.	399	403	399	403
Aromatics, vol. % (ASTM)	41	44	44	47
Olefins, mole %	1.3	1.5	1.4	1.0
Octane No.				
CFRM clear	73.2	79.2	80.3	82.4
CFRR clear	80.3	88.0	89.5	92.2
CFRR + 3 ml. TEL	93.5	98.3	99.2	101.0
10-lb. RVP gasoline				
Octane No.				
CFRM clear	73.9	79.5	80.4	82.4
CFRR clear	81.1	88.3	89.7	92.2
CFRR + 3 ml. TEL	94.5	98.6	99.4	101.0

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Table IX. Pilot Plant Data on Fluid Catalyst Hydroforming

(204/373° F. mid-continent heavy naphtha Kellogg MoO_3 on Al_2O_3 gel catalyst)

Experiment No.		1	2	3	4
Operating conditions					
Pressure, lb./sq. inch		500	500	500	250
Temperature, ° F.		884	900	932	928
Yields on feed					
Total liquid (100% C_4), wt. %		90.4	88.0	83.8	87.4
Dry gas (C_4-free), wt. %		7.7	11.6	16.0	12.2
Carbon, wt. %		0.29	0.43	0.25	0.39
Weight balance, %		97.8	97.3	97.4	98.0
Total liquid (100% C_4), vol. %		91.2	87.3	82.8	85.3
Butanes, vol. %		4.3	5.9	8.7	6.4
Gasoline (10-lb. RVP), vol. %		98.3	91.1	82.4	88.7
Extra. butanes for 10-lb. RVP, vol. %		7.1	3.8	−0.4	3.4
Hydrogen produced, standard cu. ft./bbl.		450	453	449	681
Dry gas (C_4-free), standard cu. ft./bbl.		686	833	993	1066
Mole % H_2		65.6	54.4	45.2	63.8
Mole % CH_4		13.0	18.1	23.4	15.0
Mole % C_2		11.4	15.0	17.1	11.4
Mole % C_3		10.0	12.5	14.3	9.8
Corrected gasoline inspections, 100% C_4 gasoline	Feed Stock				
Gravity, °API	56.1	50.8	50.0	53.7	51.5
Reid vapor pressure, lb./sq. inch	1.0	5.7	7.6	10.2	7.9
ASTM (D + L) at 158° F., vol. %	..	8.0	10.3	18.5	12.9
Aromatics, vol. %	8	33.0	37.5	44.5	46.0
Olefins, mole %	..	0.9	0.7	0.9	1.2
Octane No.					
CFRM clear	39	..	75.3	82.2	81.1
CFRR clear	41	76.6	82.2	91.3	90.2
CFRR + 3 ml. TEL	..	(91.2)	94.7	100.3	99.0
10-lb. RVP gasoline					
Octane No.					
CFRM clear		..	76.0	82.2	81.5
CFRR clear		77.5	83.0	91.3	90.7
CFRR + 3 ml. TEL		(92.0)	95.5	100.3	99.6

Table X. Pilot Plant Data on Fluid Catalyst Hydroforming of East Texas Naphtha

(Kellogg MoO_3 on Al_2O_3 gel catalyst)

Experiment No.	5	6
Feed stock	East Texas 236/430° F. Naphtha	
Operating conditions		
Pressure, lb./sq. inch gage	500	500
Temperature, ° F.	902	921
Yields on feed		
Gasoline (100% C_4), wt. %	87.1	88.6
Total liquid, wt. %	90.2	90.6
Dry gas, C_4-free, wt. %	9.5	9.2
Carbon, wt. %	0.27	0.20
Weight balance, %	97.9	97.9
Gasoline (100% C_4), vol. %	87.3	88.4
Total liquid (100% C_4), vol. %	89.8	90.0
Butanes, vol. %	5.1	4.6
Gasoline (10-lb. RVP), vol. %	92.4	94.7
Total liquid (10-lb. RVP), vol. %	94.9	96.3
Extra. butanes for 10-lb. RVP, vol. %	5.1	6.3
Hydrogen produced, standard cu. ft./bbl.	342	326
Dry gas produced, C_4-free, standard cu. ft./bbl.	682	651
Mole % H_2	50.2	50.2
Mole % CH_4	22.1	21.7
Mole % C_2	14.9	14.9
Mole % C_3	12.9	13.2
Corrected gasoline inspections, 100% C_4 gasoline		
Gravity, °API	49.2	48.5
Reid vapor pressure, lb./sq. inch	6.8	5.9
ASTM (D + L) at 158° F., vol. %	20.4	19.5
ASTM end point, ° F.	394	401
Aromatics, vol. % (ASTM)	47	48.5
Olefins, mole %	1.1	1.1
Octane No.		
CFRM clear	78.6	78.1
CFRR clear	87.8	87.3
CFRR + 3 ml. TEL	98.0	(97.6)
10-lb. RVP gasoline		
Octane No.		
CFRM clear	79.3	78.9
CFRR clear	88.5	88.1
CFRR + 3 ml. TEL	98.9	(98.7)

tane number of the postaviation fraction was greater than 100 CFRR. The clear research octane number of the total liquid product containing all the butanes was determined to be 95.6 CFRR. The yield of this material was 83 volume %.

Fluid Hydroforming Economics

The economics of the fluid catalyst process represent a considerable improvement over the conventional fixed-bed process. This is attributed to reduced investment and operating costs in addition to the improved yield picture. The investment cost now visualized is very nearly the same as that for the thermal reforming plus catalytic polymerization combination mentioned previously. Consequently, the "pay-out" times are now shorter than for that process in high or low fuel cost areas.

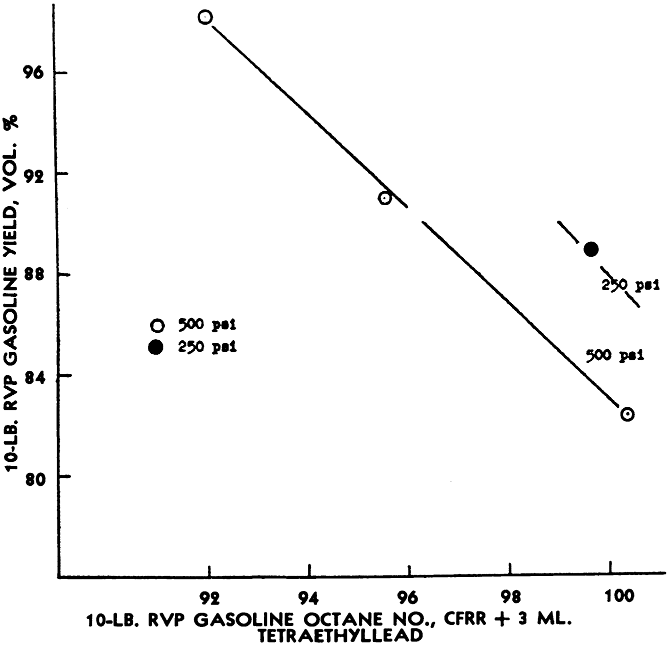

Figure 5. Fluid Catalyst Hydroforming

204/373° F. mid-continent heavy naphtha
Kellogg MoO_3 on Al_2O_3 gel catalyst
10-lb. RVP gasoline yield vs. leaded research octane
Mid-continent feed stock

° API	56.1
I.b.p., ° F.	204
E.p., ° F.	373
Aniline point, ° F.	133
Octane	
CFRM, clear	39.1
CFRR, clear	40.9
Sulfur, wt. %	0.031

An economic balance sheet for fluid catalyst hydroforming employing an East Coast construction, operating cost, and price structure is presented as Table XII. The motor gasoline has a 10-pound Reid vapor pressure and an octane rating of 95 CFRR + 3 ml. of tetraethyllead per gallon. The feed stock has an ASTM boiling range of 204/373° F., a 56.1°API gravity, a 138° F. aniline point, and an octane number of 39.1 CFRR. The economics indicate a pay-out time of one year.

Table XI. Fluid Catalyst Hydroforming for Aromatics or 115/145 Grade Aviation Gasoline Production

[214/291° F. virgin naphtha (predominantly East Texas). Kellogg MoO_3 on Al_2O_3 gel catalyst]

Operating conditions	
Pressure, lb./sq. inch gage	250
Temperature, ° F.	934
Yields on feed	
100% C_4 liquid, vol. %	83.0
C_4 fraction, vol. %	6.9
Butanes	0.1
Isobutane	2.9
n-Butane	3.9
C_5 fraction, vol. %	7.2
Isopentane	3.8
n-Pentane	3.4
Depentanized liquid, vol. %	68.9
Preaviation blending agent (125/232° F.), vol. %	22.8
Aviation blending agent (232/286° F.), vol. %	33.5
Postaviation blending agent (286+ ° F.), vol. %	12.6
Dry gas, wt. %	13.6
Carbon, wt. %	0.37
Hydrogen produced, standard cu. ft./bbl.	741
Dry gas produced, standard cu. ft./bbl.	1196
Vol. % H_2	61.9
Vol. % CH_4	17.4
Vol. % C_2	11.3
Vol. % C_3	9.4
Benzene, vol. %	1.6
Toluene, vol. %	15.8
C_8 aromatics, vol. %	15.4
C_9 aromatics, vol. %	6.8
Inspections of products	
Debutanized liquid	
Aromatics, vol. %	59
Octane No., CFRR clear	95.2
Preaviation blending agent	
Reid vapor pressure, lb./sq. inch	2.9
ASTM distillation	
I.b.p., ° F.	164
10%	178
50%	190
90%	210
E.p.	226 d.p.
Aromatics, vol. %	25.8
Octane No.	
CFRR clear	73.4
CFRR + 3 ml. TEL	91.8
Blending octane No., F-3 + 4.6 ml. TEL	94.2
Blending index No., F-4 + 4.6 ml. TEL	89.5
Aviation blending agent	
Reid vapor pressure, lb./sq. inch	0.4
ASTM distillation	
I.b.p., ° F.	234
10%	242
50%	250
90%	266
E.p.	277
Aromatics, vol. %	86.3
Blending octane No., F-3 + 4.6 ml. TEL	100
Blending index No., F-4 + 4.6 ml. TEL	216
Postaviation blending agent	
Reid vapor pressure, lb./sq. inch	0.5
ASTM distillation	
I.b.p., ° F.	292
10%	298
50%	306
90%	320
E.p.	369
Aromatics, vol. %	95.5
Octane No., CFRR clear	>100

Summary

The new process offers the following advantages:

Higher gasoline yield.

Considerably reduced investment and operating costs. This has been brought about mainly through elimination of multiple reactors and accessory equipment, elimination of time cycle controllers, greatly simplified method of regeneration, and elimination of reheat furnaces.

Longer on-stream time, due to the ability to control any decline of catalyst activity with age by periodic additions of fresh catalyst.

A very high octane "ceiling." Debutanized gasolines with an octane number of over 95 Research clear have been produced, with attendant carbon yields of less than 0.4%. Such octane numbers come about largely because of the ability of the process to produce

Table XII. Economic Balance Sheet for Fluid Catalyst Hydroforming of 204/373° F. Mid-Continent Naphtha

[Production of 10-lb. RVP gasoline of 95 octane (CFRR+3 ml. TEL/gal.) 7500-barrel-per-day unit, East Coast price structure]

	Unit Cost/Bbl.	Bbl./Day	Vol. %	Cost/Day,$
Credits				
10-lb. RVP gasoline	$5.04	6800	92.0	34,800
Fuel gas (fuel oil equivalent)	$1.90	803	10.7	1,525
Total credits				36,325
Debits				
Stock cost				
Naphtha	$3.36	7500	100.0	25,200
Extra. butanes	$2.42	300	4.0	726
Direct operating cost				
Total process costs				1,868
Ethylizing	0.2 cent/ml. TEL/gal.			1,713
Taxes and insurance	2% of investment			123
Royalties	7 cents/bbl.			462
Total debits (before depreciation)				30,092
Credits less debits (before depreciation				6,233
Investment, $				2,250,000
Payout time, years				0.99

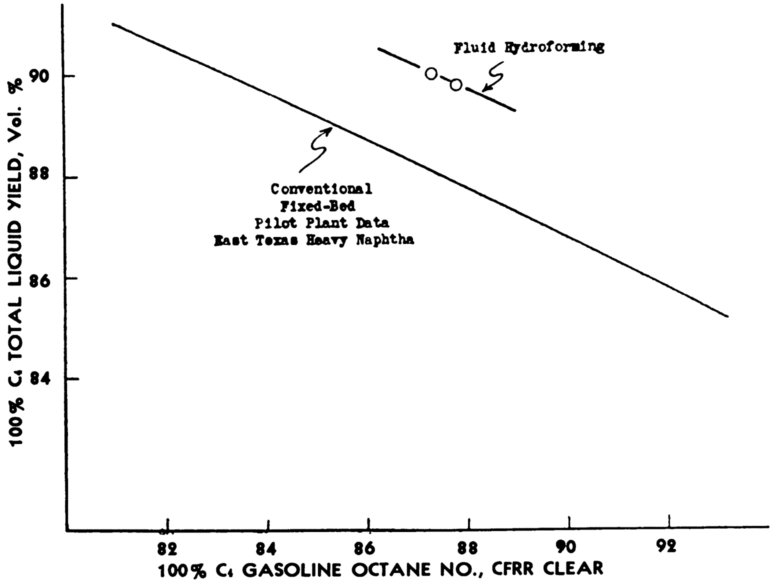

Figure 6. Fluid vs. Conventional Fixed-Bed Hydroforming of East Texas Naphthas

100% C_4 total liquid yield vs. CFRR octane, pilot plant data

high aromatic yields. A high yield of aviation blending agent for 115/145 grade aviation gasoline results from such operation.

Considerable flexibility with regard to feed stock boiling range and composition. It is possible to handle both cracked and virgin heavy stocks without difficulty.

Essentially isothermal operation and elimination of "channeling" result in better utilization of catalyst than is possible in the fixed-bed units.

The general use of automotive engines now being marketed with compression ratios higher than 7 or 8 to 1 awaits the widespread production of motor fuels on the order of 95 CFRR octane clear (*1*). The fluid catalyst hydroforming process is capable of meeting this challenge.

Acknowledgments

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Fluid Hydroforming

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The Standard Oil Development Co. has been active in the field of Fluid hydroforming, and the results obtained in general parallel those presented by the authors of the previous paper. Data are presented on the operation of a 50-barrel-per-day large scale Fluid hydroforming pilot plant.

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The excellent work of The M. W. Kellogg Co. in adapting the Fluid technique to hydroforming has been well summarized by McGrath and Hill. The Standard Oil Development Co. has also been active in this field and the results presented by the authors in general parallel those found in its laboratories. Its interest in this process dates back to World War II, and since that time considerable data have been obtained in the laboratory on the development of a Fluid hydroforming process. This work, as in the studies by Kellogg, has shown the process to possess the basic advantages of an isothermal reactor, continuous operation, and the simplicity inherent in the Fluid technique.

The results of several years of operation of a 4-barrel-per-day Fluid hydroforming pilot plant were reported by E. V. Murphree at the World Petroleum Congress at The Hague in June 1951. More recently, a 50-barrel-per-day large scale Fluid hydroforming pilot plant has been placed in operation at the Esso Laboratories at Baton Rouge, La. The operation of this pilot plant has been very satisfactory from the start. Good catalyst flow has been maintained along with excellent retention of catalyst in the system. Isothermal reactor and regenerator operation have been obtained, and no difficulty has been experienced with catalyst attrition or catalyst regeneration. The product distribution data have been essentially equal to those obtained in the smaller pilot plant work.

Results of operation on the 50-barrel pilot unit are presented in Table I. Figures from the Kellogg report are shown for reference purposes, although strictly these cannot be compared with the 50-barrel-per-day results because of considerable difference in feed stock type, and because the molybdenum catalysts used were not identical.

The feed stock for the Kellogg run was derived from mid-continent crude, whereas

Table I. Results of Operation

	50 Bbl./Day Unit	Kellogg Table 9, Expt. 4
10-lb. RVP gasoline		
CFRR ON, clear	95.0	90.7
+ 3 ml. TEL	...	99.6
Yields on feed		
Gasoline (10 lb. RVP), vol. %	90.3	88.7
Extraneous C_4 for 10 lb. RVP, vol. %	4.5	3.4
Total liquid (100% C_4^+), vol. %	85.8	85.3
Butanes, vol. %	5.5	6.4
Dry gas, wt. %	10.5	12.2
Carbon, wt. %	0.8	0.4
Feed		
I.b.p., ° F.	208	204
F.b.p.	344	373
° API	55.2	56.1
ON—CFRM	50.4	39
CFRR	51.5	41

the 50-barrel-per-day plant charged mixed Louisiana naphthas. As optimum operating conditions have not yet been fully established on the 50-barrel-per-day unit, these results are not necessarily the best obtainable. Emphasis is placed on production of maximum liquid yields, and minimum carbon formation is not critical in Fluid hydroforming as in fixed-bed operation.

Kellogg has reported that the investments for Fluid hydroforming are about the same as for thermal reforming plus polymerization. Figures which the Standard Oil Development Co. has prepared indicate that investments for the Fluid hydroforming route are considerably below those for thermal reforming, particularly when the investment for loss in gasoline capacity through thermal reforming is taken into account at higher octane levels.

In its work, the Development Co. has been impressed by the flexibility of the process. As no functional process limitations such as maximum carbon or restrictive high temperatures in regeneration exist in the Fluid system, units can be designed for any octane number product or any type of feed. Moreover, the merits of improved catalysts can be exploited to maximum advantage.

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Comparison of Platforming and Thermal Reforming

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A comparison has been made of Platforming and of thermal reforming from the standpoint of yield–octane number relationships, product properties, hydrocarbon types, and with respect to the nature of chemical reactions responsible for improvement of octane number. Comparison is based on studies of thermal reforming in a commercial operation at a Pennsylvania refinery and in a pilot plant on a mid-continent naphtha; and in pilot plants and laboratory Platforming on the same stocks.

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Two methods of upgrading straight-run gasolines are Platforming and thermal reforming. Platforming utilizes a supported platinum catalyst and is conducted in the presence of recycled hydrogen. Thermal reforming employs heat and pressure. The comparison in this study is made on the basis of product distribution, hydrocarbon-type analysis, and yield-octane relationship. Because thermal reforming, in many instances, is carried out in conjunction with polymerization of the gaseous by-products of the operation, the comparison has been extended to a yield-octane relationship including the polymerization step following thermal reforming.

Thermal Reforming

Thermal reforming of virgin gasoline fractions for octane number improvement had become an established commercial refining tool in the early thirties (*4, 8, 14*). Essential features of the process flow in use today do not differ markedly from those employed in those early plants. In 1933, Egloff and Nelson (*4*) pointed out that in certain instances some advantages were obtained by removing the high octane number light ends of a virgin gasoline by prefractionation, and reforming only the heavier low octane number naphtha. They also pointed out that, as the octane number of the final blended product is increased, a point is eventually reached where the advantage of prefractionation disappears. It then becomes more economical to reform the entire gasoline. Egloff, Nelson, and Zimmerman (*5*) present experimental data to illustrate these points.

Correlations presented in the middle thirties enabled the prediction of octane number improvement resulting from thermal reforming (*7, 21*). They have continued to appear in the literature (*6, 20*). Improvement of the octane number of naphthas has been the principal function of thermal reforming, but Egloff (*3*) discusses its usefulness also for the production of light olefins which provide feed stocks for alkylation or polymerization processes. To show the distinct improvement in the yield-octane relationship realized by the catalytic polymerization of C_3 and C_4 olefins produced by thermal reforming, Mase and Turner (*16*) present experimental data at various reforming severities for two naphthas.

Because the octane number of straight-run gasoline can be improved to a certain extent by either a process involving chemical change or by the addition of tetraethyllead,

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Advances in Chemistry; American Chemical Society: Washington, DC, 1951.

the refiner must establish the optimum extent of each operation producing the desired octane number at minimum expense. Economical appraisal of thermal reforming and tetraethyllead addition for octane improvement was discussed in an early paper by Gary and Adams (*7*), and more recently by Feuchter (*6*).

The economics of thermal reforming and hydroforming of sweet and sour heavy straight-run naphthas have been compared recently by McLaurin, McIntosh, and Kaufman (*15*). They concluded that the relative economics of the two processes were virtually the same for both feed stocks.

Most thermal reforming operations are performed at cracking coil transfer temperatures in excess of 1000° F., and at transfer pressures in the range of 500 to 1000 pounds per square inch. Equipment following the cracking heater resolves the heater effluent into a residuum, gasoline, and appropriate light hydrocarbon fractions. Often this fractionation equipment is common with other thermal cracking processes in the refinery. In a few instances straight-run gasolines are charged with light recycle to the light oil coil of two-coil thermal cracking units in order to accomplish mild reforming.

Platforming

Since the announcement of the Universal Oil Products Co. Platforming process in April 1949 (*17*), a number of publications (*1, 2, 9–13, 19*) have described the operating variables and chemistry of the process. Particular features of the Platforming process involve use of a platinum catalyst and the recycling of a hydrogen-rich gas. The following reactions take place in Platforming: dehydrogenation, hydrocracking, isomerization, desulfurization, dehydrocyclization.

These reactions are relatively selective in character, so that high yields of high octane fuels can be realized. Furthermore, these reactions can be made to proceed to different extents, so that fuels of variable aromaticity and volatility can be produced. A basic reason for this is the relatively low temperature of operation employed in Platforming, permitting the elimination of undesirable thermal decomposition effects.

In view of the number of reactions that take place, the process is not limited to selected charging stocks. A highly naphthenic stock is upgraded largely by the production of

Table I. Commercial Thermal Reforming of Pennsylvania Gasoline Laboratory Inspections of Feed and Liquid Products

	Straight-Run Gasoline Charge		Debutanized Thermal Reformate	Blend of Thermal Reformate and Polymer Gasoline		
	As received	Debutanized		As produced	Debutanized	Residuum
API	63.6	60.7	57.8	62.1	58.1	12.5
Total sulfur, wt. %	0.07	0.07	0.06	0.06	0.07	0.06
Mercaptan sulfur, wt. %	0.004	0.0068	..	0.014	0.0107	..
Reid vapor pressure	10.3	3.1	..	12.4	4.4	..
Bromine number	..	..	..	52.0	60.3	..
Octane No.						
F-1 clear	50.7	44.4	77.3	82.4	80.0	..
F-1 + 3 ml. TEL/gal.	70.2	65.2	89.0	91.2	89.9	..
F-2 clear	49.8	43.9	69.2	75.1	72.2	..
F-2 + 3 ml. TEL/gal.	68.9	64.4	80.6	83.2	81.1	..
Viscosity, S.U.S. at 210° F.	..	..	..	..	..	50.2
100 ml. distillation						
Initial boiling point, ° F.	96	128	124	93	123	268
5%	137	167	147	122	151	463
10	159	180	155	137	161	512
30	217	220	186	180	193	585
50	255	254	227	224	229	634
70	294	292	273	269	270	671
90	345	336	327	342	332	727
95	370	355	354	384	361	..
End point	389	384	385	402	403	..
% recovered	96.5	98.5	98.0	96.5	98.5	..
% bottoms	1.2	1.2	1.0	1.2	1.2	..
% loss	2.3	0.3	1.0	2.3	0.3	..
Light hydrocarbon content, vol. %						
C_3H_8	1.5	..	..	0.8	..	..
C_4H_8	..	..	..	2.7	..	..
C_4H_{10}	5.5	..	..	7.0	..	..
Total C_5	8.5	..	..	13.5	..	..
C_6+	84.5	..	..	76.0	..	..

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Table II. Over-all Material Balance on Thermal Reformer and Polymerization Unit

	Bbl./Day	Vol. %	°API	Lb./Hour	Wt. %
Straight-run gasoline charge	1683	100.0	63.6	17,779	100.0
Products					
Total fuel gas (37,635 standard cu. ft./hour)				2,904	16.3
Reformate + polymer blend (12.4 lb. RVP)	1333	79.2	62.1	14,194	79.8
Residuum	20	1.2	12.5	286	1.6
Product recovery				17,384	97.7

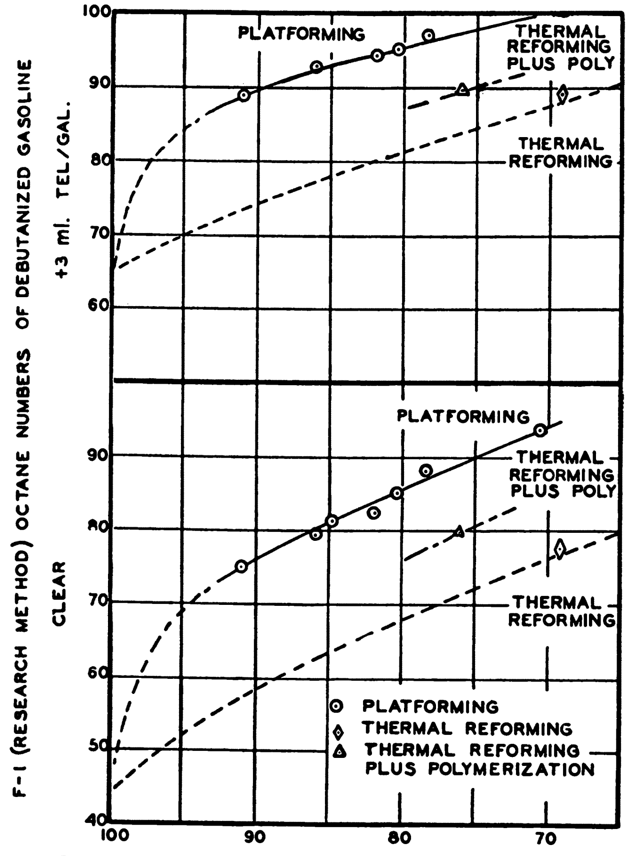

Figure 1. Comparison of F-1 (Research Method) Octane Numbers of Debutanized Gasolines from Platforming and Thermal Reforming of Pennsylvania Straight-Run Gasoline

Table III. Over-all Material Balance on Thermal Reformer and Polymerization Unit

(Debutanized basis)

	Bbl./Day	Vol. %	°API	Lb./Hour	Wt. %
Debutanized gasoline charge	1565	100.0	60.7	16,786	100.0
Products					
C_4 and lighter gas	. .	. .	. .	3,049	18.2
Debutanized polymer gasoline	108	6.9	60.5	1,160	6.9
Debutanized thermal reformate	1085	69.3	57.8	11,917	71.0
Residuum	20	1.3	12.5	286	1.7
Product recovery				16,412	97.8
Debutanized reformate + polymer	1193	76.2	58.1	13,077	77.9

[a] Over-all material balance was calculated assuming that C_4 and lighter hydrocarbons in actual gasoline charged, passed through reformer without change.

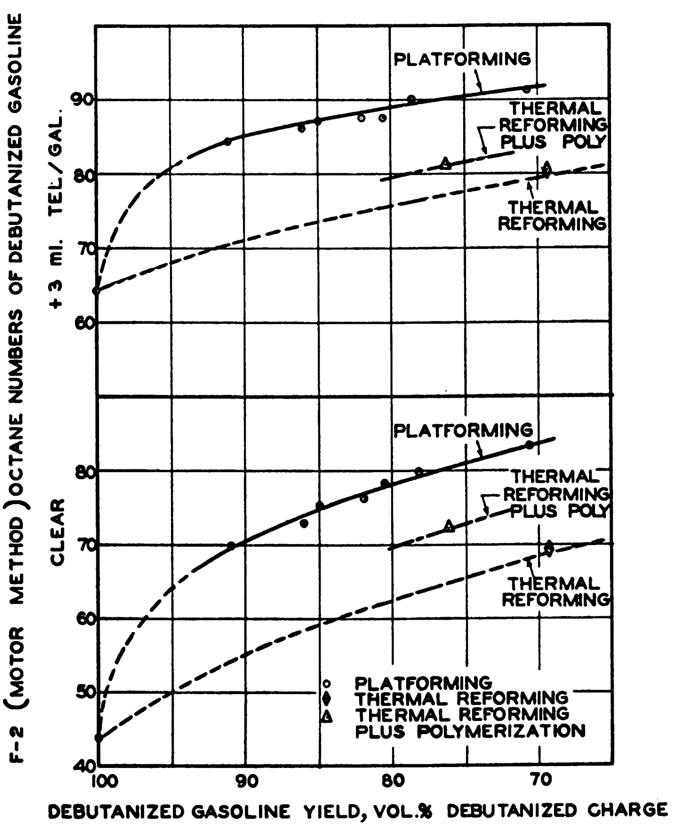

Figure 2. Comparison of F-2 (Motor Method) Octane Numbers of Debutanized Gasolines from Platforming and Thermal Reforming of Pennsylvania Straight-Run Gasoline

aromatics, and a highly paraffinic stock is upgraded to a considerable extent by the hydrocracking, isomerization, and dehydrocyclization reactions.

Information recorded on the relative rates of dehydrogenation, hydrocracking, and isomerization (*12*), show that dehydrogenation is a faster reaction than isomerization and the latter is faster than hydrocracking. Work on pure compounds (*11*) has shown that in the Platforming of *n*-heptane the tendency to split at the C_1-C_6, C_2-C_5, and C_3-C_4 linkages is in the ratio of 3:5:26, indicating a selective effect of splitting paraffinic molecules at the center linkages. In the case of aromatic hydrocarbons, the major reactions are those of removing large alkyl groups and redistributing small alkyl groups, thus producing polymethylated benzenes.

Further work on Platforming has established the operability of utilizing blends of straight-run and cracked gasolines to produce Platformates of a quality similar to that resulting from Platforming straight-run stocks. Similarly, Platforming of fractions from catalytically cracked gasolines has been shown to produce aviation gasoline base stocks (*18*).

Another application of the Platforming process has been to produce aromatic hydrocarbons. Of particular interest is the production of benzene. It has been shown (*10*) that yields up to 92% of theoretical based on methylcyclopentane and cyclohexane content can be obtained from light straight-run fractions. Similarly, toluene and xylenes are produced in high yields from the corresponding C_7 and C_8 fractions.

Commercial application of Platforming for the production of motor fuel was begun at the Old Dutch Refining Co., Muskegon, Mich., in October 1949. Two runs have been

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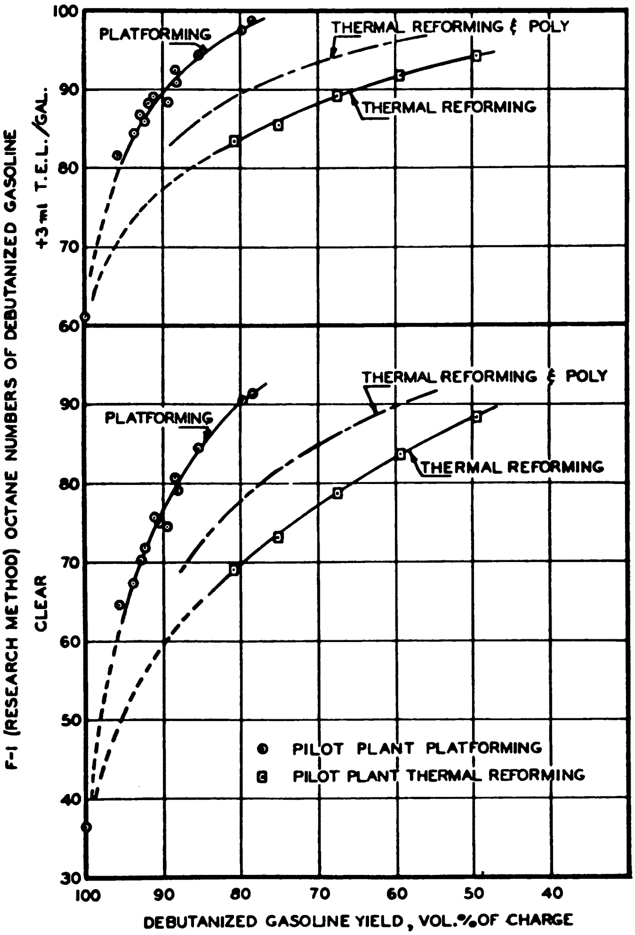

Figure 3. Comparison of F-1 (Research Method) Octane Numbers of Debutanized Gasolines from Platforming and Thermal Reforming of Mid-continent Straight-Run Naphtha

completed. The first amounted to 45 barrels of charge per pound of catalyst and the second to 42.3 barrels per pound. Actual catalyst cost for the operation was about 9 cents per barrel of feed. Performance tests on the commercial unit have indicated yields of 95% by volume based on the charge and leaded research octane numbers of 92 to 94. A number of Platforming plants have been licensed, varying in size from 900 to 16,000 barrels per day throughput (*1*).

Comparison between Platforming and Thermal Reforming

Thermal Reforming of Pennsylvania Gasolines. The operation of a commercial thermal reformer that processes a full boiling range Pennsylvania straight-run gasoline was selected for this study. Process flow through the equipment in this reforming unit of conventional design is such that a debutanized thermal reformate is prepared, and the entire debutanizer overhead is processed in a U.O.P. catalytic polymerization unit. Main column receiver gas is scrubbed at 75 pounds per square inch in an absorber which discharges lean gas to the refinery fuel line. The polymerization unit prepares a stabilized 35-pound Reid vapor pressure polymer gasoline which is combined, before storage, with the debutanized thermal reformate. The poly stabilizer overhead gas together with the absorber lean gas forms the metered total fuel gas stream. A small amount of residuum is separated from the reformer heater effluent in a quenched flash chamber following the heater in the process flow.

During a test period the thermal reforming unit processed a full boiling range Pennsylvania straight-run gasoline at a transfer temperature of 1040° F. Laboratory inspections of the feed stock, the debutanized thermal reformate, the blend of the polymer gasoline with the thermal reformate, and the residuum are presented in Table I. The feed stock contained 7 volume % of C_4 and lighter hydrocarbons. Table I also shows the inspections of laboratory debutanized samples of the feed stock and of the thermal reformate blend with polymer gasoline.

The over-all material balance, prepared for the test period on the combined operation of the thermal reformer and the polymerization unit, appears in Table II. It is based on the streams actually fed and produced. Table III shows the debutanized reformate and debutanized polymer streams separately and as a combined stream. Laboratory inspections of the debutanized reformate and of the debutanized reformate plus polymer blend are presented in Table I.

The octane numbers of the debutanized thermal reformate, observed yield of which

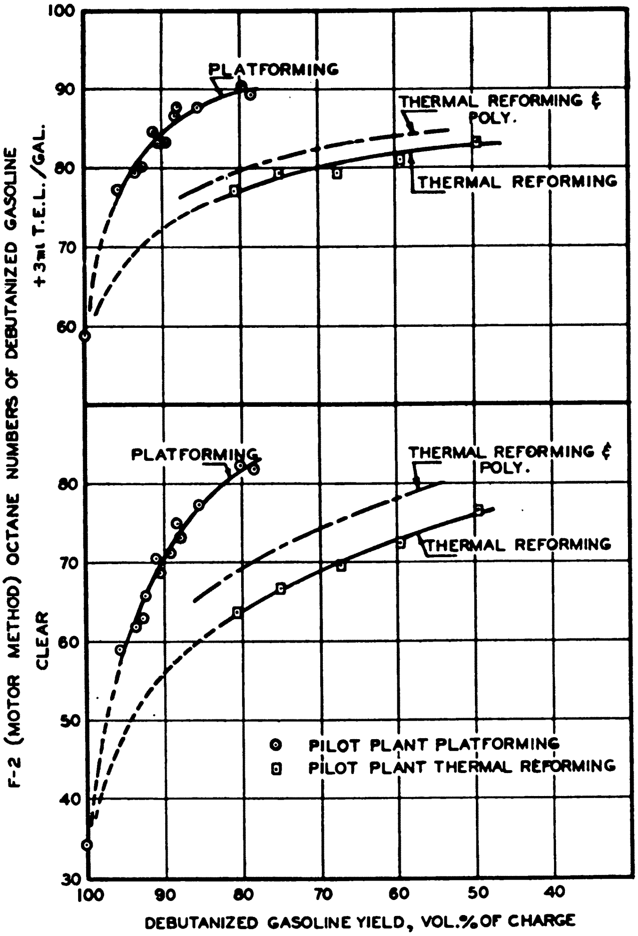

Figure 4. Comparison of F-2 (Motor Method) Octane Numbers of Debutanized Gasolines from Platforming and Thermal Reforming of Mid-continent Straight-Run Naphtha

was 69.3 volume % of the debutanized feed, are plotted as points on the yield-octane charts of Figures 1 and 2. Dotted lines drawn through or near these points were derived from generalized thermal reforming correlations; the predicted yield-octane relationship is in good agreement with the observed points.

Similarly, the measured octane numbers of the debutanized blend of thermal reformate with polymer are plotted in Figures 1 and 2 at the observed yield of 76.2 volume % for the debutanized blend.

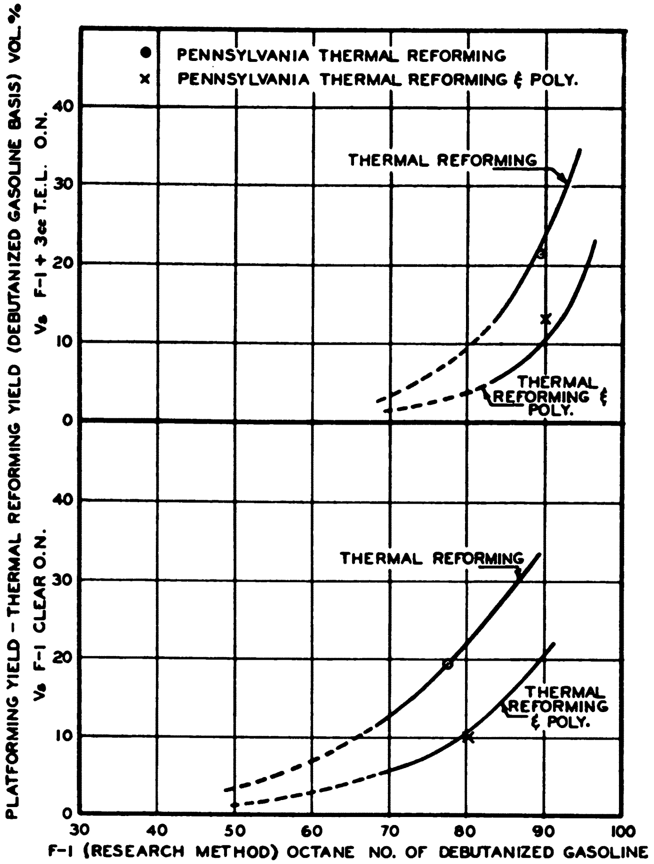

Figure 5. Difference in Yield of Platformate and Thermal Reformate at Various Levels of F-1 Octane Numbers of Mid-continent Naphtha

Thermal Reforming of Mid-Continent Naphtha. Pilot plant tests were made on a straight-run mid-continent naphtha having a nominal boiling range of 200° to 400° F. and a clear octane number of 35. The thermal reforming tests were made in a 2-barrel-per-day pilot plant consisting of a 24-tube cracking coil, a main fractionating column to separate residuum boiling above 400° F. end point gasoline, and a stabilizer column which prepared a debutanized thermal reformate. Results of this test work, made at a coil pressure of 500 pounds per square inch and at transfer temperatures of 1000° to 1040° F., are plotted in Figures 3 and 4 as yield-octane relationships.

Polymer gasoline yields were estimated for each of the test periods, using recoveries of 70 and 95% for the C_3 and C_4, respectively, and a polymerization conversion of 90%. The estimated yield-octane relationship for the combination of thermal reforming and catalytic polymerization is represented by the broken line in Figures 3 and 4.

Platforming of Pennsylvania Straight-Run Gasoline. Table IV presents the results obtained from Platforming the Pennsylvania straight-run gasoline. The product was debutanized in the unit and rather complete analyses were obtained on the debutanized product.

The results shown in Table IV indicate that over the range of severities investigated the clear research octane number increases from 75 at the lowest severity to 94 at the highest severity. This is accompanied by an increase in aromatic content from about 30% to about 57%, and an increase in the amount of liquid product boiling below 212° F. from 42 to 52%, as compared to 25% in the charge. Aromatic production based on the charge is of interest, because the values shown indicate a continual trend of increased aromatic production as the severity is increased. Tables I and IV show that the reduction in sulfur content by thermal reforming is small, amounting to about 15%, and Platforming attains a reduction of about 97%.

Discussion

Yield-Octane Relationships. Figures 1 and 2 show the yield-octane relationship for the three operations on the basis of clear and leaded research and motor octane numbers. The tabular data obtained on pilot plant thermal reforming and on Platforming of a mid-continent naphtha, are not shown in this paper; instead, a yield-octane relationship is presented in Figures 3 and 4. The incremental yield of the Platforming operation over the thermal reforming and the thermal reforming and polymerization operations are shown in Figures 5 and 6. These show clearly the difference in the yield-octane relationship. At a leaded research octane number of 91 the Platforming yield exceeds the thermal

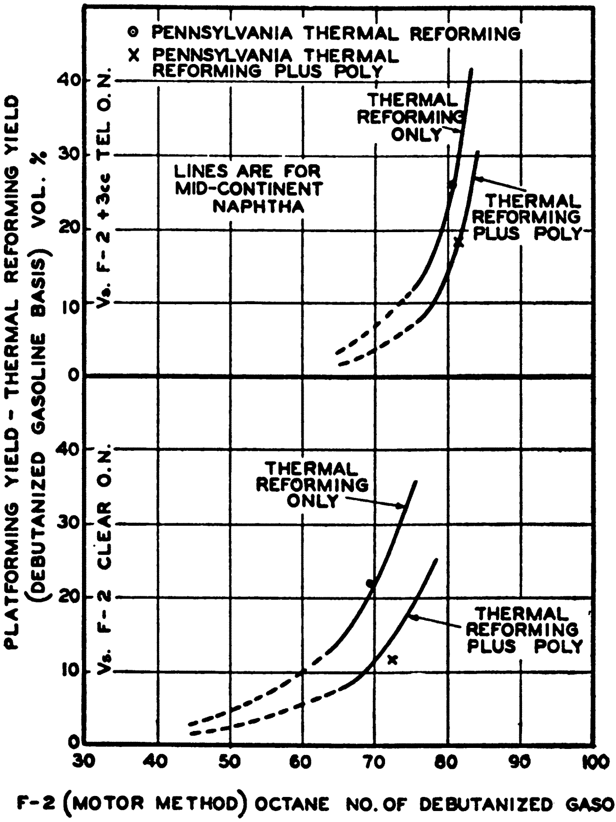

Figure 6. Difference in Yield of Platformate and Thermal Reformate at Various Levels of F-2 Octane Numbers

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reforming yield by about 27% based on charge, while it exceeds the thermal reforming plus polymerization yield by about 13% based on the charge. The data are based on the results obtained with the mid-continent charge stock; however, the single points obtained

Table IV. Platforming of Debutanized Pennsylvania Straight-Run Gasoline

	Charge	Test Number 1	2	3	4	5	6	7
Product yield								
Charge, wt. %								
H_2 C_1-C_3	..	4.9	7.7	7.4	9.6	10.7	10.7	16.4
C_4	0.0	3.2	5.5	5.9	7.3	7.7	8.7	10.2
C_5+	100.0	91.9	86.8	86.7	83.1	81.6	80.6	73.4
Charge, vol. %								
C_4	..	4.0	7.0	7.9	9.8	9.8	11.4	13.0
C_5	7.7	12.7	14.9	14.0	15.8	16.5	16.5	18.0
C_6+	92.4	78.3	71.0	70.9	66.0	63.9	61.9	52.6
Total C_4+ gasoline	..	95.0	92.9	92.8	91.6	90.2	89.8	83.6
Total C_5+ gasoline	100.0	91.0	85.9	84.9	81.8	80.4	78.4	70.6
Properties of C_5+ Platformate								
API °gravity	60.7	59.1	58.4	57.3	58.4	57.7	56.0	52.9
Sulfur, wt. %	0.07	..	0.002	..	..	..	..	..
Reid vapor pressure	3.1	5.6	5.6	5.6	6.0	6.1	6.3	6.9]
Aromatic content, wt. %	8.7	29.6	34.9	39.3	39.0	41.3	47.8	57.4
Aromatic content, wt. % of charge	8.7	27.3	30.2	33.9	32.3	33.5	38.3	41.7
Octane No.								
F-1 clear	44.4	75.0	79.7	81.6	82.9	85.2	88.3	94.0
F-1 + 3 cc. TEL/gal.	65.2	89.0	92.9	93.4	94.7	95.2	97.2	Iso + 0.03
F-2 clear	43.9	70.0	72.9	75.4	76.3	78.3	79.7	83.6
F-2 + 3 cc. TEL/gal.	64.4	84.6	86.3	87.4	87.8	87.8	90.3	91.7
Engler distillation:								
Initial boiling point	140	116	126	120	118	116	113	106
5%	170	143	143	142	134	134	132	124
10	184	155	152	152	144	144	141	135
30	222	190	181	183	173	171	169	160
50	257	228	221	223	213	210	212	210
70	293	268	263	265	257	257	261	267
90	338	320	319	321	314	316	319	321
95	354	344	341	345	343	338	347	348
End point	390	385	395	401	390	394	412	419
% bottoms	1.2	1.0	1.0	1.3	1.0	1.0	1.0	1.0
% loss	0.3	0.5	0.5	0.2	0.5	0.5	0.5	0.5
% over at 212° F. + loss	25.3	42.0	45.2	44.7	50.0	51.5	50.5	51.5

Table V. Octane Numbers of 20% Cuts from Pennsylvania Straight-Run Gasoline, Thermal Reformate, and Two Platformates

Cut No.	Distillation Cut Temp., ° F.	Vol. % Cut in Gasoline	Properties of Cut: A.P.I. gravity	F-1 + 3 ml. TEL/gal. octane number
		Pennsylvania Straight-Run Gasoline		
1	174	19.6	82.3	84.3
2	221	20.0	63.7	75.1
3	270	19.7	58.6	67.6
4	318	19.8	53.9	57.6
5	..	20.9	50.1	40.5
Total		100.0	60.7	65.2
		Thermal Reformate from Commercial Unit		
1	140	19.8	84.8	96.8
2	177	19.7	65.5	91.6
3	234	19.6	56.2	87.0
4	289	19.8	50.0	86.2
5	..	21.1	42.2	79.0
Total		100.0	57.8	89.0
		Platformate from Test Period 2		
1	136	19.5	89.4	94.8
2	178	19.3	73.0	88.3
3	226	19.5	59.8	87.3
4	286	19.5	47.8	93.1
5	..	22.2	36.1	98.1
Total		100.0	58.4	92.9
		Platformate from Test Period 6		
1	113	19.4	90.7	96.0
2	158	19.2	77.1	89.9
3	221	19.4	59.1	89.3
4	279	20.0	41.9	0.075 ml. TEL in iso-C_8
5	..	22.0	31.1	0.23 ml. TEL in iso-C_8
Total		100.0	55.7	97.2

in the commercial operation on the Pennsylvania stock are in good agreement with the mid-continent data.

The lead susceptibility of Platformates is better than that of olefinic thermal reformates. This is shown clearly in Figures 7 and 8 where the leaded octane numbers are plotted against clear octane numbers for the Platforming and the thermal reforming tests on the mid-continent naphtha. At a given clear octane number, the leaded octane number of the Platformate is distinctly higher than that of the thermal reformate. This difference becomes greater as the octane number level is increased. The points obtained from Platforming and thermal reforming of the Pennsylvania stock would be nearly coincidental on these plots with those shown for the mid-continent naphtha.

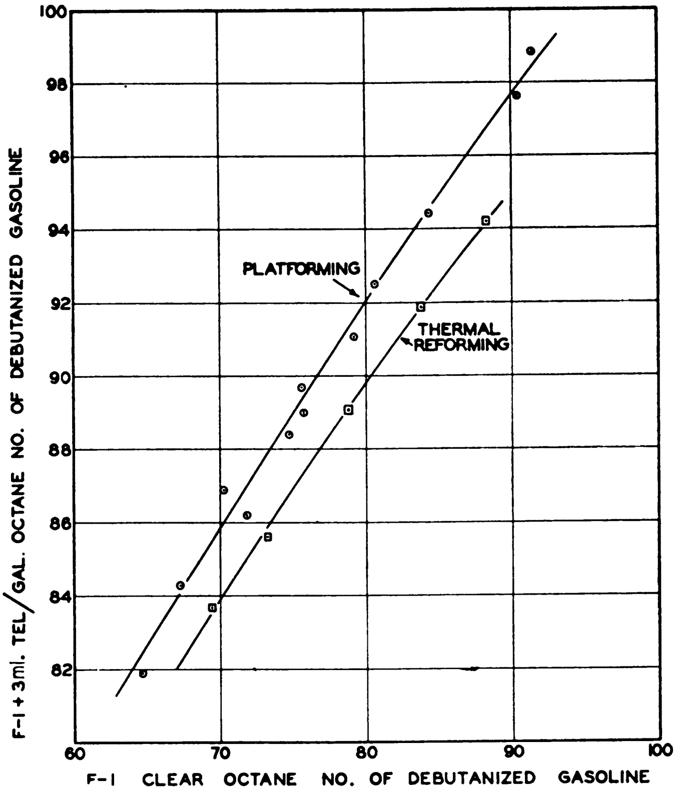

Figure 7. Lead Response (Research Method) of Platformate and Thermal Reformate from Mid-continent Naphtha

The plot of Figure 9 shows that to reach a given octane number there is a smaller change in volatility in Platforming than is experienced in thermal reforming. For the specific case of Figure 9, the lowering of the 260° F. 10% distillation temperature of the mid-continent naphtha resulting from Platforming on one hand and from thermal reforming on the other is plotted against the octane number of the product. At low product octane numbers the 10% point of the feed stock is lowered as much as 50° F. more by thermal reforming than it is by Platforming. At high octane number levels the lowering of the 10% point becomes more nearly equal for the two processes. These effects occur because Platforming is able to raise octane numbers to a considerable extent by naphthene dehydrogenation and isomerization reactions, neither of which is destructive in nature. Thermal reforming, however, depends almost entirely on cracking reactions to improve octane numbers. As the highest octane number levels are approached, the hydrocracking

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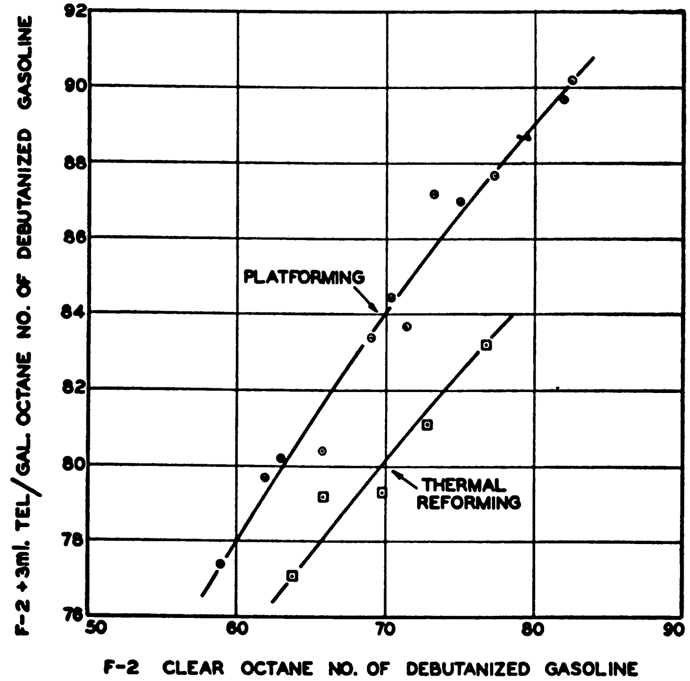

Figure 8. Lead Response (Motor Method) of Platformate and Thermal Reformate from Mid-continent Naphtha

reactions taking place in the Platforming process account for the more rapid drop in the 10% point of the Platformate.

At a given octane number the concentration of aromatics in Platformates is greater than in thermal reformates, as shown in the plot of Figure 10 for the processing of a mid-

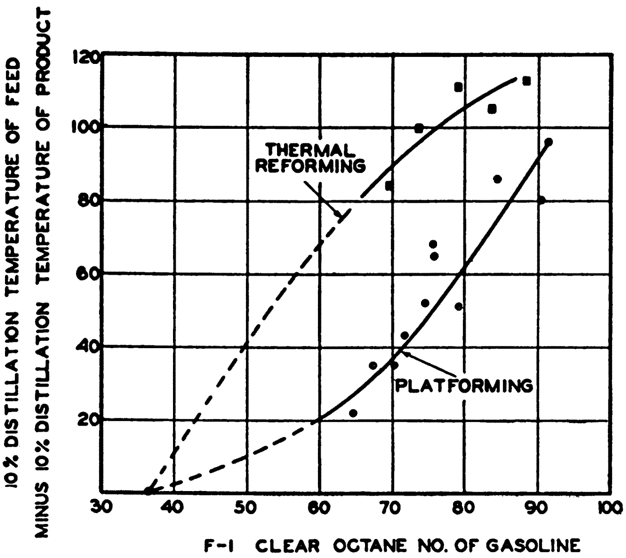

Figure 9. Difference in Volatility of Platformate and Thermal Reformate Produced from Mid-continent Naphtha

continent naphtha by the two methods. In thermal reforming there is a very small net production of aromatics based on the feed, possibly owing to the thermal dehydrogenation of naphthenes, and a sharp rise in aromatic concentration in the reformate at high octane numbers because of the destruction of nonaromatic material. In Platforming, however, there is a pronounced net production of aromatics over the entire range of operating severity, and their concentration in the Platformate increases rather smoothly to over 60% at the highest octane numbers reached in the mid-continent tests shown in Figure 10.

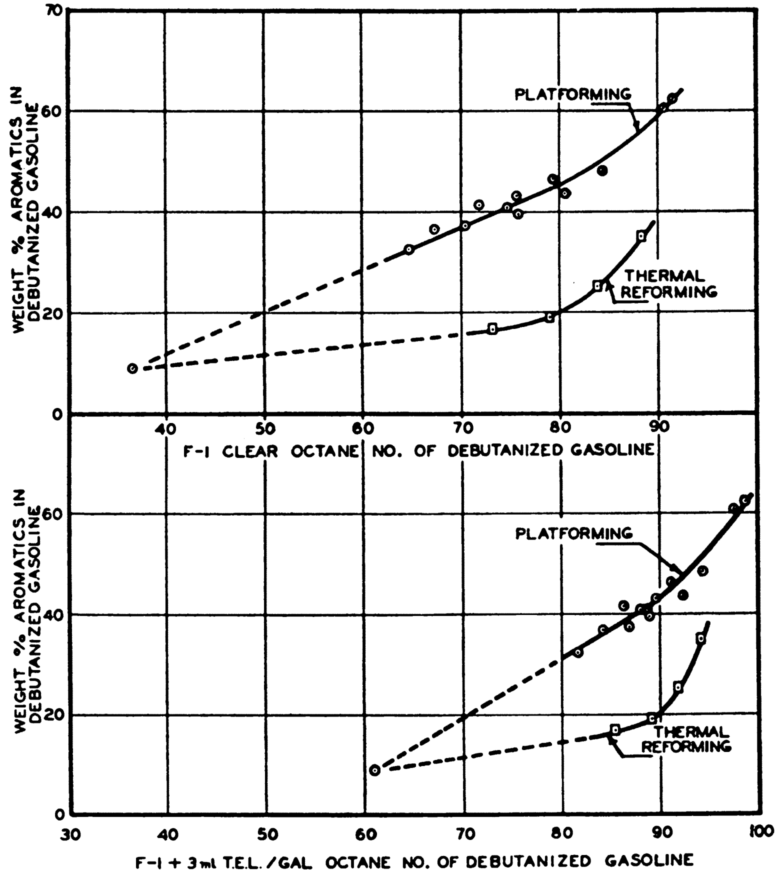

Figure 10. Aromatic Contents of Platformate and Thermal Reformate from Mid-continent Naphtha

Octane numbers of 20% cuts prepared from a Pennsylvania straight-run gasoline and from three of its refined products are shown in Table V. The debutanized feed stock and thermal reformate described in Table I, and Platformates from tests 2 and 6 in Table IV were resolved into 20% cuts by distillation in a 30-inch packed column at a 10 to 1 reflux ratio based on product. Octane numbers of the straight-run drop rather smoothly from a value of 84 down to about 40 as the boiling point of the cut is increased. The objective of the commercial thermal reforming operation was to reach leaded F-1 octane numbers of the order of 90. The entire straight-run gasoline was reformed because there are no fractions in the virgin material that have this octane number, and there would be no advantage in prefractionation.

In a comparison of the 89 octane number thermal reformate with the 92.9 octane number Platformate it is to be noted that the octane numbers of the light half of the ther-

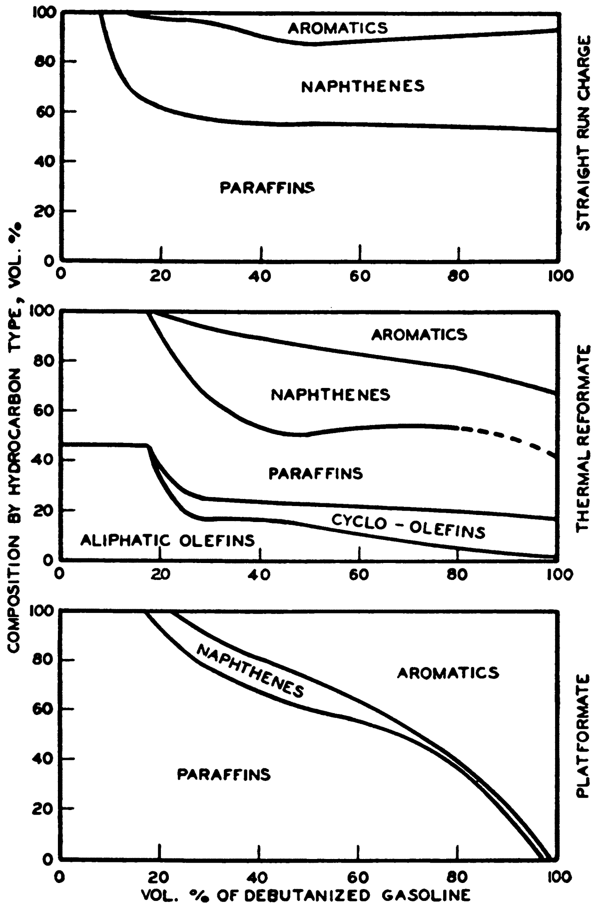

Figure 11. Hydrocarbon-Type Content of Debutanized Pennsylvania Straight-Run Gasoline, Platformate, and Thermal Reformate

mal reformate are slightly higher than those of the corresponding fractions of the Platformate.

The reason for the relatively slight difference in leaded octane numbers is: The light thermal reformate is highly olefinic and the low boiling olefins have a very high octane number. If this fraction were hydrogenated the octane number would be appreciably lower. The same fraction from a Platformate contains substantial amounts of branched paraffins and the octane number of this fraction is considerably higher than that of a hydrogenated light thermal reforming fraction. There is only a small difference between the octane numbers of a light olefinic material containing large amounts of normal hydrocarbons and a light paraffinic fraction containing large amounts of branched hydrocarbons. Octane numbers of the heavy half of the Platformate, however, are distinctly higher than those of the thermal reformate, and this difference is well over 20 units as the end point is approached.

Table V shows that in the Platformate a fairly uniform octane number is attained over the entire boiling range as compared to a decreasing octane number over the boiling range for the thermal reformate. This characteristic of the Platformate is particularly desirable because the octane number of the fuel to the various engine cylinders is relatively uniform regardless of intake manifold distribution effects.

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Table V indicates that as the octane number of the Platformate was raised from 92.9 to 97.2 by more severe operating conditions, the octane numbers of the fractions in the light half were raised only slightly, but there was a large increase in the octane numbers of the fractions in the higher boiling half of the Platformate.

Hydrocarbon-Type Analysis. The results of work done on the determination of the composition by hydrocarbon types of the Pennsylvania straight-run gasoline and of the thermal reformate and Platformate derived from that stock are shown in Table VI and Figure 11. The method of analysis will be published by the Universal Oil Products Co. laboratories. The lines shown in Figure 11 were drawn through concentrations plotted at the volumetric mid-point of each fraction examined in the laboratory. Although they appear as smooth lines on the plot, they may only approximate actual concentrations to be found in very narrow cuts. The charging stock (Figure 11) is predominantly paraffinic, and the naphthene distribution is fairly uniform in the 20 to 100% of the material. The aromatic content is also rather uniform in the 40 to 100% of the stock.

Table VI. Hydrocarbon-Type Analysis of Debutanized Pennsylvania Straight-Run Gasoline, Platformate, and Thermal Reformate

	Cut Number							Vol. % Yield Based on Feed to Process
Pennsylvania straight-run gasoline	1	2	3	4	5	Bottoms	Tota	
Boiling range of cut, ° C.	I.b.p.-46	46–65	65–85	85–107.3	107.3–134.2	134.2-e.p.	I.b.p.-e.p.	
Total gasoline, vol. %	7.7	5.0	9.1	19.9	20.1	38.2	100.0	
Vol. % in cut								
Paraffins	100	80.4	64.7	54.6	57.3	55.1		
Naphthenes	..	19.6	33.0	40.0	29.4	35.4		
Aromatics	..	..	2.3	5.4	13.3	9.5		
	100	100.0	100.0	100.0	100.0	100.0		
Total gasoline, vol. %								
Paraffins	7.7	4.0	5.9	10.9	11.5	21.1	61.1	61.1
Naphthenes	..	1.0	3.0	7.9	5.9	13.5	31.3	31.3
Aromatics	..	..	0.2	1.1	2.7	3.6	7.6	7.6
	7.7	5.0	9.1	19.9	20.1	38.2	100.0	100.0
Thermal reformate from commercial unit								
Boiling range of cut, ° C.	I.b.p.-46	46–85	85–115	115–149		149-e.p.	I.b.p.-e.p.	
Cut in total gasoline, vol. %	17.5	19.2	21.7	21.4		20.2	100.0	
Vol. % in cut								
Paraffins	53.2	46.0	28.0	33.5		11.8[a]		
Aliphatic olefins	46.8	17.0	15.0	7.5		3.2		
Cyclo-olefins	..	8.6	7.4	12.8		15.3		
Naphthenes	..	23.0	35.5	26.3		41.8[a]		
Aromatics	..	5.4	14.1	19.9		27.9		
	100.0	100.0	100.0	100.0		100.0		
Total gasoline, vol. %								
Paraffins	9.3	8.8	6.1	7.2		2.4	33.8	23.4
Aliphatic olefins	8.2	3.3	3.2	1.6		0.6	16.9	11.7
Cyclo-olefins	..	1.7	1.6	2.7		3.1	9.1	6.3
Naphthenes	..	4.4	7.7	5.6		8.5	26.2	18.2
Aromatics	..	1.0	3.1	4.3		5.6	14.0	9.7
	17.5	19.2	21.7	21.4		20.2	100.0	69.3
Platformate from test 2								
Boiling range of cut, ° C.	I.b.p.-46	46–85	85–115	115–149	149-e.p.		I.b.p.-e.p.	
Cut in total gasoline, vol. %	16.9	20.2	25.9	20.9	16.1		100.0	
Vol. % in cut								
Paraffins	100	80.9	60.7	45.2	13.0			
Naphthenes	..	11.9	12.2	3.3	3.0			
Aromatics	..	7.2	27.1	51.5	84.0			
	100	100.0	100.0	100.0	100.0			
Total gasoline, vol. %								
Paraffins	16.9	16.3	15.7	9.5	2.1		60.5	52.0
Naphthenes	..	2.4	3.2	0.7	0.5		6.8	5.8
Aromatics	..	1.5	7.0	10.7	13.5		32.7	28.1
	16.9	20.2	25.9	20.9	16.1		100.0	85.9

Approximate split between paraffins and naphthenes.

The product from thermal reforming contains a substantial amount of lower boiling aliphatic olefins. The concentration of these olefins is gradually reduced as the boiling range increases. An increasing quantity of cyclo-olefins is found in the higher boiling cuts, however, and the over-all olefin concentration is not substantially decreased. The aromatic concentration is also increased as the boiling range is increased. The over-all result of a comparison of charge analysis and product analysis based on charge indicates that paraffins are most susceptible to reforming; about 62% of the original paraffinic material is converted as compared to a 42% disappearance of the naphthenes. The net increase in aromatics is very small, amounting to only 2% based on the charge. The small amount of aromatics produced may have come in part from the cracking of the paraffins and it becomes apparent that in thermal reforming the dehydrogenation of naphthenes to form aromatics is almost insignificant. The ratio of aliphatic olefins in the product (based on charge) to the paraffins in the charge is approximately the same as the ratio of cyclo-olefins in the product (based on charge) to the naphthenes in the charge. The over-all picture is that both paraffins and naphthenes undergo cracking and dehydrogenation to produce lower paraffins and olefins along with higher cyclo-olefins and with a negligible amount of aromatics.

Product Distribution. The first 20% of the Platformate is paraffinic, and the remainder consists of almost equal amounts of Paraffins and aromatics along with a small amount of naphthenes. In the 20 to 100% of the product the paraffins are gradually reduced in concentration, while the aromatics are gradually increased. The highest boiling fraction is essentially completely aromatic. An over-all balance (based on the charge) shows that about 85% of the paraffins present in the charge are retained in the debutanized product; 79% of the naphthenes present in the charge are converted to aromatics; 18.5% are left unconverted; and only 2.5% are hydrocracked. The above values indicate the exceedingly high selectivity of the reactions taking place. The gradual increase in the aromatic content and the gradual reduction in paraffinic content, as the boiling point of the Platformate is increased, are readily explained.

As the paraffins are hydrocracked and isomerized, their average boiling range is lowered.

As the naphthenes are dehydrogenated the average boiling range of the resulting aromatics is increased, so that a natural segregation into a lower boiling paraffin-rich and a higher boiling aromatic-rich fraction takes place.

The hydrocarbon-type analysis of the Platformate discussed above was based on the product having an octane number of 92.9 (F-1 plus 3 ml. of tetraethyllead per gallon). The aromatic content (based on charge) increases continually with increased severity. At the two highest severities, the aromatic yield (based on the charge) is in excess of the total naphthenes and aromatics present in the charge. This indicates the participation of the dehydrocyclization reaction of paraffins to form aromatics.

Acknowledgment

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Development of a Reforming Catalyst

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A catalyst for the reforming of naphthas has been developed which provides an excellent octane-yield relationship and can be operated without regeneration for long periods of time. This development started with the discovery of a catalyst for the isomerization of paraffin and naphthene hydrocarbons which was composed of a hydrogenating component, such as nickel or platinum, deposited on silica-alumina. The early catalyst would promote isomerization at nominal temperatures but was much too active as a cracking agent at temperatures required for aromatic formation. By markedly decreasing the surface area of the silica-alumina component, a reforming catalyst was developed that gives the proper balance and direction for the main reactions of reforming: isomerization, dehydrogenation, and hydrocracking.

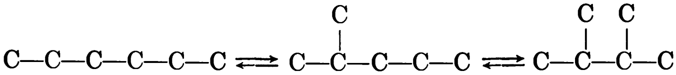
In the last 15 years of petroleum technology, reforming has moved from an operation of questionable necessity to a must for most refiners. This paper summarizes part of the chemistry of reforming and then shows how the authors have developed a new catalyst for this operation.

Reforming a naphtha to a higher octane rating must involve at least one of the following chemical reactions: (*a*) production of aromatics, (*b*) production of highly branched paraffins, (*c*) production of olefins, or (*d*) lowering the molecular weight of the hydrocarbons in the naphtha.

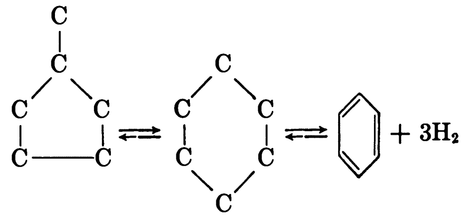
Thermal reforming relies largely on molecular weight reduction to obtain antiknock improvement. It forms some aromatics and olefins, but, in general, it is a brute force method of bringing about chemical transformations and does so at the expense of forming undesirable quantities of gas and high boiling material.

The early hydroforming catalysts were a big step forward in directing the chemical reactions of reforming to a desired end—namely, the formation of aromatics. These catalysts, however, were far from perfect. They required frequent regeneration with the attendant high plant investment cost and they fell short in octane number improvement due to a lack of isomerization ability.

The ability of a catalyst to promote isomerization plays two roles in reforming: it increases the amount of branched chain paraffins in the product and it converts naphthene hydrocarbons with cyclopentane rings into cyclohexane ring naphthenes which are necessary for the formation of aromatics by dehydrogenation.



$$\mathrm{C{-}C{-}C{-}C{-}C{-}C} \rightleftharpoons \mathrm{C{-}\overset{\overset{C}{|}}{C}{-}C{-}C{-}C} \rightleftharpoons \mathrm{C{-}\overset{\overset{C}{|}}{C}{-}\overset{\overset{C}{|}}{C}{-}C}$$



The octane number improvement obtained by isomerization of paraffin hydrocarbons is not great since the amounts of the more highly branched paraffins formed at equilibrium are small at the temperatures employed in catalytic reforming (*5*). Naphthene isomerization, on the other hand, plays a more important role in reforming. In most naphthas about 50% of the naphthene hydrocarbons are of the cyclopentane type (*4*) so that in order to obtain the maximum aromatic formation, isomerization of these rings to cyclohexane rings must be promoted by the catalyst.

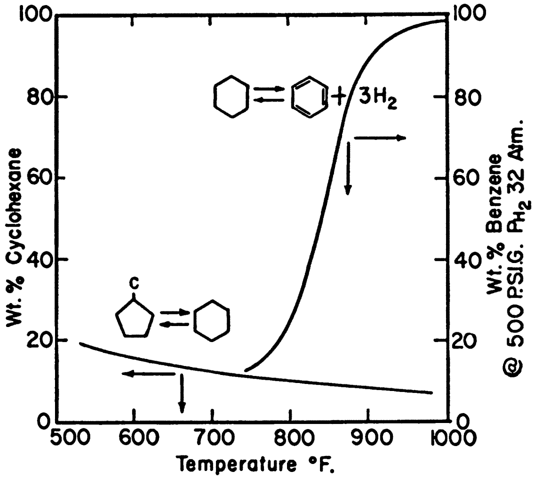


Figure 1. Methylcyclopentane-Cyclohexane and Cyclohexane-Benzene Equilibria

At temperatures where substantial dehydrogenation of naphthene hydrocarbons to aromatics can take place, the isomerization equilibrium of cyclopentane naphthenes to cyclohexane naphthenes is greatly in favor of the cyclopentane compounds. However, the dehydrogenation of the cyclohexane rings superimposes its equilibrium on the former reaction giving an over-all conversion of the alkyl cyclopentane hydrocarbons into aromatics. This is illustrated in Figure 1. In this figure, the calculated equilibrium concentrations of cyclohexane formed from methylcyclopentane (*1*) and of benzene from cyclohexane (*7*) are plotted against the reaction temperature. Experimental data have indicated that the benzene-cyclohexane curve in Figure 1 may be somewhat in error since higher yields of benzene from cyclohexane have been obtained at 800° to 900° F. than that predicted by this curve.

The Platforming catalyst is a vast improvement over the older hydroforming catalysts. It produces less carbon so that frequent regeneration is unnecessary and it promotes the isomerization required for extensive aromatic formation. In one way of looking at the development of this catalyst, assuming that its composition is that described in the patent literature (*6*), one can say that Haensel and his associates started with a dehydrogenating component on a carrier that is relatively inert for isomerization and cracking and added an isomerization–mild cracking component. Over the past several years, the authors have also developed a reforming catalyst that simultaneously isomerizes,

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dehydrogenates, and cracks. The history of its development, which will be the subject of the remainder of this paper, is about the reverse of that of the Platforming catalyst in that it started with a discovery of a good isomerization and dehydrogenating agent, but one which was much too active in its cracking behavior, and decreasing the latter to suit the needs of reforming.

Several years ago, one of the authors found that nickel, platinum, and some other hydrogenating agents, when deposited on fresh synthetic silica-alumina cracking catalyst, made a new catalyst that would isomerize paraffin and naphthene hydrocarbons in the presence of hydrogen at elevated pressures and nominal temperatures. Table I shows some early typical results calculated from mass spectrometer analyses of the products obtained by passing methyl cyclopentane, cyclohexane, and *n*-hexane over a catalyst composed of 5% nickel in silica-alumina at the indicated reaction conditions. Isomerization of a number of other hydrocarbons has also been studied and reported elsewhere (*2*).

Table I. Isomerization of Saturated Hydrocarbons in the Presence of Nickel-Silica-Alumina Catalysts

Catalyst: 5% nickel on silica-alumina
Pressure: 350 lb./sq. inch gage
Liquid space velocity: 1.0 vol./vol./hour
H_2:HC, mole ratio: 4.0

Hydrocarbon	*n*-Hexane	Methylcyclopentane	Cyclohexane
Reaction temp., ° F.	700	650	650
Products, mole % of charge			
C_5's and lighter	2.5	0.9	0.4
2,2-Dimethylbutane	3.9	2.6	0.0
2,3-Dimethylbutane	5.5		
2-Methylpentane	29.7		
3-Methylpentane	22.0		
n-Hexane	37.5		
Cyclohexane	...	14.9	30.7
Methylcyclopentane	...	82.1	68.9
Benzene	...	0.3	0.5
Conversion, mole % of charge	62.5	17.9	69.3
Isomer yield, mole % of charge	61.1	14.5	68.9

Platinum was found to be the most efficient hydrogenating component for the isomerization catalyst from the standpoint of amount required and resistance to sulfur poisoning.

From this beginning, an extensive study of the isomerization of *n*-heptane was made with platinum on silica-alumina catalysts. Figure 2 shows curves plotted from the data obtained illustrating the total isomer yield versus conversion and the temperatures that produced these conversions. The conversion–isomer yield curve follows closely the 45° theoretical yield line, goes through a maximum at about 65% isomer yield, and then drops sharply because of cracking. The temperature at which the maximum yield of isomers was obtained was about 660° F.

If this catalyst were to be used in the temperature range of 850° to 950° F. where extensive aromatic formation may be obtained, one would be operating in a range far to the right of the peak isomer yield and in a region where very severe cracking of paraffin hydrocarbons occurs. In fact, it is questionable whether much of the paraffin hydrocarbons in a naphtha would survive such treatment.

Hence, the problem became one of decreasing the cracking activity of the catalyst without harming its isomerization ability. This was accomplished by reducing the surface area of the silica-alumina component prior to platinization by treating it with superheated steam (*3*). Figure 3 shows the results obtained on a study of the total isomer yield obtained from passing *n*-heptane over five catalysts of decreasing surface area plotting the isomer yields against the reaction temperature. These data show that the temperatures required for isomerization increase as the surface area of the catalysts decreases and that the extent of isomerization obtained by catalysts of reduced surface area is essentially the same as that obtained with an undeactivated base within the limits of accuracy of the analytical methods employed.

Figure 4 illustrates the surface area–reaction temperature relationship for maximum isomer yield in the *n*-heptane isomerization experiments. The curve shows the reaction temperatures at which the maximum isomer yields were obtained—i.e., the inflection points of the curves in Figure 3—as a function of the surface area of the catalysts. This curve points out that the catalyst should have a surface area below 65 or 70 square meters per gram, as determined by the Brunauer-Emmett-Teller technique, in order to serve the purpose of catalyzing both isomerization and dehydrogenation without overcracking.

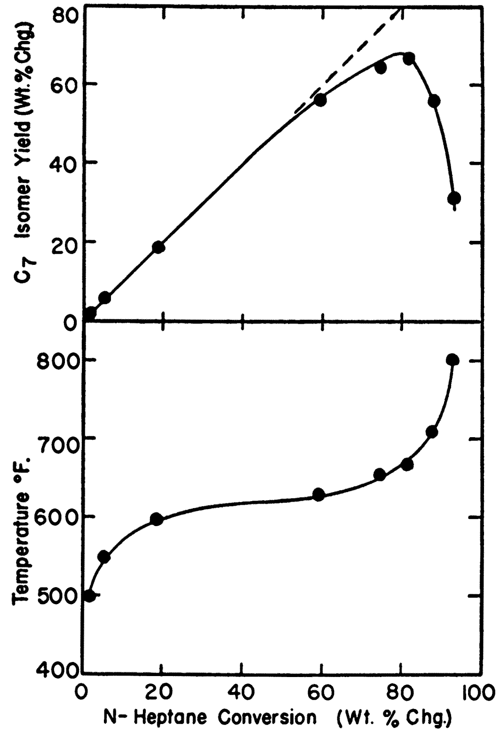

Figure 2. Isomerization of *n*-Heptane

Curves plotted from data obtained illustrating total isomer yield *vs.* conversion and temperatures that produced these conversions

The fact that the catalyst can promote dehydrogenation as well as isomerization is shown in Figure 5, where the weight per cent benzene in the products of experiments on dehydrogenation of cyclohexane is shown plotted against the reaction temperature. These results are compared to Von Muffling's (7) calculated equilibrium line. The

Table II. Hydrocracking of Pure Hydrocarbons in the Presence of Nickel-Silica-Alumina Catalysts

Catalyst: 5% nickel on silica-alumina
Pressure: 350 lb./sq. inch gage
Liquid space velocity: 1.0 vol./vol./hour
H_2:HC, mole ratio: 4.0

Hydrocarbon	*n*-Heptane	*n*-Octane
Reaction temp., ° F.	700	690
Products, mole % of charge		
Methane	0.6	0.7
Ethane	0.7	0.0
Propane	30.5	22.6
Butanes	33.6	56.8
Pentanes	0.6	22.8
Hexanes	0.7	0.8
Conversion, mole % of charge	78.8	100
Isomer yield, mole % of charge	44.4	47.5

authors' yields of benzene are definitely higher than those predicted by Von Muffling's calculations, indicating an error in the latter. The authors' calculations of this equilibrium fall very close to the experimental data.

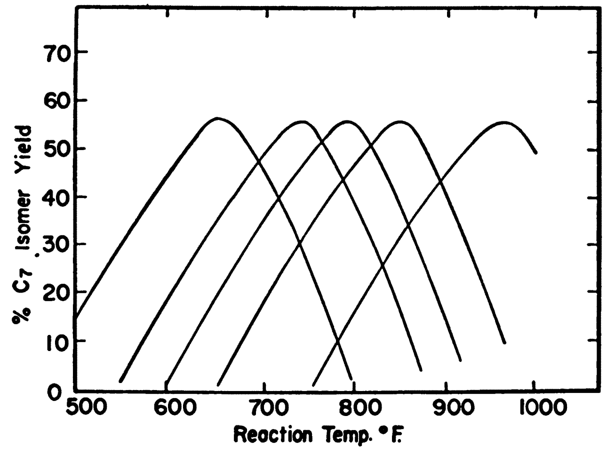

Figure 3. Isomerization of *n*-Heptane

Total isomer yield obtained from passing *n*-heptane over five catalysts of decreasing surface vs. reaction temperature

Besides dehydrogenation of naphthenes and the isomerization of both naphthenes and paraffins, a reforming catalyst should be capable of controlling the hydrocracking reaction to minimize the formation of ethane and methane. The catalysts developed in this work promote cleavage of the paraffin chains near the central carbon atoms, and hence help maintain a high yield of useful hydrocarbons. This is most clearly demonstrated in Table II which shows the products obtained from *n*-heptane and *n*-octane when operating at high conversions with an undeactivated catalyst. This observation has been confirmed

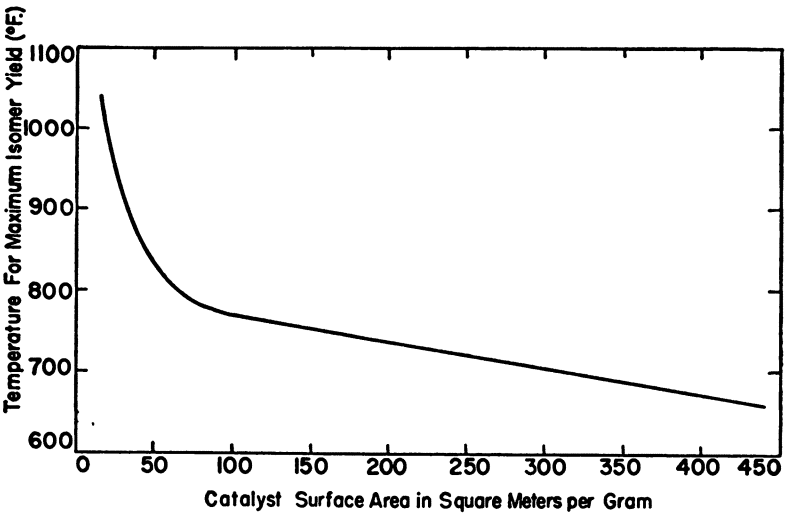

Figure 4. Isomerization of *n*-Heptane

Surface area–reaction temperature relationship for maximum isomer yield in *n*-heptane isomerization experiments

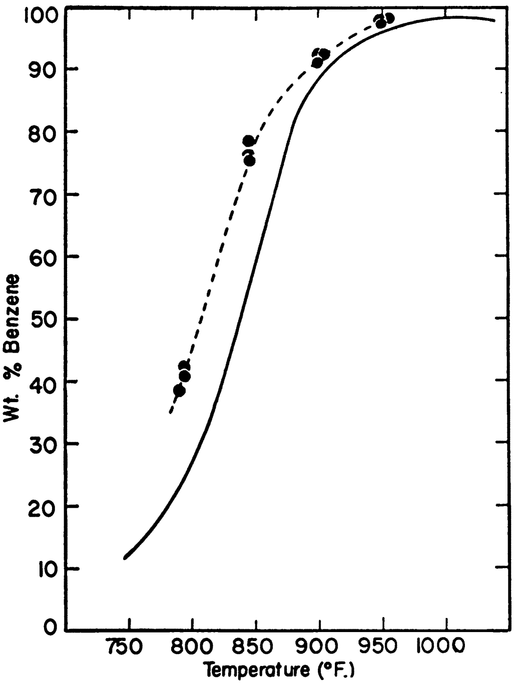

Figure 5. Benzene-Cyclohexane Equilibrium

Pressure, 500 lb./sq. inch gage, H_2:HC mole ratio, 10; liquid space velocity, 2.0 vol./vol./hour

by subsequent pilot plant operation on deactivated catalysts which has consistently shown a 97 to 98% hydrogen purity on the recycle gas stream formed by an equilibrium flash separation at 500 pounds per square inch gage at 100° F.

The purpose of a reforming catalyst is, after all, to provide as favorable a yield–octane number relationship as possible, and all the foregoing can be summed up by the yield–octane number curves shown in Figure 6. These data were obtained in a pilot plant investigation of the reforming of an East Texas naphtha of 53 research octane number at 880° to 950° F., 500 pounds per square inch gage, 5.0 weight space velocity, and a 10 to 1 hydrogen to hydrocarbon mole ratio. Thus by establishing the proper balance and direction of the main reactions—isomerization, dehydrogenation, and hydrocracking—a greatly improved efficiency for octane improvement has been achieved.

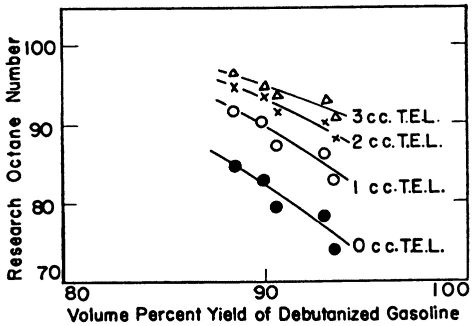

Figure 6. Catalytic Reforming of East Texas Naphtha

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Polymerization of Hydrocarbon Gases to Motor Fuels

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The Pure Oil Co., Chicago, Ill.

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Processes for the polymerization of hydrocarbon gases to motor fuel were developed to a commercial level in the early 1930's. Thermal polymerization plants, employing temperatures of 900° to 1200° F. and pressures of 60 to 3000 pounds per square inch, were developed first, closely followed by catalytic units operating at temperatures of 280° to 475° F. and pressures of 200 to 1200 pounds per square inch. Currently, thermal polymerization finds its greatest application in combination with thermal reforming of naphtha. Catalytic polymerization has proved highly successful, as is indicated by the fact that one company alone has licensed over 150 plants to date.

The past twenty-five years have seen a great increase in the volume of hydrocarbon gases produced in petroleum refineries as a consequence of the enlarged cracking capacity of the industry. Early during this period refiners used cracked and natural gases (also being produced in increasing volume) as fuel and in some cases wasted the excess gas. With the availability of this low priced charge stock as an incentive, research was directed simultaneously by several organizations toward the conversion of these low molecular weight hydrocarbons to motor fuel by polymerization. Development work first bore fruit in 1931 when a unit capable of producing up to 100 barrels a day of gasoline from refinery gas started operation at the Toledo Refinery of The Pure Oil Co. (*24*). The process was subsequently licensed by Alco Products, Inc. This was followed in 1934 by a unit of about 1000 barrels a day at the Alamo Refinery of the Phillips Petroleum Co. (*2*), Borger, Tex., operating on either cracked or natural gas fractions. The Polymerization Process Corp. was formed to license the process which incorporated the results of research by Phillips Petroleum, Standard Oil (Indiana), Standard Oil (New Jersey), Texas Co., and M. W. Kellogg Co. These were both thermal units relying on comparatively high heat and pressure to effect conversion. In 1935 catalytic polymerization of olefins to motor fuel boiling fractions was accomplished on a commercial level at the East Chicago Refinery of the Shell Oil Co., using the polymerization process of the Universal Oil Products Co. and employing more moderate conditions. The use of catalytic polymerization spread uniformly throughout the following decade until almost every refinery having cracking facilities employed polymerization of cracked gases. There are now more than 150 Universal Oil Products (U.O.P.) catalytic polymerization plants in operation.

A combination of the thermal polymerization process and the U.O.P. catalytic process was introduced in 1937 at the Shamrock Oil and Gas Co., Sunray, Tex. (*23*). In 1934 the Shell Development Co. introduced the cold acid process (*13*), which selectively polymerizes isobutene, using sulfuric acid as catalyst. The hot acid process was also developed by them and differed from the cold acid process in polymerizing all C_4 olefins. Both products are predominantly the dimer. The cold acid process produces a large pro-

Publication Date: January 1, 1951 | doi: 10.1021/ba-1951-0005.ch009

portion of almost pure iso-octene which readily hydrogenates to iso-octane. The hot acid process produces a mixture of isomeric octenes which in turn may be hydrogenated to hydrocodimer. Iso-octane and hydrocodimer from sulfuric acid plants, as well as from some U.O.P. catalytic plants designed to selectively polymerize isobutenes or butenes, were of notable importance during World War II as components of aviation gasoline.

During 1931–41, additional plants of all these types were built, but the logical combination of catalytic dehydrogenation of paraffins to olefins, followed by catalytic polymerization of olefins, was not commercially realized although the literature abounds with references to dehydrogenation catalysts (*6*). It was not until 1941, under the stress of war, that the Houdry process for dehydrogenating isobutane to isobutene was first used by Imperial Chemical Industries in England. Today, dehydrogenation of propane or butane still finds no place as a step in making motor gasoline.

A further application of polymerization lies in the valuable combination of the thermal polymerization process with thermal reforming of naphtha for octane number appreciation. An outgrowth of such combination was first used at the Gulf Oil Corp.'s Pittsburgh refinery in 1936 and called Polyforming. A gas reversion process was brought out by Phillips Petroleum Co. and installed in their Kansas City Refinery in 1937. These processes, which will be explained later, largely replaced thermal polymerization and found considerable application until the advent of catalytic reforming in the last few years.

Thermal Polymerization Processes

Thermal polymerization processes were developed simultaneously and independently by the Phillips Petroleum Co. and The Pure Oil Co., the former dealing more particularly with the conversion of C_3 and C_4 hydrocarbons containing a low proportion of olefins, and the latter a somewhat higher proportion. Operating condition limits for the former were 800 to 3000 pounds per square inch gage and 900° to 1100° F. with the flow arrangement shown in Figure 1. The latter company employed conditions of 60 pounds per square inch gage and 1150° F. to 1200 pounds per square inch gage and 1100° F. with flow arrangement as in Figure 2. The exothermic conditions of the polymerization with olefins make it preferable to have the reaction coil in a separate setting to allow controlled heat

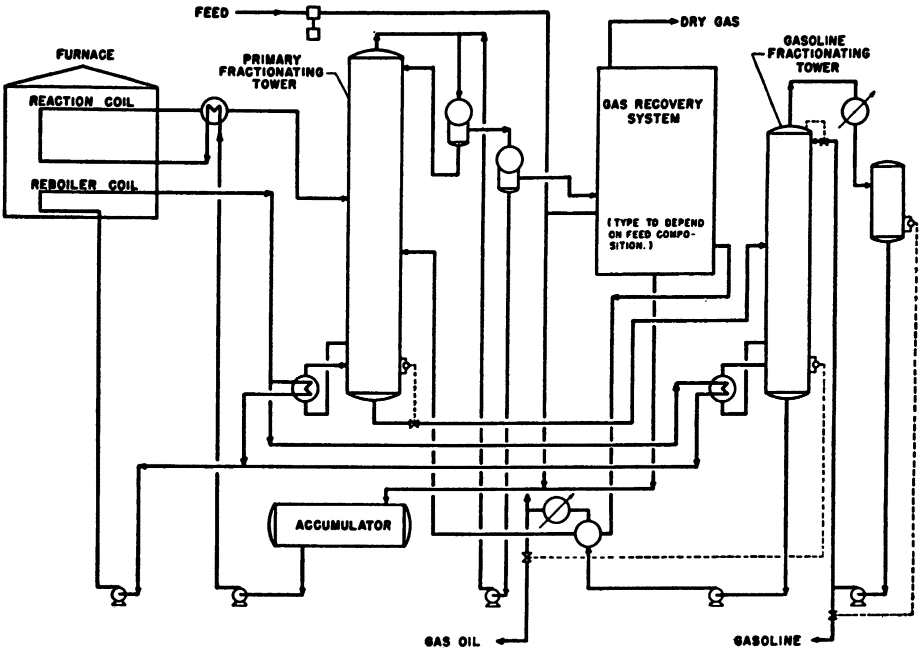

Figure 1. Unitary Polymerization Process

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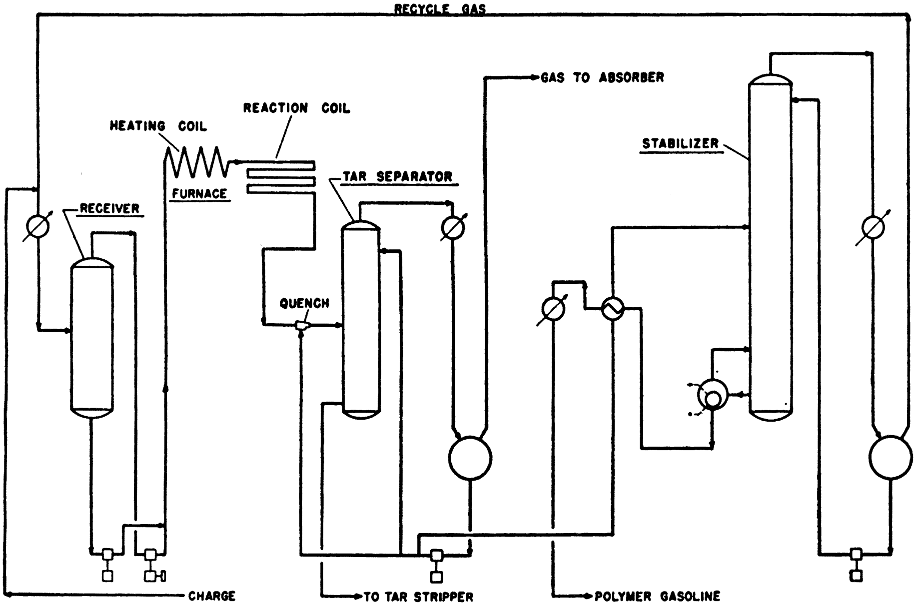


Figure 2. Thermal Polymerization of Olefin-Containing Gas

dissipation. At the lowest pressure and highest temperature when charging a gas containing 35% C_3 and C_4 olefins (*17*), the total liquid product is largely aromatic and has the true boiling point (T.B.P.) distillation shown in Figure 3, curve *A*, having distinct plateaus at benzene and toluene. By increasing the pressure to 400 pounds per square inch gage and reducing the temperature to 1070° F., a polymer having a T.B.P. distillation, curve *B*, is made which no longer exhibits marked aromaticity. For comparison the T.B.P. distillation curve of the crude polymer produced from a C_3–C_4 feed containing 64% olefins, using a phosphoric acid catalyst at 400° F. and 200 pounds per square inch gage is shown as curve *C* on Figure 3 (*12*). In the operating range required to produce maximum yields of motor fuel (which increases with operating pressure) the two thermal processes become technically indistinguishable.

Although liquid polymers boiling in the gasoline range can be made from methane, ethane, and ethylene, the yield has been too low and the operating conditions too severe to make gasoline from them economically.

In predicting yields, an empirical mechanism has to be resorted to since the chemistry of the pyrolysis of mixtures of C_3 and C_4 hydrocarbons is still at least partly conjecture.

A method for computing ultimate yields and product distribution worked out by H. C. Schutt and others of Stone & Webster Engineering Corp., heretofore unpublished, involves the estimation of the hydrogen content of the residue gas, the total liquid polymer as a function of the operating conditions, subsequent simultaneous application of an over-all material and hydrogen balance to determine the yield of gasoline and tar products from a given charging stock.

Weight % total polymer is found by solving

$$P_T = 100 \times \frac{(H_G - H_F)}{(H_G - H_P)}$$

where P_T = weight % total polymer; H_G = weight % hydrogen in C_3-free residue gas; H_P = weight % hydrogen in C_4-free polymer; and H_F = weight % hydrogen in net fresh feed. Weight % hydrogen in the C_3-free residue gas is obtained from Figures 4, 5, and 6 which relate weight % C_2 in the furnace feed to mole % C_2 in the C_3-free residue gas, operating pressure to ethylene to ethane ratio, and operating temperature to hydrogen to methane ratio, respectively. Although the correlations given in Figures 4 and 6 apply quite generally, the validity of the relationship in Figure 5 is limited to the temperature range prescribed thereon; however, practical operating temperatures are included.

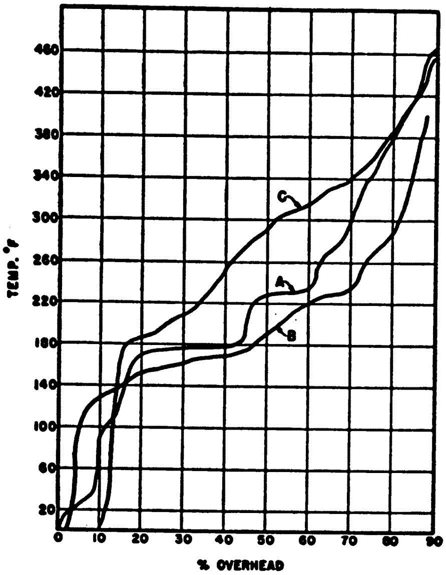


Figure 3. True Boiling Point Curves of Polymers

A and *B* = Thermal
C = Catalytic

Figure 7 permits the estimation of the hydrogen content of the C_4-free polygasoline as a function of operating pressure and weight % total C_4-free polymer per pass on combined throughput including the C_2 recycle. The specific gravity of the C_4-free 400° F. end point gasoline is also given. The relationship clearly illustrates the beneficial effect of pressure on yield and the deceleration of this benefit as pressure increases, so that a discreet limit is soon reached. The range of total polymer yield per pass is limited by the rate of carbon deposition on the high end and the size of equipment on the low end. The range given is that residing between these two uneconomic extremes.

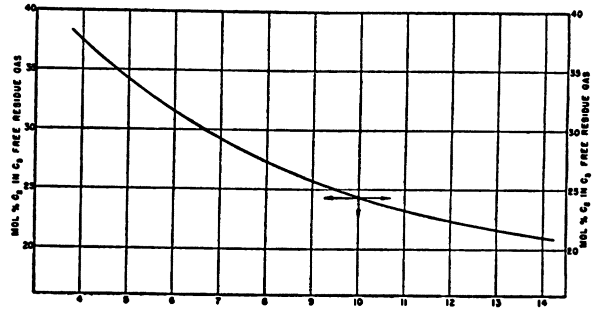
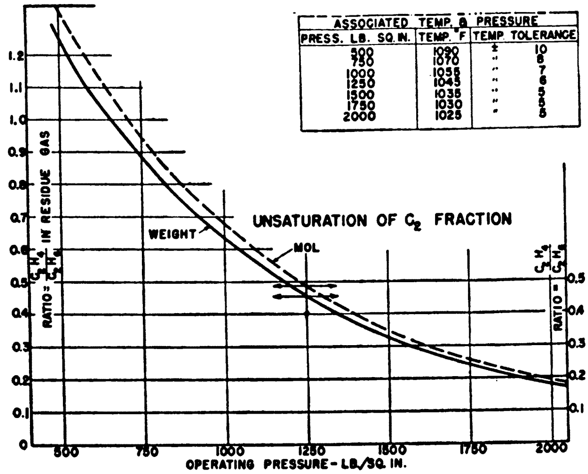


Figure 4. Ethane-Ethylene in Residue Gas

Tar is defined as the part of the polymer product boiling above 400° F. end point gasoline, and the weight % may be determined from Figure 8 as a function of total polymer per pass and operating pressure for net fresh feed compositions shown on Figure 8. Further, Figure 8 illustrates the penalty of high conversions by overpolymerization. Pressure promotes a favorable gasoline to tar ratio. The hydrogen and material balances may be completed by finding the hydrogen content and specific gravity of the tar as a function of operating temperature from Figure 9.

Time and temperature are to some extent interchangeable to attain a certain conversion per pass. Preferred reaction time is, however, in the 50- to 100-second range.



ASSOCIATED TEMP. & PRESSURE		
PRESS. LB. SQ. IN.	TEMP. °F	TEMP. TOLERANCE
500	1090	± 10
750	1070	" 8
1000	1055	" 7
1250	1045	" 6
1500	1035	" 5
1750	1030	" 5
2000	1025	" 5

Figure 5. Residue Gas Composition

Gas Reversion Process. The reforming of naphtha for octane improvement is conducted under temperatures and pressures of the same order as those for thermal polymerization. Whereas reforming is a once-through operation, the term Polyforming applies when the C_3 fraction produced in the reforming process and that part of the C_4 fraction not required for gasoline blending are recycled, in a sense combining reforming and thermal polymerization. Polyforming can be extended to include outside C_3 and C_4 stocks.

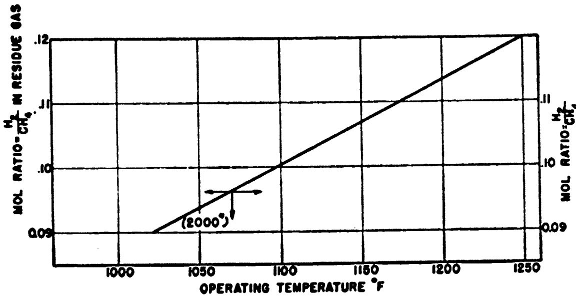
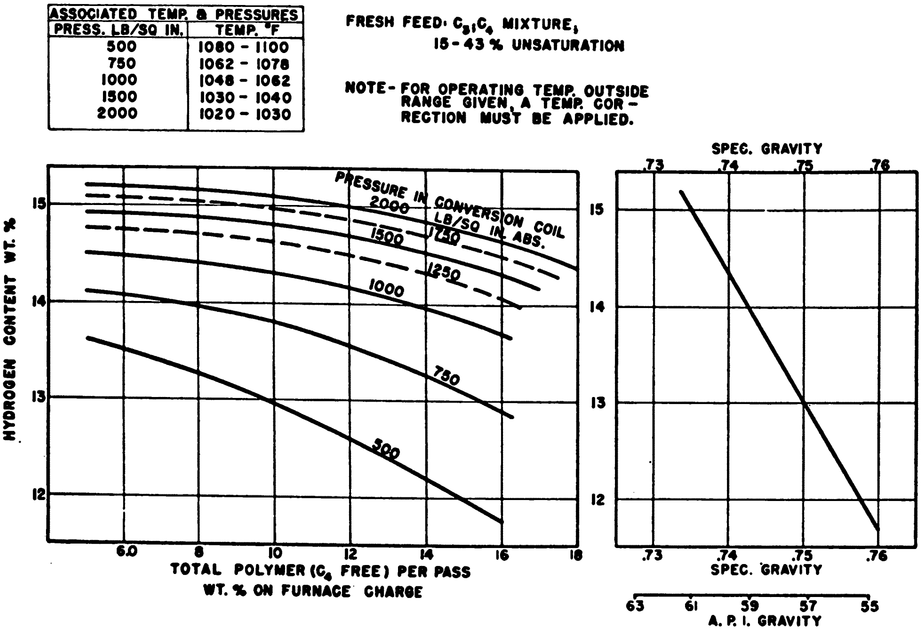


Figure 6. Hydrogen-Methane Ratio

In the gas reversion process the recycle and outside C_3–C_4 stocks are heated separately for partial conversion before admixture with the naphtha. This bridges the difference in reaction velocity between the two types of charge and is helpful since the conversion rate of naphtha is approximately four times that of propane and twice that of butane, thereby decreasing the volume of C_3–C_4 recycle. Figure 10 shows a simplified flow diagram of a typical gas reversion operation. The extent to which outside C_3–C_4 stocks can be utilized is not limited, and the process can revert to thermal polymerization as the proportion is



ASSOCIATED TEMP. & PRESSURES	
PRESS. LB/SQ IN.	TEMP. °F
500	1080 - 1100
750	1062 - 1078
1000	1048 - 1062
1500	1030 - 1040
2000	1020 - 1030

Figure 7. Composition of Gasoline—400° F. End Point, C_4-Free

increased to the final exclusion of naphtha. Gas oil may be substituted for naphtha, particularly if of a refractory nature, such as recycle stocks from catalytic cracking. In the combination of processes both the reforming severity and octane appreciation may be increased before rate of carbon deposition becomes a limiting factor. Also, the rate of conversion of C_3 fraction and C_4 fraction to motor fuel is increased by alkylation and synthesis reactions with the naphtha.

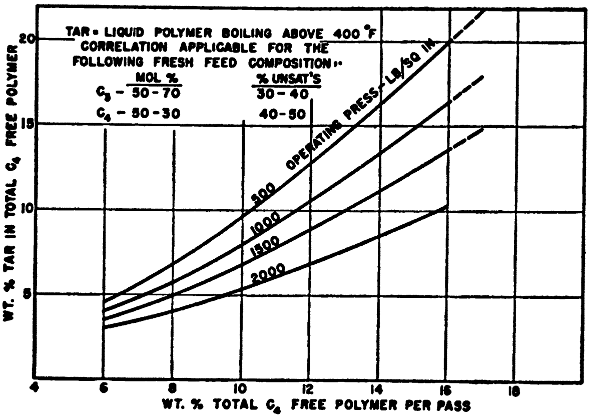


Figure 8. Tar Yields

Recent literature contains detailed correlations of the yield and quality of the gasoline product with operating conditions, quality of naphtha charge, and extent of outside additions of C_3 and C_4 fractions (*7*, *14*).

The method of calculation employs several correlations of C_2 and lighter fractions expressed as weight % of heater feed, known as "severity factor." The first correlation determines the yield of C_3, C_4, C_5, and C_6 to 400° F. end point fractions from the naphtha alone, followed by others determining the yields of gasoline components from the C_3 and C_4 fractions from the naphtha and from outside gas which are added to those of the naphtha.

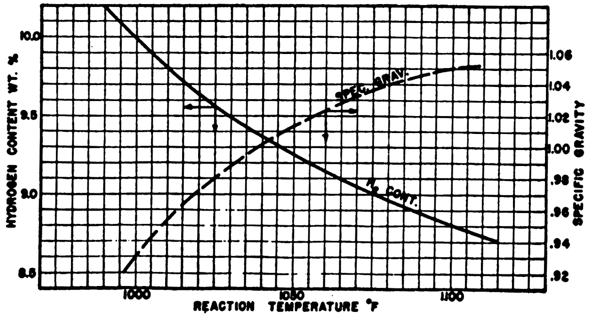


Figure 9. Tar Composition

In gas reversion the outside gas is subjected separately to mild thermal polymerization, limited by tar production, insufficient to advance materially the rate of carbon deposition in the coil after naphtha admixture. By combining the yield mechanism given for thermal polymerization with that for Polyforming, the process may be evaluated. In general, preferred operating conditions are 1020° to 1120° F. and 1500 to 2000 pounds per square inch gage in the reversion section, followed by 1025° to 1125° F. and 1000 to 2000 pounds per square inch gage in the naphtha Polyform section. According to Bogk, Ostergaard, and Smoley (*1*) the yield-CFR-ASTM octane number relationship of straight reforming, Polyforming, and gas reversion of 40 octane number straight run gasoline is given in Figure 11.

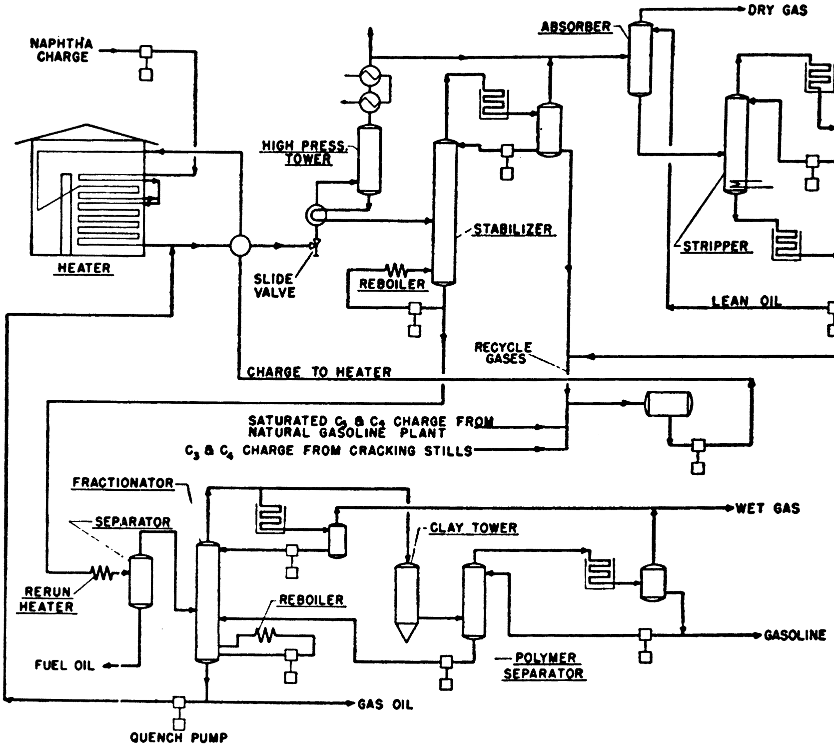


Figure 10. Gas Reversion Process

Gasoline boiling range distillates from thermal polymerization and gas reversion are not suitable for use as motor fuels without further treatment owing to high gum content and low induction periods. Finishing is usually accomplished by percolation through fuller's earth in the vapor phase (Gray process) as shown in Figure 10.

Catalytic Polymerization Processes

The more significant commercial catalytic polymerization processes have proved to be phosphoric acid processes and sulfuric acid processes.

The Universal Oil Products Co. process is based on the successful development of phosphoric acid catalysts by Ipatieff, initially as a liquid (*8*, *9*, *11*), later on a solid adsorbant (*10*). The first U.O.P. polymerization plants operated at pressures of about 200 pounds per square inch, temperatures of about 400° F. with a 100° F. temperature rise through the catalyst bed. A number of catalyst towers were used in series for the catalyst had to be regenerated, usually one tower at a time while the remaining ones continued on stream. The regeneration was accomplished by oxidizing the coke and heavy polymer deposit with a controlled concentration of oxygen in an inert gas followed by steaming of the catalyst for the purpose of restoring the water of hydration necessary for high conversion and extended life of the catalyst.

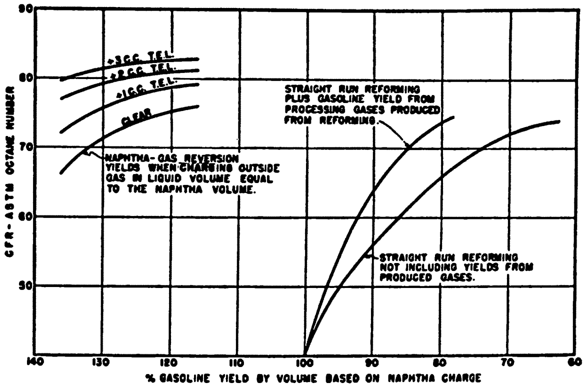


Figure 11. Yield-Octane Relationship for Naphtha-Gas Reversion and Reforming of Straight-Run Gasoline

Gray and Hutchinson County, Tex., Crudes

By 1939 a Midget chamber-type polymerization process (*20*) had been developed that economically employed feed rates as low as 250,000 cubic feet per day, whereas the older units were uneconomical at feed rates below about 2,000,000 to 3,000,000 cubic feet per day. Midget units proved successful because it was found that when operating the polymerization reaction at pressures of 500 pounds per square inch a sufficient amount of feed remained in a dense phase to wash the catalyst clear of most of the heavy polymer, thus extending catalyst life and eliminating catalyst regeneration.

Figure 12 is a simplified flow diagram of a chamber-type unit. In this instance the feed is taken only from the cracking plant stabilizer overhead although some plants also include the absorber overhead gas in the feed. If a predominantly C_3–C_4 charge is polymerized the recovery section can be modified to yield a propane stream for liquefied petroleum gas sale as well as butane by the use of a de-ethanizer (if required), a depropanizer, and a debutanizer.

A further improvement was the development of the reactor type unit using multiple tube-and-shell reactors for better temperature control (*25*). This type of reactor proved useful in larger installations and for selective polymerization of either C_3 or C_4 olefins only. The larger reactor type units are so arranged that the steam produced in the reactor shell by the exothermic reaction is used to preheat the feed to the proper inlet temperature. The tubes usually are from 2 to 6 inches in diameter.

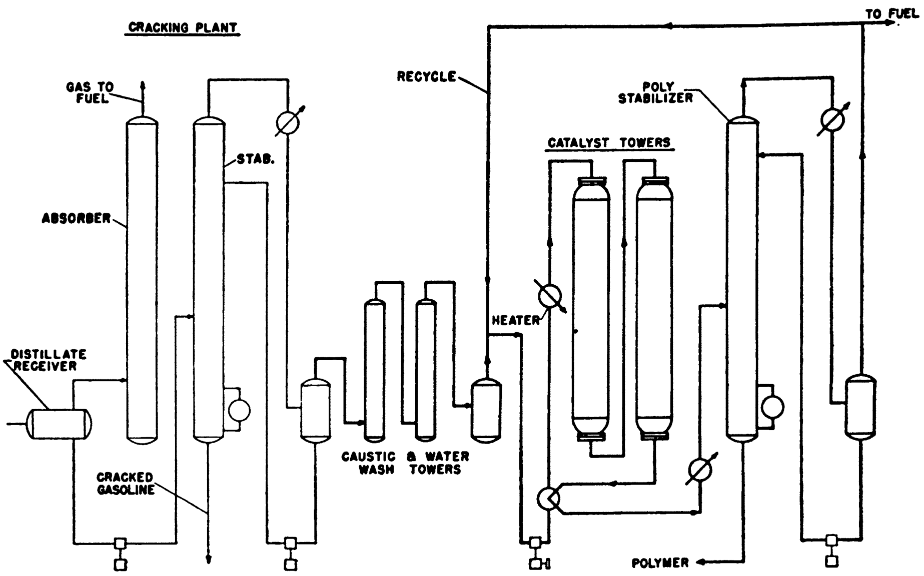


Figure 12. U.O.P. Catalytic Polymerization Process—Chamber Type

The principal operating variables in the U.O.P. catalytic polymerization process are feed composition, pressure, temperature, space velocity, and water content of the feed.

The type of feed that can be used varies widely. In nonselective polymerization in chamber-type plants a C_3–C_4 olefin content of about 20 to 25%, is practical. When the olefin content of the fresh feed rises above 25%, enough spent gas of low olefin content must be recycled in order to limit the olefin content of the total feed. Reactor-type plants can employ a higher olefin content in the feed, the exact value depending on the cooling efficiency of the reactor.

The ease of polymerization of olefins, in the order of increasing reactivity, is ethylene, propylene, 1-butylene, 2-butylene, and isobutylene. The presence of isobutylene apparently accelerates the polymerization of *n*-butylenes, and the presence of butylenes has a similar effect on propylene (*8*, *11*, *25*).

Polymerization is accompanied by a decrease in volume and therefore is promoted by elevated pressures. Also, raising the pressure lowers the temperature at which satisfactory conversion can be obtained; and low temperatures are preferred because they minimize the formation of heavy polymers and coke, thus increasing catalyst life. Older units operated at about 200 pounds per square inch and 400° F. at the inlet, using cracked gases without further compression. The newer chamber-type units operate at about 500 pounds per square inch, inlet temperatures of 350° to 400° F., and 450° to 475° F. at the outlet, with temperature control by means of recycling and quenching at intermediate points with spent gas. Reactor-type units operate at 700 to 1200 pounds per square inch with about 400° F. inlet and limit the temperature rise to approximately 15° F. When selectively polymerizing C_4 olefins, the temperature of a reactor-type unit may be as low as 280° to 375° F., depending on the pressure used and whether dimers only or also trimers are desired.

The space velocity is generally chosen to give conversions of 85 to 95% of the olefins charged. Higher conversions are possible, but uneconomical, as more catalyst is required and catalyst life is reduced. Space velocities, based on total feed, may range from about 0.3 to 0.5 gallon per hour per pound of catalyst or 4.5 to 7.0 cubic feet per hour per pound of catalyst, depending on olefin content of feed and other process variables.

The addition of the proper amount of water to the feed is of great importance. An

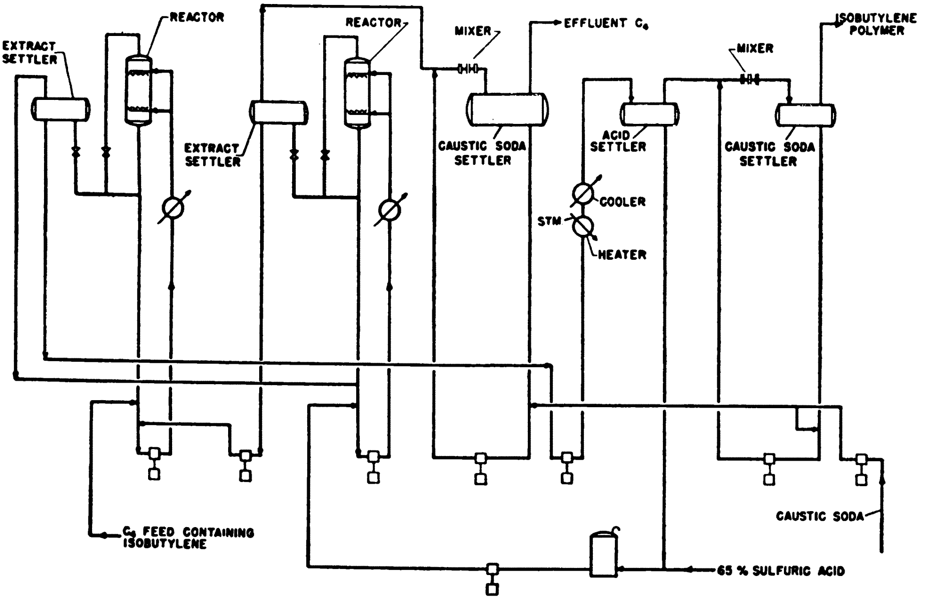


Figure 13. Shell Cold Acid Polymerization Process

underhydrated catalyst promotes heavy polymer and coke deposition on the catalyst (*25*), thus shortening catalyst life, decreasing its activity, and increasing the pressure drop. Overhydration results in softening of the catalyst, often to the point of plugging the reactor.

Reduction in activity of the catalyst may be caused by polymer and coke deposition due to excessive temperature, low pressure, insufficient water in the feed, or too low a space velocity (*25*). The presence of diolefins, oxygen, caustic, or nitrogen bases, such as ammonia or amines in the feed, also causes loss of catalyst activity.

For chamber-type plants the useful catalyst life expected is 100 gallons of polymer per pound of catalyst and about twice that for reactor-type plants (*25*). The quality of operating procedures can affect the catalyst life to a considerable degree.

The polymerization of light olefins using copper pyrophosphate is licensed by The M. W. Kellogg Co. under patents of the Polymerization Process Corp. The process is essentially the same as the U.O.P. process but instead uses a copper pyrophosphate catalyst (*18*). The first plant was built in 1939 (*22*) and several more have been put into operation since that time. A correlation of operating variables for this process was published in 1949 (*21*); it shows how conversion is influenced by catalyst activity, temperature, ratio of propene plus *n*-butene to isobutene, and the space velocity of olefins and of total feed when operating at 900 pounds per square inch gage pressure. A catalyst life of 100 to 150 gallons of polymer per pound of catalyst is claimed (*15*).

The catalyst is sometimes diluted with charcoal in the ratio of 1:1 to 2:1 of catalyst to charcoal (*21*). The charcoal acts as an adsorbent for the phosphoric acid released under operating conditions and distributes the acid over a larger portion of the bed. The phosphoric acid acts as the actual catalytic agent.

The reactor inlet temperature is about 400° F. for nonselective operation or about 350° to 370° F. for codimer production from butenes. The temperature rise is of the order of 20° to 50° F.

A recent commercial development in catalytic polymerization of olefins has been made by the California Research Corp. This process employs a reaction chamber filled with crushed quartz which is coated with liquid phosphoric acid in situ. The catalyst is reported to have a life of 100 gallons of polymer per pound of 75% by weight phosphoric acid solution; it is renewed by washing with water and steam and recoating with 75% phosphoric acid solution without disturbing the quartz. The catalyst is understood to be rugged, permitting operation without recycle on feed of any olefin content obtained in normal refinery operations. The exothermic heat of reaction is controlled by quenching with cold feed at spaced points throughout the bed as required. It is claimed that the process is easy to control, requires a minimum of pretreatment of feed stock, and accomplishes conversion of 90% or better of the olefins to polymer with most normal feed stocks.

Polymerization with Sulfuric Acid. In the early 1930's development work on sulfuric acid–catalyzed polymerization was undertaken by a number of research organizations. The most widely used process is that developed by the Shell companies (*13*).

The cold acid process was developed first and effects polymerization of isobutene only. Figure 13 shows a simplified flow diagram of the process. Two contact stages are generally used in counterflow. In the second stage the freshly regenerated acid contacts the hydrocarbons from the first stage, and the intermediate acid contacts the fresh feed in the first stage. The acid, with absorbed isobutene, is heated to cause polymerization, then cooled; the polymer which forms a separate phase is withdrawn, and the acid then is ready for re-use.

The absorption step occurs at a temperature of about 68° to 104° F. and whatever pressure is necessary to maintain the hydrocarbon feed in the liquid phase. When using a 65% acid about 90 to 95% of the isobutene is absorbed. Polymerization takes place at a temperature of 200° to 220° F., producing approximately 75 to 80% dimer, the rest trimer. Thus about 67% of the isobutene in the feed is converted to iso-octenes.

The hot acid process was developed as a logical outgrowth of the cold acid process (*13, 15, 16*). The hydrocarbon is contacted with acid, varying from 63 to 72% in strength, at a temperature of 167° to 212° F. At this temperature the n-butenes as well as isobutene are absorbed, polymerized almost at once, and the higher molecular weight olefins so formed are preferentially reabsorbed by the hydrocarbon phase, minimizing further polymerization. Figure 14 is a flow diagram for a typical plant.

To promote the cross polymerization of olefins the concentration of the more reactive isobutene is kept low by recycling a stream of hydrocarbon-acid emulsion having a low iso-

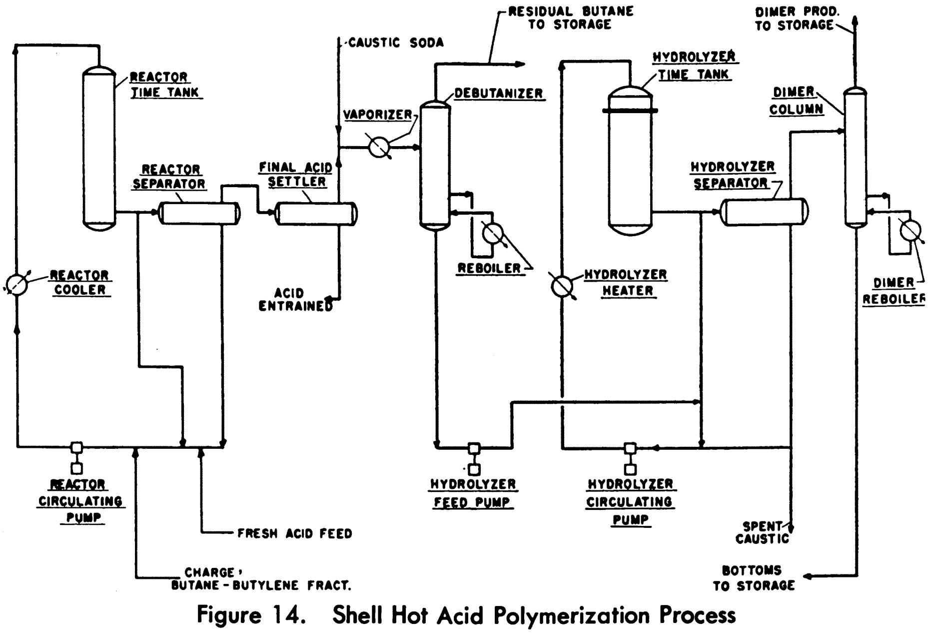


Figure 14. Shell Hot Acid Polymerization Process

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Table I. Inspection of Typical Thermal Polymer Gasolines

Process	Thermal Polymerization				Gas Reversion
	(*17*)	Pure Oil Co. data		(*2*)[a]	(*1*)
Temperature, ° F.	1154	1090	1040	..	..
Pressure, lb./sq. inch	61	625–500	1225	..	..
Feed	C_1–C_4	C_3–C_4	C_3–C_4	..	Naphtha: gas ratio 1: 1
Unsaturates, %	47	35–45	35	..	
Inspection of gasoline					
Gravity, ° API	34.4	69.4	68.9	62.5	62.0
ASTM Dist.					
I.B.P., ° F.	120	106	100	104	93
10%	167	123	116	127	123
50%	212	143	152	179	210
90%	298	228	245	303	345
E.p., ° F.	399	348	378	428	406
RVP[b], lb./sq. inch	..	9.1	10.7	8.9	8.5
Composition, vol. %					
Olefins	..	36.1	40	..	..
Aromatics	47	3.4	5	..	..
Naphthenes	..	31.3	17	..	..
Paraffins	..	29.2	38	..	..
Octane No.					
Motor, clear	..	72.2	77.0	77.5	69.0
With 3 cc. TEL	..	78.6	..	..	80.5
Research, clear	..	..	89.2	..	..
With 3 cc. TEL	..	..	..	..	..

[a] Clay treated.
[b] Reid vapor pressure.

butene content. At contact times of 10 to 15 minutes, about 85 to 90% of the C_4 olefins are converted to polymer containing up to 90 or 95% octenes.

Sulfuric acid polymerization plants found their greatest application in the aviation gasoline program. Cold acid plants were generally converted to the hot acid type because the yield of the latter is much higher with only a very small sacrifice in octane value of the hydrogenated dimer.

Properties of Polymer Motor Fuel

Some of the properties of typical polymer gasolines are shown in Tables I and II. Inspections are given for thermal as well as catalytic polymer gasolines. Catalytic polymer gasolines are characterized by their high olefin content, high octane values in straight-run blends, and their high gum-forming tendencies. However, the gasoline is very susceptible to the action of inhibitors and requires no rerunning. No noticeable effect of space velocity on the octane number of nonselective polymers is observable (*3*). The composition of thermal gasolines is influenced primarily by reaction temperature.

Mechanism of Polymerization of Alkenes (Olefins)

Thermodynamic calculations have shown the areas of temperature and pressure in which polymerization will tend to take place. The free energy ($\Delta F°$) of polymerization of normal olefins (above ethene) has been expressed by

$$\Delta F° = -20{,}320 + 33.26T \text{ (19)}$$

Other thermodynamic equations indicate that pressure favors polymerization. Although the free energy of polymerization is more favorable at low temperatures, rather high temperatures, or powerful catalysts must be used to overcome the passivity of olefins and to increase the rate of polymerization.

The mechanism of catalytic polymerization of alkenes to motor fuel recently has been ably discussed by Schmerling and Ipatieff in one chapter of a current book on catalysis (*5*).

Many theories have been proposed but three have received considerable attention: Whitmore's carbonium ion theory (*26*) postulates that a carbonium ion (positive hydrocarbon ion) adds to an olefin to form a higher molecular weight carbonium ion which then yields the olefin polymer by elimination of a proton (H^+). With acid catalysts—for example, sulfuric acid—the initial carbonium ion is formed by addition of a hydrogen ion from the acid to the extra electron pair in the double bond of the olefin. A second pro-

Table II. Inspection of Typical Catalytic Polymer Gasolines

(Phosphoric acid catalyst)

Process	Nonselective (*25*)	Nonselective (*25*)	Nonselective (*25*)	Selective (*25*)	
Temperature, ° F.	..	..	375–450	330–350	
Pressure, lb./sq. inch	1000	1000	500	900	
Feed	C_3	C_4	C_3–C_4	C_4	
Unsaturates, %	..	..	35	56	
Inspection of gasoline				Dimer	Trimer
Gravity, ° API	62.4	64.3	67.3	61.3	51.5
ASTM Dist.					
I.B.P., ° F.	144	78	90	210	261
10%	204	152	143	223	286
50%	266	258	225	228	329
90%	330	379	367	234	379
E.p., ° F.	402	416	422	257	434
RVP[a], lb./sq. inch	4	11	11		
Composition, vol. %					
Olefins	..	..	94.1[b]	..	..
Aromatics	..	..	0.8	..	..
Naphthenes Paraffins	..	..	5.1	..	..
Octane No.					
Motor, clear	..	..	82.5	95.1[c]	..
With 3 cc. TEL	..	..	85.0	..	..
Research, clear	..	..	97.0	..	..
With 3 cc. TEL	..	..	100.0	..	..

[a] Reid vapor pressure.
[b] C_6 + gasoline.
[c] Hydrogenated dimer.

posed mechanism is quite similar to the carbonium ion mechanism but differs from it in that it assumes that the condensation takes place by way of addition of an alkyl ester to the olefin to form a higher molecular weight ester which then dissociates to form the polymer and regenerate the acid. For the polymerization of olefins catalyzed by phosphoric acid, Ipatieff (*8*) has proposed that the polymerization involves the interaction of two molecules of phosphoric acid ester with the elimination of phosphoric acid and the production of polymer by the union of the two hydrocarbon radicals.

Farkas and Farkas (*4*) have introduced a promising technique for the unraveling of the mechanism of polymerization. These investigators employed a phosphoric acid catalyst in which the three hydrogens were replaced by deuterium (heavy hydrogen). The deuterium thus served as a tracer element and thereby enabled the investigators to obtain more specific information about olefin polymerization. They suggest a modification of Ipatieff's theory. Their experiments are not entirely conclusive, but they suggest a very promising method of attack for future researches on the mechanism of polymerization of alkenes.

Future Research

The polymerization of gaseous olefins is a relatively simple process. Its increased utilization will depend on an ample supply of light olefins. This suggests further investigation into the problem of producing light olefins from gaseous paraffins at low cost.

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Commercial Alkylation of Isobutane

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All phases of the process for the alkylation of isobutane with olefins as practiced in modern petroleum refining are discussed. The discussion covers the chemistry of the reaction, as well as the technological items relating to feed stock composition, catalyst types, reaction variables, and commercial adaptations. A previously unpublished correlation relating alkylate quality to operating conditions is presented. The research problems requiring solution for commercial survival of the process when jet-type aircraft utilizing low octane fuels displace the reciprocating type are outlined.

The use of thermal and catalytic cracking processes for the production of high-octane motor gasolines is accompanied by the production of quantities of light hydrocarbons such as ethylene, propylene, butene, and isobutane. These materials are satisfactory gasoline components octane-wise, but their vapor pressures are so high that only a portion of butanes can actually be blended into gasoline. Alkylation is one of several processes available for the utilization of these excess hydrocarbons.

In broad terms, alkylation refers to any process, thermal or catalytic, whereby an alkyl radical is added to a compound. In the petroleum industry, however, the term alkylation generally refers to the catalytic process for alkylating isobutane with various light olefins to produce highly branched paraffins boiling in the gasoline range. This specific process will be discussed in this paper.

The alkylation process had its first commercial application in the late 1930's and has become an important commercial process for two reasons. First, the product of the reaction is an excellent aviation gasoline blending stock, because of its high aviation octane ratings, desirable boiling range, high heat of combustion per pound, good storage stability, and low sulfur content. Secondly, it is, in effect, a process for the conservation of resources, for it converts fuel gas components to gasoline components.

The growth of this process has been accelerated by the increased availability of light hydrocarbons resulting from the simultaneous growth of catalytic cracking processes. Military demands for aviation gasoline during World War II were responsible for rapid expansion of these processes by the petroleum industry. Since aviation gasoline production is limited by alkylate supply, rapid development of the alkylation process was required to supply the expanded requirements of aviation gasoline (*5*). At the end of the war there were 59 alkylation plants in the country with a rated capacity of 178,000 barrels per day of aviation alkylate (*9*).

Chemistry of the Reaction

The reaction between isobutane and olefins in the presence of an alkylation catalyst results in a product that is essentially paraffinic, and consists of a mixture of isoparaffins ranging from pentanes to decanes and higher regardless of which alkylating olefin is used.

Component analyses of a typical alkylation product are presented in Table I. The formation of all of these compounds cannot be explained by the simple addition of an olefin molecule to an isobutane molecule. Even the formation of some of the specific isomers having the expected molecular weight cannot be accounted for by simple molecular addition. The mechanism of the reaction, therefore, must be rather complex.

Table I. Chemical Composition of a Typical Butene Alkylate (3)

Component	B.P. at Atmospheric Pressure, ° C.	Volume % Concn. in Alkylate
Pentanes and lighter	< 58.0	8.9
2,3-Dimethylbutane	58.0	4.7
2-Methylpentane	60.3	1.1
3-Methylpentane	63.3	0.4
2,2-Dimethylpentane	79.2	0.2
2,4-Dimethylpentane	80.5	3.4
2,2,3-Trimethylbutane	80.9	0.2
2,3-Dimethylpentane	89.8	2.3
2-Methylhexane	90.1	0.3
3-Methylhexane	92.0	
2,2,4-Trimethylpentane	99.2	24.3
2,2-Dimethylhexane	106.8	0.2
2,5-Dimethylhexane	109.1	6.6
2,4-Dimethylhexane	109.4	
2,2,3-Trimethylpentane	109.8	1.2
2,3,4-Trimethylpentane	113.5	13.0
2,3,3-Trimethylpentane	114.8	12.3
2,3-Dimethylhexane	115.6	3.0
3,4-Dimethylhexane	117.7	0.4
2,2,5-Trimethylhexane	124.1	4.5
2,3,5-Trimethylhexane	131.4	0.9
Isoparaffins	> 131.4	12.1
		100.0

Of the several theories proposed for the mechanism of the alkylation reaction (*2*, *4*, *7*), the "carbonium ion" theory is probably the most widely accepted. Although a complete discussion of this theory is beyond the scope of this paper, an outline of the mechanisms it proposes as applied to known alkylation products is presented.

A carbonium ion is defined by this theory as a molecule containing a carbon atom which is deficient two electrons in its outer shell, and consequently carries a positive charge. The carbonium ion is highly reactive, and can undergo several transformations and reactions, among which are the following:

1. Loss of a proton to form an olefin
2. Reaction with an olefin to form a carbonium ion of higher molecular weight
3. Proton shift from another carbon atom in the molecule to the carbon atom deficient in electrons to form a new carbonium ion
4. Methyl group shift from another carbon atom in the molecule to the carbon atom deficient in electrons to form a new carbonium ion having a different carbon-to-carbon skeleton
5. Cleavage of carbon-to-carbon linkage to form an olefin and another carbonium ion of lower molecular weight
6. Reaction with isobutane to form a paraffin molecule and a tertiary butyl carbonium ion

The above transformations and reactions can be used to explain the formation, as an example, of different heptane isomers when alkylating isobutane with propylene. As the first step in the mechanism, a tertiary butyl carbonium ion derived from isobutane reacts with a propylene molecule to form a carbonium ion of seven carbon atoms as outlined in reaction 2. This ion may then react directly with a molecule of isobutane as in reaction 6 to form the expected heptane molecule and to convert the isobutane molecule to a tertiary butyl carbonium ion. This seven-carbon carbonium ion, however, may undergo isomerization by the mechanism outlined in reaction 3 or 4 before reacting with isobutane to form an isomeric heptane molecule.

The proposed mechanisms may also be used to explain the formation of paraffins having both lower and higher molecular weights than would be expected from simple addition of olefin molecules to isobutane molecules. A typical example is the formation of heptanes and nonanes when isobutane is alkylated with butene. The first step consists of a reaction between a butene molecule and a tertiary butyl carbonium ion derived from isobutane to form a carbonium ion of eight carbon atoms by reaction 2. This ion may then undergo isomerization as in reactions 3 and 4, followed by carbon-to-carbon cleavage, as in reaction 5, to form an isomeric pentene molecule and an isopropyl carbonium ion. The pentene molecule then reacts with a tertiary butyl carbonium ion to form a nine-carbon carbonium ion, which in turn reacts with isobutane as in reaction 6 to form a product nonane molecule and a tertiary butyl carbonium ion. The isopropyl carbonium ion, on the other hand, may react with another butene molecule to form a seven-carbon carbonium ion, which is converted to a product heptane molecule by reaction with isobutane.

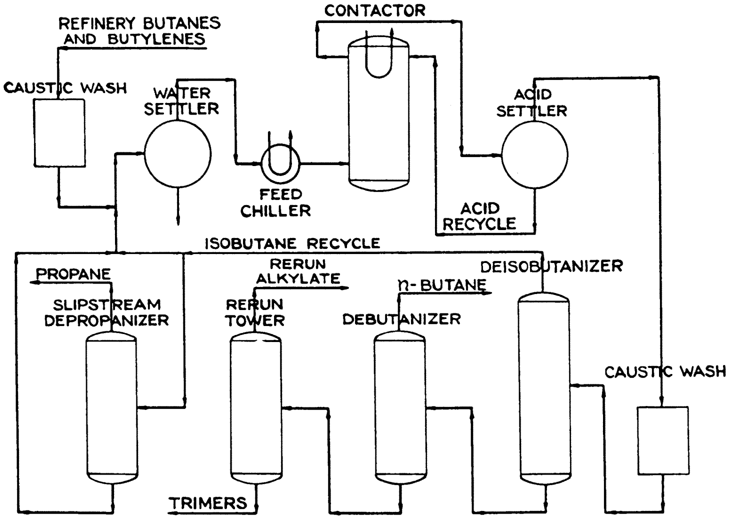

Figure 1. Sulfuric Acid Alkylation Plant

It will be noted from the above examples that the tertiary butyl carbonium ions required for the reaction are constantly being replenished to establish a chain reaction. It is assumed that the reaction is initiated by olefin molecules accepting protons from the catalyst to form carbonium ions which react with isobutane to produce the necessary active tertiary butyl carbonium ions.

Sulfuric Acid Alkylation

Commercial alkylation may be divided into three distinct types depending on whether the catalyst used is sulfuric acid, hydrofluoric acid, or aluminum chloride. These types of alkylation are similar in many respects but have some outstanding differences. In 1946 there were 32 plants in the United States employing the sulfuric acid process, 27 using the hydrofluoric process, and one using aluminum chloride (*1*, *9*). Since sulfuric acid alkylation is the most widely practiced of the three, it will be discussed first.

Figure 1 presents a schematic flow diagram for a typical sulfuric acid plant for the alkylation of isobutane with butenes. The olefin feed stock is a depropanized refinery butane-butenes stream from catalytic and/or thermal cracking containing about 50% olefins and composed essentially of isobutane, normal butane, and butenes with minor amounts of propane and isopentane. This olefin stock undergoes a caustic treatment for removal of mercaptans and hydrogen sulfide. Removal of these compounds is necessary to prevent the formation of free sulfur which would result in a corrosive product, to reduce acid consumption, and to prevent octane degradation of the leaded product. This stock then combines with the recycle isobutane stream and goes to the reactor.

The alkylation reactor or contactor serves to bring isobutane and olefin into intimate

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contact with the liquid catalyst for a sufficient length of time to obtain the desired product. Provision must also be made either in the reactor proper or in the reactor system to remove the heat of reaction liberated in the process. Several types of reactors are commonly used, and a later section of this paper is devoted to that subject.

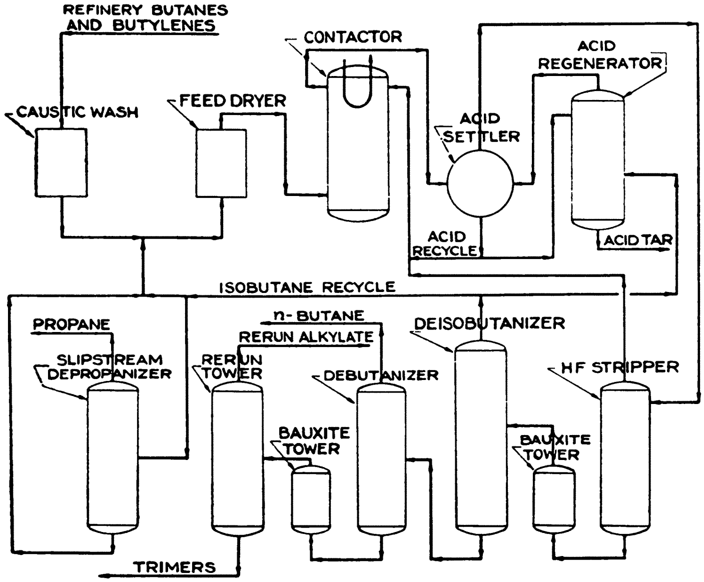

Figure 2. Hydrofluoric Acid Alkylation Plant

The mixture leaving the reaction zone is in the form of a hydrocarbon-acid emulsion and passes to an acid settler for separation of acid and hydrocarbon phases. This acid settler is usually a separate vessel from the reactor itself, although it is an integral part of one type of system. The hydrocarbon-free acid from the acid settler recirculates to the reactor. The hydrocarbon layer, which consists of alkylate, excess isobutane, and the inert diluents introduced with the feed, receives a caustic treatment and goes to the fractionating section of the plant. Caustic treatment is necessary at this stage of the process to neutralize acidic components, such as sulfur dioxide, which are formed in small quantities by catalyst degeneration.

The fractionation section of the alkylation plant consists of a deisobutanizer, a debutanizer, and a rerun tower in series, and a depropanizer. The deisobutanizer overhead, which contains about 90% isobutane, recycles to the reactor. The deisobutanizer bottoms stream passes to the debutanizer, which removes normal butane diluent as an overhead stream. The debutanizer bottoms or raw alkylate stream then goes to a rerun tower for removal of the high boiling alkylate bottoms or "trimers." The rerun overhead requires no further treatment to be satisfactory as an aviation gasoline blending stock. The depropanizer removes propane diluent from a "slip-stream" portion of the recycle isobutane stream to prevent propane build-up in the reaction system.

In the alkylation of isobutane with butenes, several variables have an important bearing on the quality of the alkylate produced. The most important is the concentration of isobutane in the reactor. Although theoretically only equimolecular ratios of isobutane and butene are required for the reaction, a large excess of isobutane in the reaction zone has been found necessary to suppress undesirable side reactions which result in loss of yield and octane number. Over-all isobutane-olefin ratios of 5 to 1 or higher are necessary for the production of high quality aviation alkylate.

Temperature is an important variable in the alkylation process. When alkylating isobutane with butenes, a reaction temperature of 40° to 50° F. produces the highest quality alkylate with the lowest catalyst consumption. Commercial operation has been successfully carried on at temperatures as high as 70° F., but the alkylate produced has been of inferior quality and the catalyst consumption has been excessive.

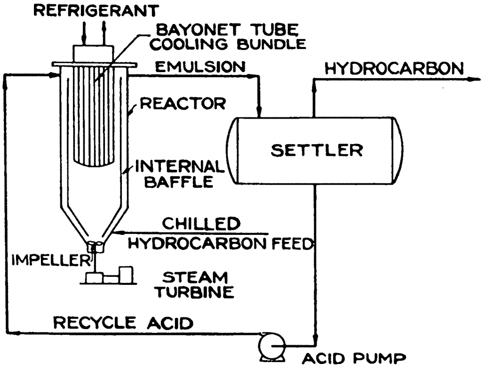

Figure 3. Impeller-Type Reactor System

The amount of acid in the acid-hydrocarbon reaction mixture also has an important bearing on the alkylate quality. If the reaction mixture contains less than 40% acid by volume, an acid-in-hydrocarbon emulsion results. Above this 40% inversion point, a hydrocarbon-in-acid emulsion is formed. The latter type produces the better product and consequently an acid volume of 60 to 70% of the reaction mixture is normally maintained.

The effect of reaction pressure is negligible, the pressures used being sufficient to keep the reaction mixture in the liquid phase.

The catalyst usually employed for sulfuric acid alkylation is 98% sulfuric acid, although concentrations as high as 100% are equally satisfactory. The use of fuming acids is not desirable since the excess sulfur trioxide reacts with isobutane and does not serve as a catalyst. It is possible to use sulfuric acid of concentrations as low as 90%, but the use of these weaker acids has an adverse effect on the alkylate quality and catalyst life.

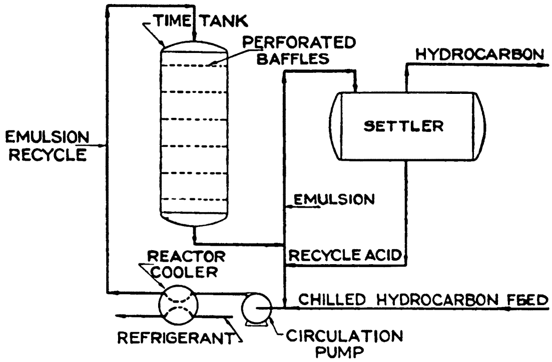

Figure 4. Time-Tank Reactor System

As the alkylation catalyst ages, its titratable acidity decreases because it becomes diluted with water from the feed stock and with water and complex hydrocarbon oils produced by side reactions. The catalyst is ordinarily discarded when its titratable acidity drops to 85 to 88%. If the catalyst is used further, the quality of the alkylate deteriorates rapidly, and the hydrocarbon-acid emulsion becomes so stable that separation difficulties are encountered in the acid settler.

There are two methods ordinarily used for maintaining the acidity of the catalyst. The first of these is the continuous method where fresh acid is added to the circulating acid stream continuously at a rate sufficient to maintain the titratable acidity at the desired level of 88 to 90%. Spent acid is constantly withdrawn to maintain the level in the acid settler. In this type of operation the catalyst strength is constant during processing.

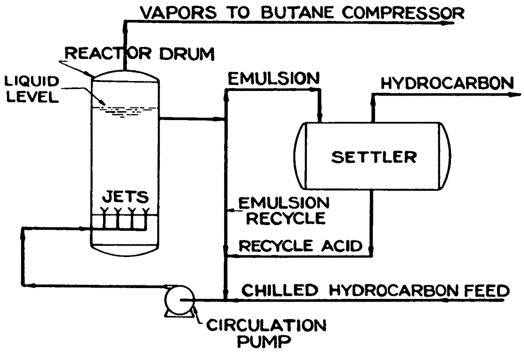

Figure 5. Autorefrigerated Jet-Type Reactor System

In the second method of acid addition, the fresh acid is charged batchwise to two acid settlers which are alternately used in the reactor system. When the acid reaches the desired discard strength, the settler in use is removed from service and is replaced with a freshly charged one. The second settler is kept in service until the acid has again become depleted, at which time it is replaced by the original settler recharged with fresh acid. In this operation the acid strength starts at 98% and gradually decreases to 88% for each batch of acid used. While batchwise handling of the catalyst requires an extra acid settler, it has two distinct advantages over the continuous method in that the average acid strength during processing is higher, resulting in higher alkylate octanes, and the catalyst consumption is decreased because the rate of acid depletion is most rapid at low titratable acidities.

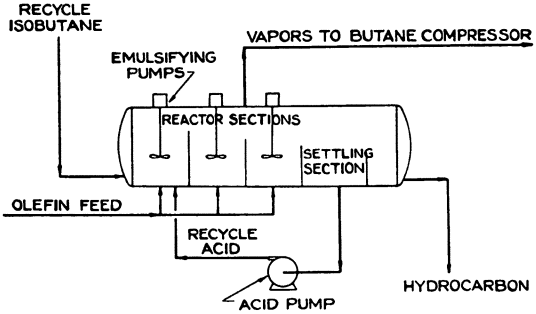

Figure 6. Autorefrigerated Integral Reactor-Settler System

The catalyst consumption for sulfuric acid alkylation is expressed in terms of pounds of fresh acid depleted per barrel of alkylate produced. When alkylating isobutane with butenes at 50° F. and maintaining an isobutane-olefin ratio of 5 to 1, the acid consumption will average 35 to 40 pounds per barrel when charging 98% acid and discarding 88% acid in a batchwise operation.

Commercial operation of sulfuric acid alkylation plants has been relatively trouble-free and shutdowns for reasons other than normal inspection and maintenance are seldom required. Many plants operate on a one-year regular shutdown and high on-stream efficiencies are obtained. In spite of the fact that a strong acid is used as catalyst, corrosion problems are not serious because the water content of the catalyst remains low. Consequently, unusual materials of construction are not required and ordinary carbon steel is used extensively for construction of these plants.

Hydrofluoric Acid Alkylation

Figure 2 presents a schematic flow diagram for a typical hydrofluoric acid alkylation plant. Since processing with hydrofluoric acid is very similar to processing with sulfuric acid, this discussion will point out only the significant differences in the two processes.

The feed preparation differs from that for sulfuric acid by the inclusion of a hydrocarbon feed dryer. Due to the very corrosive nature of hydrofluoric acid–water mixtures, a feed dryer is necessary to prevent water from entering the system. Activated alumina is a typical drying agent used in this service.

As in sulfuric acid alkylation, the hydrocarbon-acid emulsion passes from the contactor into an acid settler for separation of acid and hydrocarbon phases and the acid layer recirculates to the reactor. Unlike sulfuric acid, however, hydrofluoric acid is appreciably soluble in hydrocarbons, and as much as 1% by weight may be retained in the hydrocarbon layer. The necessity of recovering this acid from the hydrocarbon phase results in another difference between hydrofluoric and sulfuric acid processing in that a hydrofluoric acid stripper is required. This stripper is ordinarily packed with aluminum rings which serve not only as tower packing but also as a catalyst for the decomposition of organic fluorides into hydrocarbons and free hydrofluoric acid.

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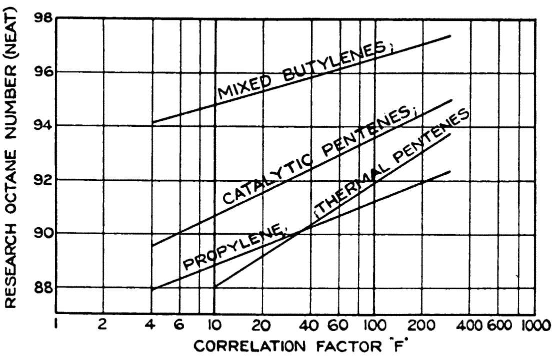

Figure 7. Sulfuric Acid Alkylate Octanes, ASTM Research (CRC-F-1)

The stripper overhead returns to the reactor, and the bottoms pass to a bauxite tower for removal of the remaining organic fluorides. Removal of these dissolved organic fluorides is essential because they impart corrosive properties to the resulting alkylate and lower its octane ratings. Their removal is accomplished by passing the hydrocarbon in the liquid phase through a bauxite-packed tower where they combine with the alumina. A low silica grade of bauxite must be used to prevent the formation of volatile silicon tetrafluoride which would migrate and cause condenser fouling in the fractionating section. Often lime is added to these towers to neutralize traces of free hydrofluoric acid and to aid in the control of silicon migration.

The fractionation section of the plant is identical to that for sulfuric acid alkylation except that another bauxite treatment is given the total alkylate before rerunning.

As in sulfuric acid alkylation, the important reaction operating variables are isobutane concentration, catalyst purity, acid-hydrocarbon ratio, and reaction temperature. Normally these variables are maintained at the same level as in sulfuric acid alkylation except for temperature. Most commercial plants operate from 75° to 100° F. This higher operating temperature often allows cooling water rather than the usual vaporizing refrigerants to be used.

In contrast to the sulfuric acid process, regeneration of the catalyst in hydrofluoric acid alkylation is continuous. During processing, both hydrofluoric acid and sulfuric acid become diluted with tarry materials and water, but since hydrofluoric acid is rather volatile, it is readily purified by distillation. Consequently, a portion of the circulating catalyst stream is continuously charged to an acid regeneration tower. Hydrofluoric acid of high purity is flashed overhead and returned to the reaction zone while water and tars are drawn as bottoms.

The catalyst acidity in the reactor can be maintained at any desired strength by regulation of the acid regeneration tower feed rate. For the production of aviation grade alkylate, the titratable acidity of the circulating acid is usually maintained in the range of 85 to 90% hydrofluoric acid.

Fresh hydrofluoric acid used for catalyst make-up is anhydrous and of 99.5%+ purity. Since the acid in the unit is continually being regenerated, the only hydrofluoric acid consumed in the process is that which is absorbed in the bauxite towers, lost to the acid tar, lost in handling, or lost through venting equipment and lines for maintenance access. Typically, hydrofluoric acid consumption, including losses to all sources, will average about 0.5 to 0.8 pound per barrel of alkylate.

Because of its corrosive nature and high volatility, the introduction of hydrofluoric acid as a commercial catalyst was attended by many problems in design and operation. Among the more serious problems was the effective sealing of pumps and valves in hydrofluoric acid service, and the prevention of valve sticking caused by iron fluoride deposits. In such equipment as the acid regeneration tower, where a hydrofluoric acid–water mixture occurs, the corrosion problem was particularly troublesome. From several years experience with the process, it has been found that ordinary carbon steel is satisfactory for hydrofluoric acid service where water concentrations are low, and where moving parts are not involved. Materials containing silica, such as cast iron, are not suitable because they are readily attacked by hydrofluoric acid. Monel has been found to be excellent in hydrofluoric acid service, even where water–hydrofluoric acid mixtures are encountered, and is used extensively for valves, valve trims, pumps, and for lining the acid regeneration tower. With the use of these materials in plant construction, the service record of hydrofluoric acid alkylation plants has been satisfactory, and on-stream efficiencies of 96% are not unusual (*8*).

Commercial Reactor Systems

Schematic sketches of four types of reactor systems commonly used for the commercial alkylation of isobutane are shown in Figures 3, 4, 5, and 6.

A typical system using an impeller type of reactor is depicted by Figure 3. In this system mixing is accomplished by internal recirculation of the mixture, cooling by heat exchange within the reactor, and phase separation by use of an auxiliary settling vessel. The reactor consists of a vertical cone-bottomed vessel with a pump-type impeller in the bottom and an internal concentric baffle arranged to produce a rapid and turbulent circulation of the reaction mixture. A refrigerated tube-bundle is suspended from the top of the vessel into the central zone of the reactor to maintain the mixture at the desired temperature.

Figure 4 illustrates a reaction system using a "time-tank" reactor. This system uses external recirculation to provide orifice mixing of the catalyst and reactants, and cooling is accomplished by an external heat exchanger in the recirculation stream. Acid separation is again carried on in an external settling vessel. The reactor consists of a vertical vessel containing numerous multiple orifice plates through which the reaction mixture is circulated by an external pump to obtain a high degree of turbulence.

A jet-type reactor system is shown in Figure 5. Here external recirculation is used to obtain jet mixing and cooling is obtained by evaporation of a portion of the butanes in the reactor, resulting in an autorefrigerated system. An auxiliary settling vessel is again employed. The reactor proper consists of a vertical vessel with jet nozzles in the bottom through which the reaction mixture is circulated to obtain turbulent mixing. The refrigerating butane vapors from the reactor are compressed, condensed, and returned to the system.

An integral type of reactor system is presented in Figure 6. Internal agitation is used to obtain mixing in this system and autorefrigeration is again employed. The settling section is an integral part of the reactor vessel. The reactor is a horizontal vessel having

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several reaction sections and a settling section separated by vertical baffles which allow a cascade flow through the vessel. Special emulsifying pumps enter from the top of the reactor into each reaction zone to provide the necessary mixing.

Of course, combinations and variations of these systems are in use; however, those outlined represent some of the more common installations. All of these systems can be used for sulfuric acid alkylation but only the types using tube-bundle refrigeration can be used with hydrofluoric acid since its high volatility precludes the use of an autorefrigerated system.

Olefins Used for Alkylation

Although the preceding discussion of the sulfuric and hydrofluoric acid processes has been confined to butene alkylation, isobutane has also been alkylated commercially with other olefins. Ethylene, propylene, pentenes, and dimers of butenes have been used for this purpose. It is also possible to use these olefins for the alkylation of isopentane. Such an operation, however, has not achieved commercial acceptance because it produces an inferior alkylate with a high catalyst consumption, and because isopentane is a satisfactory aviation gasoline component in its own right.

Because propylene is highly volatile and must be marketed as fuel gas rather than as gasoline, it is low in cost and would appear to be a desirable alkylation feed stock. Balanced against its low cost, however, are the increased catalyst consumption and decreased product quality encountered in its alkylation. Consequently, its inclusion in alkylation feed is usually limited to minor quantities by the alkylate quality required for the maximum production of aviation gasolines.

Pentene alkylation also has the disadvantages of increased catalyst consumption and decreased alkylate quality. A further disadvantage is that pentenes are a satisfactory motor gasoline blending stock and are thus a more expensive alkylation charge stock. For these reasons, commercial alkylation of pentenes is not extensively practiced.

Butenes can also be alkylated in the form of various polymers, such as the by-product diisobutene polymers from butadiene plants. In this operation, each octene molecule appears to react as two individual butene molecules, and the high alkylate quality and low catalyst consumption characteristic of butene alkylation are obtained. For the most part, polymers have been alkylated only as supplemental feed stocks from external sources in periods of high aviation gasoline demand.

Product inspections and yield data for typical alkylates produced from propylene, butenes, and pentenes are presented in Table II. In general, the optimum operating con-

Table II. Properties and Yields of Typical 360° F. End Point Rerun Alkylates[a]

Feed, olefin	Propylene	Butenes	Mixture of thermal and catalytic pentenes
Gravity, ° API at 60° F.	72.3	69.0	66.5
100 cc. ASTM distillation			
Initial b.p., ° F.	108	115	124
10% recovered	179	197	227
50% recovered	196	224	247
90% recovered	241	261	281
End point	360	360	360
Inspection tests			
Reid vapor pressure	4.0	3.5	1.5
Sulfur content, wt. %	<0.03	<0.03	<0.03
ASTM gum, mg./100 ml.	<0.5	<0.5	<0.5
Net heat of combustion, B.t.u./lb.	19,000	19,000	19,000
Octane ratings			
ASTM research octane No. (CRC-F-1), net	89	95	90
ASTM aviation blending octane No. (CRC-F-3)[b]	103	106	103
ASTM supercharge blending index No. (CRC-F-4)[b]	122	151	127
Yields			
Rerun alkylate, vol. % on total	95	95	90
Total alkylate, vol. % on olefin consumed	170	165	172
Isobutane consumed, vol. % on olefin consumed	125	105	110
Catalyst consumption, lb./bbl. of total alkylate	140	40	80
Heat of reaction, B.t.u./lb. of alkylate	350	315	250

[a] Propylene and butene alkylates on debutanized basis; pentene alkylate on depentanized basis.

[b] 4.6 cc. tetraethyllead per gallon.

ditions for these olefins are similar to those used for butene alkylation. Consequently, they can be alkylated simultaneously in all proportions and commercial operations are normally carried out on combined olefins. The product obtained when employing a combined olefin feed is similar to that obtained by blending the products from alkylation of the individual olefins.

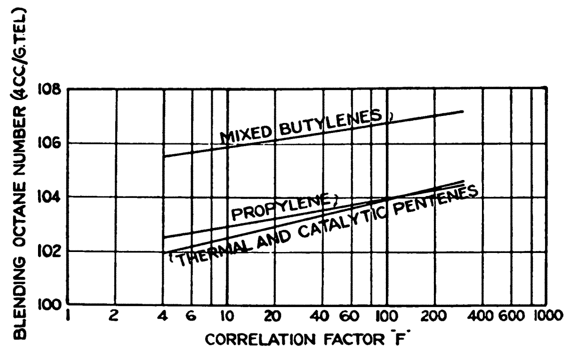

Figure 8. Sulfuric Acid Alkylate Octanes, ASTM Aviation (CRC-F-3)

Successful catalytic alkylation of isobutane with ethylene has been accomplished in one commercial installation using aluminum chloride catalyst (*1*). The chief product of the reaction is 2,3-dimethylbutane, a hydrocarbon having very high aviation octane ratings. Ethylene has also been alkylated with isobutane in a thermal process to give 2,2-dimethylbutane as the chief product component (*6*). When sulfuric or hydrofluoric acid alkylation with ethylene is attempted, the ethylene forms a strong bond with the acid, and fails to react with isobutane. The net result is the formation of little or no product, accompanied by excessive catalyst deterioration.

Correlation of Alkylate Quality

For purposes of plant design and for optimum operation consistent with feed stock availability, it is necessary to be able to predict accurately the octanes of the alkylate produced under varying operating conditions. Such a correlation developed from several hundred pilot plant and commercial plant tests is presented in Figures 7, 8, and 9. This correlation is applicable to sulfuric acid alkylation of isobutane with the indicated olefins, and was developed specifically for the impeller-type reaction system, although it also appears to be satisfactory for use with some other types of reactors.

This correlation is based on a factor which combines those variables exerting the greatest influence on alkylate quality in any specific operating unit. The correlating factor has been called F and is defined as follows:

$$F = \frac{(I)_E \times (I/O)_F}{100(SV)_O}$$

where $(I)_E$ = liquid volume per cent isobutane in reaction effluent
$(I/O)_F$ = volumetric isobutane-olefin ratio in reaction feed
$(SV)_O$ = olefin space velocity in volumes per hour per reactor volume

A change in any one of the three included variables which improves the quality of the product will increase the numerical value of the factor; hence, the larger the factor, the better the alkylate quality. In ordinary commercial operation F will vary from about 10 to 40. Acid content of the reaction mixture and reaction time, while not directly a part of the factor, are so interrelated that if the acid content is maintained above 40%, the olefin space velocity term correlates the effects of these variables satisfactorily. While reaction temperature has an important effect on product quality, it has not been included in this factor since this variable is ordinarily held constant at an optimum value for any well-

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designed unit. A separate correction factor may be applied to the curves as presented to cover variations in temperature and in other variables affecting alkylate quality.

Research octane numbers are shown to be proportional to the log of the correlation factor *F* in Figure 7. Single lines are obtained for refinery mixtures of butenes regardless of their source but separate lines are required for pentenes depending on whether they are derived from thermal or catalytic cracking operations. The alkylates produced from butenes are considerably superior to those produced from either propylene or pentenes. Figures 8 and 9 present aviation and supercharge octane ratings in the same manner as Figure 7, and in general the same quality trends are noted for the alkylates produced from the different olefins. The correlations as presented are specific for a plant operating with a reaction temperature of 50° F., using batch acid operation over the 98 to 88% titratable acidity range. The octanes are presented for 360° F. end point debutanized alkylates, except for pentene alkylate, which is on a depentanized 360° F. end point basis.

Future Aspects

The major use of alkylate up to the present time has been as a component of the high octane aviation gasolines required by modern reciprocating aircraft engines. Since the trend in aircraft engine development is toward the jet-type engines which do not require expensive high octane fuels, it is probable that alkylate will not be used in aircraft fuels in the long-range future. Consequently, if the alkylation process is to continue to find commercial application, alternative uses may have to be developed for alkylate.

Although inclusion in motor gasolines is the most obvious alternative use for alkylate, this process would have to be economically competitive with processes such as polymerization, which also convert gaseous hydrocarbons to gasoline. Since the chief obstacle to the use of alkylate in motor gasolines is its high processing cost, it would appear that future research should be directed toward improvements in the process which will reduce these costs.

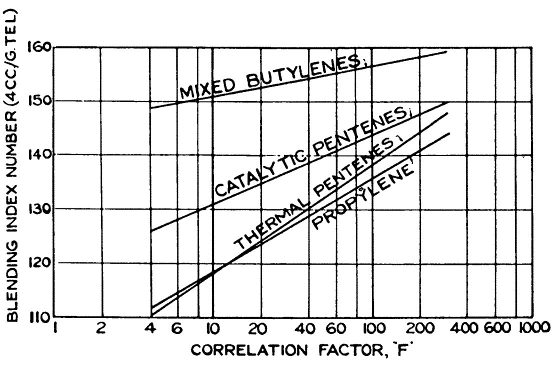

Figure 9. Sulfuric Acid Alkylate Octanes, ASTM Supercharge (CRC-F-4)

One of the major items contributing to the high processing cost is the cost of the catalyst consumed. This is particularly true for propylene alkylation, where the catalyst cost is about 2.5 to 3.0 cents per gallon of alkylate produced. Several courses that research might follow in order to reduce catalyst consumption would be the development of a more efficient reactor, a more efficient catalyst, or an additive which would retard catalyst degeneration.

High catalyst costs in sulfuric acid alkylation are also a result of the fact that the spent catalyst is of little value, even though it contains a high concentration of acid. In the past, this spent acid was often utilized for lubricating oil treating operations, but modern lubricating oil refining techniques no longer provide an outlet for this material. Recovery of the acid by conventional means of water dilution, hydrocarbon separation, reconcentration, and fortification with fuming acid is not particularly attractive from an economic standpoint. A significant reduction in catalyst cost might be obtained by developing a use for the spent catalyst. Another approach to this problem would be the development of an economic acid recovery process, or the finding of a profitable use for the hydrocarbons released from the acid in the present recovery processes. The hydrofluoric acid regeneration process has overcome the objections offered above but the high cost of the catalyst itself has kept the costs of this process at a level comparable with the sulfuric acid process.

Another factor which contributes most to the high cost of the alkylation process is the necessity of having a large excess of isobutane in the reaction zone. This requirement results in increased capital costs for over-sized reactors, settlers, fractionators, and accessories, as well as in increased operating costs of this equipment. Process developments which would allow satisfactory operations at considerably lower isobutane-to-olefin ratios would help reduce these costs. Such developments might again involve improvements in reactors or in catalysts.

Acknowledgment

The permission of the Sinclair Refining Co. for the publication of the alkylate quality correlations is gratefully acknowledged.

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Isomerization

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Isomerization played a vital role during World War II, primarily by increasing the supply of isobutane for alkylation. Although less extensively employed, isomerization of pentanes and hexanes provided valuable blending stocks for high octane aviation fuels, and isomerization of naphthenes contributed to toluene production. Isomerization offers the best method of raising the octane levels of pentanes and hexanes, and this application can be expected to become important as performance requirements of gasolines increase. Butane isomerization would again be extensively used in a future war, and pentane and naphtha isomerization might also be employed. The current shortage of aromatics is reviving interest in naphthene isomerization.

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Isomerization is one of the important ways in which petroleum technologists have employed chemical synthesis to meet the demand for "tailor-made" fuels needed by increasingly powerful internal combustion engines.

Isomerization may be defined as the rearrangement of the molecular configuration of a hydrocarbon without change in molecular weight. Although such rearrangements are known to occur in cracking and reforming operations, the present discussion will consider only those processes in which isomerization is the basic reaction.

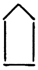
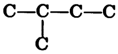
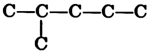
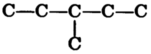
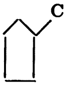
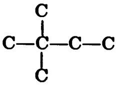
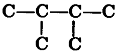
When applied to the low-boiling fractions of petroleum, containing predominantly straight-chain paraffin hydrocarbons, isomerization increases the proportion of valuable branched molecules. In the case of butane, branching leads to increased chemical activity through the availability of a reactive tertiary hydrogen atom. This is the basis for the most extensive commercial application of isomerization—the manufacture of isobutane for alkylation to high octane components of aviation gasoline. With hydrocarbons in the gasoline boiling range, rearrangement to more highly branched structures leads directly to improvement in antiknock properties. Table I illustrates this trend by relating the structures of the pentanes and hexanes to their octane ratings, as determined by the ASTM Motor method. The cyclic structures, included here for comparison, occupy an intermediate position in each group.

Isomerization has long been familiar to organic chemists, but reactions of this type have become important in petroleum chemistry only in relatively recent years. Not until 1933 did the first paper on the isomerization of individual paraffinic hydrocarbons appear in the scientific literature (*11*).

With the growing interest during the 1930's in the use of catalysts in petroleum processing, extensive exploratory work was conducted on a variety of catalytic reactions, including isomerization. Subsequent development work carried isomerization to the point where several processes could be quickly brought to full scale operation when the situation warranted. Early in World War II, the demand for high octane aviation gasoline provided the necessary incentive.

In PROGRESS IN PETROLEUM TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1951.

Table I. Effect of Hydrocarbon Branching on Octane Number

Hydrocarbon		Motor Octane Number	
		Unleaded	+3 cc. TEL
Pentanes			
n-Pentane	C—C—C—C—C	61.9	83.6
Cyclopentane		85.0	95.2
Isopentane	 $\mathrm{C{-}\underset{\substack{\mid\\ C}}{C}{-}C{-}C}$	90.3	Iso-octane + 2 cc. TEL
Hexanes			
n-Hexane	C—C—C—C—C—C	26.0	65.2
2-Methylpentane	 $\mathrm{C{-}\underset{\substack{\mid\\ C}}{C}{-}C{-}C{-}C}$	73.5	91.1
3-Methylpentane	 $\mathrm{C{-}C{-}\underset{\substack{\mid\\ C}}{C}{-}C{-}C}$	74.3	91.3
Cyclohexane		77.2	87.3
Methylcyclopentane		80.0	93.0
Neohexane	 $\mathrm{C{-}\overset{\substack{C\\ \mid}}{\underset{\substack{\mid\\ C}}{C}}{-}C{-}C}$	93.4	Iso-octane + 2.1 cc. TEL
Diisopropyl	 $\mathrm{C{-}\underset{\substack{\mid\\ C}}{C}{-}\underset{\substack{\mid\\ C}}{C}{-}C}$	94.3	Iso-octane + 1.8 cc. TEL

The first commercial isomerization plant was a butane unit at Shell's Houston refinery. It began operation in November 1941. By the end of the war, a total of 43 isomerization units had been built and placed in operation—38 in the United States and the remainder in Canada, the Caribbean area, and Arabia.

The wartime role of isomerization in the United States is summarized in Figure 1. Most of the units were built to supplement the natural supply of isobutane for alkylation. Domestic production of synthetic isobutane began in 1941 and rose in four years to more than 40,000 barrels per day. Most of the isomerization units were shut down when the military need for aviation gasoline dropped after the close of the war in Europe in May 1945.

Pentane isomerization was carried out on a much smaller scale. Isopentane, because of its high octane number and good lead response, was blended directly into aviation gasoline. It also served to increase the volatility of blends containing such high-boiling components as alkylate.

Isomerization of light naphtha—mainly pentanes and hexanes—was practiced to only a limited extent.

A fourth type of petroleum isomerization, which was commercialized on a small scale, involves the rearrangement of naphthenes. In the manufacture of toluene by dehydrogenation of methylcyclohexane, the toluene yield can be increased by isomerizing to methylcyclohexane the dimethylcyclopentanes also present in the naphtha feed. This type of isomerization is also of interest in connection with the manufacture of benzene from petroleum sources.

Basic Factors in Isomerization

Isomerization of paraffins and naphthenes is a reversible first-order reaction limited by thermodynamic equilibria. It is slightly exothermic in nature and does not take place to any appreciable extent without a catalyst (*4*). Although the mechanism of the reaction

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has been extensively studied (*15*), no clear-cut agreement has been reached among the various investigators.

Equilibria. The equilibrium distributions of butane, pentane, and hexane isomers have been experimentally determined (*5*, *16*) and are diagrammed in Figure 2. In each case, lower temperatures favor the more highly branched structures. At the approximately 200° F. temperature usually employed for isomerization, the butane equilibrium mixture contains about 75% isobutane. That for pentane contains about 85% isopentane. In the case of hexane, the equilibrium product contains about 50% neohexane and has a Motor octane rating of about 82. In all cases, of course, the yield of the desired isomers can be increased by fractionation and recycle.

For butane and hexane, the experimental equilibria agree fairly well with equilibria calculated from thermodynamic data (*17*). In the case of pentane the isomer favored thermodynamically is neopentane. This material is not obtained, however, apparently for reasons connected with the reaction mechanism.

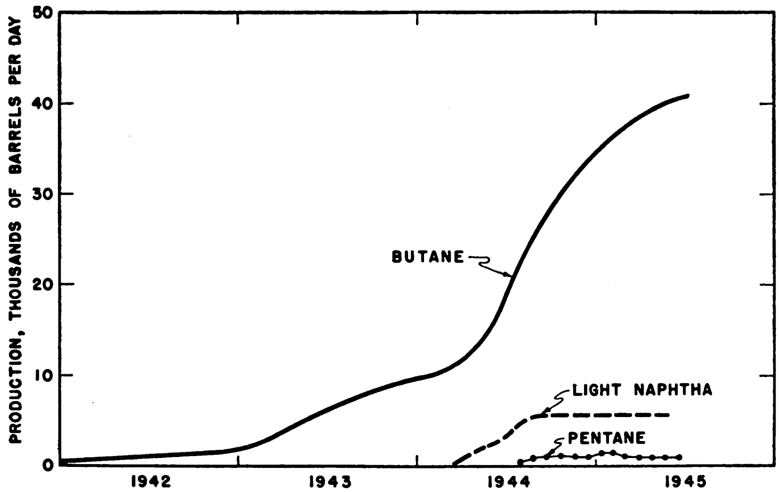

Figure 1. Wartime Growth of U. S. Commercial Isomerization

Side Reactions. The chemical problems encountered in paraffin isomerization—particularly the suppression of side reactions—become more serious as the molecular weight of the hydrocarbon increases. In addition to lowering the yield of the desired product, such side reactions shorten the effective life of the catalyst.

Butane isomerization is relatively straightforward. The butanes show no appreciable tendency to crack or disproportionate under isomerization conditions (*6*).

In the case of pentanes, disproportionation to isobutane and hexane is pronounced. This undesirable side reaction can be suppressed by the addition of small amounts of cyclic hydrocarbons or by operation under hydrogen pressure (*6*).

The hexanes undergo side reactions even more readily than do the pentanes. Although disproportionation and cracking can be suppressed to some extent by the addition of cyclic hydrocarbons, this treatment is not effective enough to ensure satisfactory catalyst life, and hydrogen at relatively high pressure must be used as the inhibitor.

The isomerization of paraffinic heptanes presents still more difficult problems, and no successful method has been found for suppressing the side reactions.

In the case of naphthenes, isomerization takes place under such mild conditions that side reactions do not interfere.

Catalyst. In all of the commercial isomerization processes applied to paraffins and naphthenes, the catalyst is aluminum chloride plus hydrogen chloride. In the pure state, these two ingredients do not associate chemically (*1*), but they become associated in the presence of certain hydrocarbons normally occurring in petroleum stocks.

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Most of the mechanisms proposed for isomerization assume formation of a transitory compound of aluminum chloride, hydrogen chloride, and the hydrocarbon undergoing isomerization. This unstable compound, which cannot be isolated, should not be confused with the liquid aluminum chloride–hydrogen chloride–hydrocarbon complex formed during the isomerization process as a result of cracking, disproportionation, hydrogen transfer, and polymerization. This liquid complex resembles heavy motor oil in appearance and viscosity. However, it has a specific gravity of about 1.5, and it is immiscible with liquid hydrocarbons. The hydrocarbon component of the complex is of relatively high average molecular weight (300 and higher) and contains an average of at least two double bonds per molecule. There may be as many as two molecules of combined aluminum chloride for each double bond. The complex is itself an active catalyst, and it may, in addition, dissolve aluminum chloride. In the presence of hydrogen chloride, this dissolved aluminum chloride increases the catalytic effect.

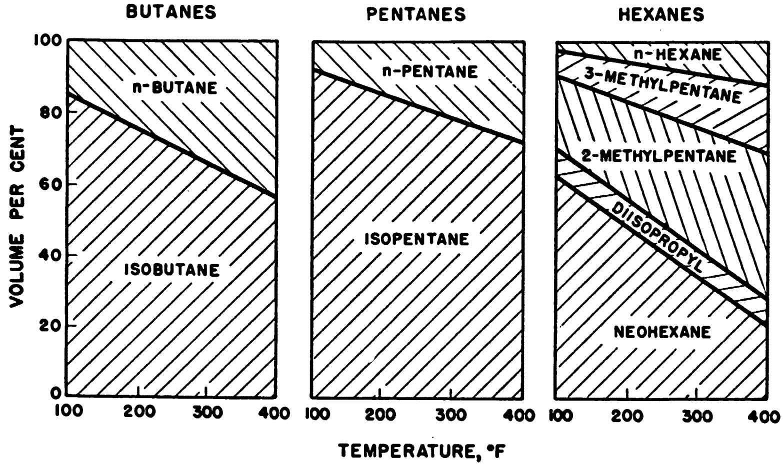

Figure 2. Experimental Equilibria

During the isomerization process the complex gradually becomes more highly unsaturated because of hydrogen transfer to lower boiling hydrocarbons formed in side reactions. As this occurs, the $AlCl_3$ appears to become more tightly bound, and the complex gradually loses catalytic activity.

Commercial Operations

This consideration of basic factors tends to oversimplify the technical problems that had to be solved before isomerization could become a successful commercial operation. Several processes resulted from largely independent work carried out in separate petroleum laboratories. As would be expected, each of these laboratories devised a somewhat different scheme—particularly in the case of butanes, which received the greatest amount of attention. A major share of the credit for the rapid commercialization of these processes can be traced to the free exchange of technical information and operating experience through the Isomerization Subcommittee of the wartime Aviation Gasoline Advisory Committee (*12*).

Butane Isomerization. Five processes for butane isomerization were in commercial use by the end of World War II. These processes differ primarily in the method of contacting the hydrocarbon with the catalyst. Two are vapor-phase processes, which require periodic discard and replacement of the catalyst bed; the other three are carried out in the liquid phase and are continuous with respect to catalyst addition and withdrawal.

The essential features of the Shell Isocel process (*2*)—the first to reach commercialization—are shown in Figure 3. In this process, the dried butane feed is vaporized and sent

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to the top of the reactor, where it picks up anhydrous hydrogen chloride. The combined vapors are charged to the reactor, which is packed with Isocel—aluminum chloride on bauxite. To recover the aluminum chloride picked up by the hydrocarbon, the reactor product is passed through a guard chamber filled with bauxite. The product is then condensed, cooled, and passed to the accumulator, from which small amounts of by-product gases lighter than butanes are vented to prevent pressure build-up in the system. The hydrocarbon is charged to the top of the stripper tower, which recovers the hydrogen chloride for recycle. Remaining traces are removed by caustic and water washing, and the hydrocarbon stream is sent to an efficient fractionating tower. The *n*-butane recovered is generally recycled.

The other vapor-phase butane isomerization process, developed cooperatively by the Anglo-Iranian Oil Co. and the Standard Oil Development Co., is somewhat similar to the Isocel process. In the AIOC-Jersey process (*13*), the reactor is initially filled with bauxite, and aluminum chloride is sublimed into the vaporized feed as necessary to maintain the desired catalyst activity. Upflow of vapor through the reactor is the customary arrangement. Since carry-over of aluminum chloride is not excessive at the usual rates of catalyst addition, about half of the commercial plants employing this process were not equipped with guard chambers.

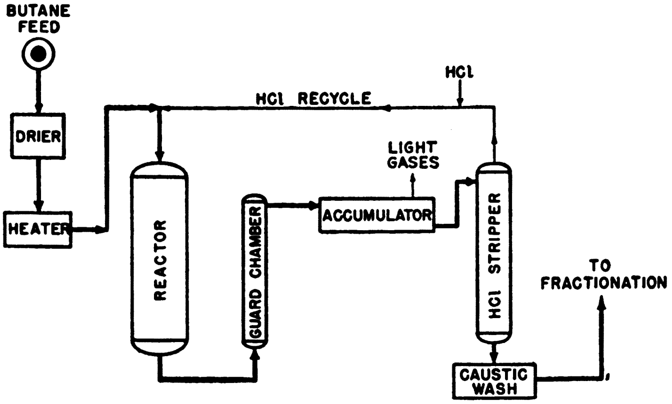

Figure 3. Vapor-Phase Butane Isomerization

Shell Isocel process

The butane isomerization process developed by the Universal Oil Products Co. is shown in Figure 4. In this process (*3*), the feed is maintained essentially in the liquid phase under pressure. Part of the feed is by-passed through a saturator, where it dissolves aluminum chloride. The feed later picks up hydrogen chloride and passes through the reactor, which is packed with quartz chips. Some insoluble liquid complex is formed, and this adheres to the quartz chips. The aluminum chloride in the feed is preferentially taken up by the complex, which thus maintains an active catalyst bed. The complex slowly drains through the reactor, losing activity en route. It arrives at the bottom in essentially spent condition and is discarded. Aluminum chloride carried overhead in the reactor products is returned to the reactor from the bottom of the recovery tower. The rest of the process is the same as in the vapor-phase processes.

A second process employing complex as the catalyst carrier was independently developed by the Standard Oil Co. (Indiana) and by The Texas Co. In this process (*19, 20*), liquid butane containing make-up aluminum chloride and recycled hydrogen chloride is bubbled upward through a bed of preformed liquid complex about 20 feet in depth. Because the aluminum chloride in the feed is effectively transferred to the complex, catalyst carry-over in the reactor effluent is low and no recovery tower is needed.

The third liquid-phase butane-isomerization process, shown in Figure 5, was developed by Shell as an improvement over the original intermittent vapor-phase process.

The aluminum chloride is handled, in this case, as an approximately 9% solution in relatively inert molten antimony trichloride; the solution has a solidification point of about 170° F. (*10*). As in the other processes, a small amount of liquid aluminum chloride–hydrogen chloride–hydrocarbon complex is continuously formed.

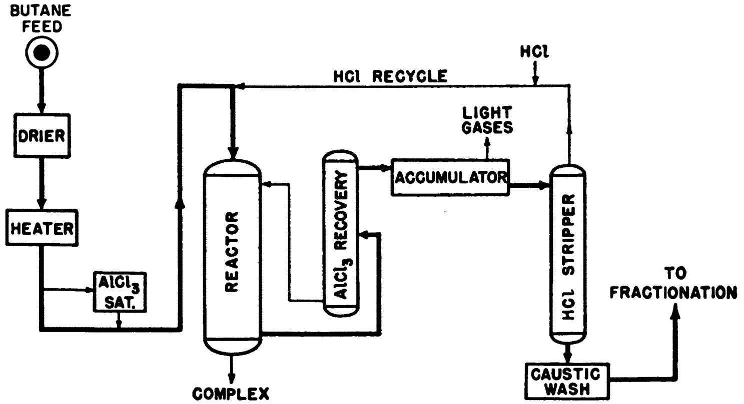

Figure 4. Liquid-Phase Butane Isomerization

U.O.P. Process

In this process, the liquid butane feed is employed first to recover aluminum chloride and antimony chloride from spent catalyst. This is accomplished in a scrubber, from which insoluble complex is continuously discarded. The butane stream then picks up recycled hydrogen chloride and enters the reactor, where mechanical agitation causes intimate contacting with an equal volume of catalyst. The undesirable complex formed in the reactor dissolves in the molten mixture of aluminum chloride and antimony chloride but is continuously rejected from the system by a small catalyst side stream passing through the scrubber. A portion of the liquid catalyst is carried with the products from the top of the contactor to a distillation tower. Here the aluminum and antimony chlorides are recovered from the products, which pass overhead and are treated as in the other processes. The proper aluminum chloride content of the molten catalyst is restored by a saturator through which part of it is passed before it is returned to the contactor.

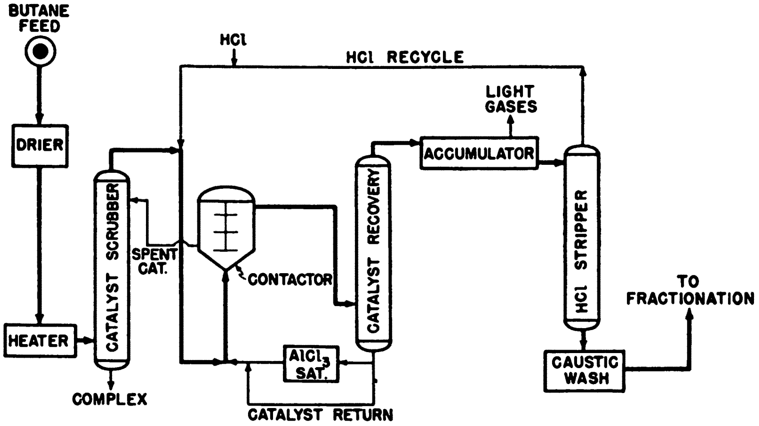

Figure 5. Liquid-Phase Butane Isomerization

Shell antimony chloride process

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A summary of commercial operations employing the five butane isomerization processes is given in Table II. The data represent typical wartime process operations rather than characteristics of any specific commercial plant.

Table II. Typical Commercial Process Data for Butane Isomerization

	Vapor-Phase		Liquid-Phase		
Process	Shell	AIOC-Jersey	U.O.P.	Indiana-Texas	Shell
Catalyst form	Impregnated bauxite	Sublimed on bauxite	Complex on quartz chips	Liquid complex	Dissolved in $SbCl_3$
Catalyst life, gal. isobutane per lb. $AlCl_3$	200	200	50–120	50–120	50–120
HCl concentration, wt. %	2–14	4	5	4	5
Once-through conversion, %	40	35	38	38	45
Reactor conditions					
Temp., ° F.	210–300	270	200	205	180
Pressure, lb./sq. in.	200	235	235	365	300
Space velocity, vol./hr./vol.	0.5–1.0	0.5–1.0	0.5	1.0	2.5
Reactor material	Carbon steel		Hastelloy B or Gunite cement		Nickel
No. of U. S. plants	7	8	14	3	2

Since the vapor-phase processes employing supported aluminum chloride contain no provision for withdrawal of spent catalyst, the feed must be practically free of impurities that would form complexes and clog the pores of the catalyst, thereby reducing catalyst activity. High-quality feeds—obtained, for example, by acid treating to remove olefins and rerunning—form virtually no complex and give substantially greater catalyst life than is obtained in the liquid-phase processes, where the discard of spent catalyst eliminates the need for special equipment for pretreating the feed. Satisfactory conversion was prolonged in the Shell vapor-phase units by gradually increasing the temperature and the hydrogen chloride concentration as the catalyst lost activity. In the AIOC-Jersey plants, catalyst activity was maintained by the addition of fresh catalyst, and run length was limited by the catalyst capacity of the reactor.

Hydrogen chloride concentrations were essentially the same in all except the Shell vapor-phase units.

Once-through conversions were generally similar, although slightly higher levels resulted from the combination of liquid catalyst and mechanical stirring in the Shell liquid-phase plants.

All the processes except the Shell vapor-phase processes used constant temperatures ranging from 180° to 270° F., depending on the process. Pressures ranged from 200 to 365 pounds.

The reactor materials reveal the comparative magnitude of the corrosion problem encountered with the five processes (7). Aluminum chloride–hydrocarbon complex is a highly corrosive material, particularly in the presence of hydrogen chloride. The vapor-phase reactors could be built of ordinary carbon steel, since essentially no complex was formed. No appreciable corrosion was encountered so long as moisture was excluded. In plants employing complex as the catalyst carrier, it was necessary to use corrosion-resistant materials in the reactor lining and in other items of equipment where conditions of temperature, turbulence, and hydrogen chloride concentration would have contributed to high corrosion rates. Relatively minor corrosion problems were encountered in the process employing antimony chloride as the catalyst carrier, and nickel was successfully used as the reactor material.

The 34 domestic commercial units employing these five butane-isomerization processes contributed substantially to the war effort.

Pentane Isomerization. Pentane isomerization, although carried out on a much smaller scale, increased the critical supply of aviation gasolines toward the end of the war. Two pentane processes—one developed by Shell and one by Standard (Indiana)—were commercialized before the end of the war. The principal differences between the butane and pentane processes are the use in pentane isomerization of somewhat milder conditions and the use of an inhibitor to suppress side reactions, principally disproportionation. In general, the problems of the butane processes are inherent also in pentane isomerization, but the quality of the feed stocks is less important. Catalyst life is much shorter than in the butane processes; only about 30 to 50 gallons of isopentane are produced per pound of aluminum chloride.

The Shell pentane process (*10*) is similar to the corresponding liquid-phase butane process. To inhibit side reactions, a hydrogen partial pressure of 60 to 70 pounds per square inch is maintained, largely by recycle. Make-up hydrogen is added as necessary to offset that lost from the system or consumed in saturating any olefins present in the feed. The molten catalyst contains only about 2% of aluminum chloride and has a lower solidification point than the butane catalyst. Typical reactor temperatures are slightly lower, but other process conditions are essentially the same as in the butane process. The only commercial plant employing this process—that of Tide Water Associated—produced an average of about 500 barrels of isopentane per calendar day during the last year of the war.

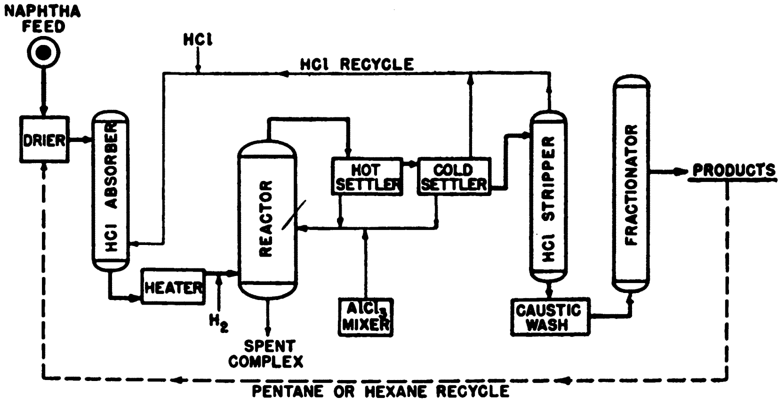

Figure 6. Naphtha Isomerization

Isomate process

The other commercialized pentane isomerization process is that of the Standard Oil Co. (Indiana) (*20*). This process differs from the Indiana-Texas butane process in that the aluminum chloride is introduced as a slurry directly to the reactor and that about 0.5% by volume of benzene is added continuously in the feed to suppress side reactions. Temperature, catalyst composition, space velocity, and hydrogen chloride concentration are generally similar to those in the corresponding butane process, but the reactor pressure is about 100 pounds lower. The Pan American Refining Co. operated the Indiana pentane isomerization process commercially during the last nine months of the war and produced about 400 barrels of isopentane per calendar day.

Napththa Isomerization. The only commercial isomerization of light naphtha was carried out in two plants employing the isomate process developed by the Standard Oil Co. (Indiana) (*20*). In this process, a feed containing normal pentane and low octane number hexanes is converted to isopentane and to hexanes of higher octane number. Pentanes and hexanes in any ratio may be processed. By recycle of selected fractions of the product, concentrates of isopentane or of neohexane and diisopropyl can be obtained as the ultimate products.

Essential features of the isomate process are shown in Figure 6. The principal departures from the Indiana pentane process are the necessary use of hydrogen as an inhibitor and the use of higher temperature and pressure. Feed-stock quality is much less important that in any other of the isomerization processes. After the dried feed picks up about 5% by weight of hydrogen chloride and is heated to 250° F., hydrogen is added at the rate of 40 to 80 cubic feet per barrel. As most of the hydrogen is consumed in a hydrocracking side reaction, no hydrogen recycle is employed. The feed enters the reactor under a pressure of 700 to 800 pounds per square inch, and the liquid hourly space velocity is about 1.3. Catalyst life varies from 50 to 100 gallons of product per pound of aluminum chloride. The presence of high-pressure hydrogen causes greater catalyst carry-over than in the corresponding butane and pentane processes, and the reactor products are passed through hot and cold settlers to remove entrained catalyst. As in the other processes, hydrogen chloride is recovered for recycle and the products are washed with caustic and fractionated.

During the last year of the war, the two commercial isomate units processed more than 5000 barrels of light naphtha per calendar day. The Standard Oil Co. (Indiana) unit at Whiting produced a mixture of hexane isomers directly and recycled *n*-pentane to convert 95% of it to isopentane; light naphtha of 69 Motor octane number was upgraded to ultimate products with an average rating of about 81. The Salt Lake City unit of the Utah Oil Refining Co. also used a 69-octane feed. Pentanes were isomerized on a once-through basis, and hexanes were recycled to increase the production of neohexane and diisopropyl. The hexane fraction of the product amounted to 80% of the total feed and had an octane number of 84.

Naphthene Isomerization. In addition to the paraffin isomerization processes, naphthene isomerization also proved useful during the war in connection with the manufacture of toluene. In the Shell dehydrogenation process for the manufacture of toluene, good yields depend upon increasing the methylcyclohexane content of the feed by isomerization of dimethylcyclopentanes. This process was employed commercially at one refinery in the Midwest and one on the Pacific Coast.

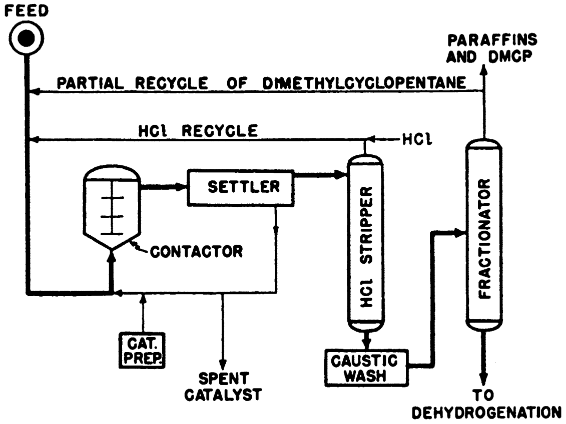

Figure 7. Shell Naphthene Isomerization Process

Essential features of the Shell naphthene isomerization process (*18*) are outlined in Figure 7. Although the contactor principle employed in the other liquid-phase Shell processes is used, the catalyst is handled in the form of hydrocarbon complex. For the manufacture of methylcyclohexane, a carefully fractionated and dried concentrate of dimethylcyclopentanes is preheated to 200° F., and about 0.1% of anhydrous hydrogen chloride is added. The feed is joined by a stream of catalyst complex and charged to the reactor under a pressure of 15 pounds per square inch gage. Isomerization takes place readily under the conditions of intimate mixing provided in the stirred reactor. The catalyst carry-over is separated from the products in the settler and recycled. In the conventional manner, the hydrocarbon stream is freed of hydrogen chloride, caustic-washed, and fractionated. A portion of the unisomerized overhead is discarded from the system to prevent the build-up of paraffins, and the balance is recycled. In commercial practice, an ultimate yield of methylcyclohexane of about 80% was obtained, and catalyst life approximated 100 gallons of feed per pound of aluminum chloride.

The naphthene isomerization process has been applied also to the conversion of methylcyclopentane to cyclohexane for subsequent dehydrogenation to benzene. Shell's Wilmington, Calif., refinery has been operating commercial equipment on this basis since March 1950 (*18*).

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Olefin Isomerization. One other type of hydrocarbon isomerization is on the threshold of commercialization—namely, that of olefins. Processes for olefin isomerization were first developed some 15 years ago (*11*, *14*, *20*) after it was recognized that highly branched olefins have higher octane numbers than do their straight-chain isomers, and that the octane numbers of olefins increase as the double bond moves toward the middle of the molecule.

The new Brownsville, Tex., plant for the manufacture of synthetic liquid fuels from natural gas makes use of this reaction to increase the octane number of its product by as much as 20 units. Synthetic naphtha produced over iron catalyst is highly olefinic and contains substantial amounts of straight-chain isomers with terminal double bonds (*8*). The shifting of these double bonds toward the center of the molecule may be accomplished by vapor-phase treatment employing synthetic cracking catalyst in the fluid state, under mild catalytic cracking conditions. Oxygenated compounds also present are converted under the isomerization conditions to hydrocarbons and water.

Significance of Isomerization

Although isomerization is now being operated commercially to only a limited extent, its significance in petroleum technology should not be underestimated.

During World War II, the demand for Grade 100/130 aviation fuel brought into play every technique known to petroleum scientists for making high octane components of aviation gasoline. Isobutane obtained by isomerization of one barrel of normal butane led to an average of 1.3 barrels of aviation alkylate; since alkylate comprised the limiting 30 to 40% in the production of Grade 100/130 gasoline, butane isomerization increased the production of the desired fuel by about four barrels for each barrel charged. In the case of pentanes, the high octane number and good lead response of isopentane permitted an increase in Grade 100/130 capacity of about three barrels for every barrel of *n*-pentane replaced by isopentane. When naphtha isomerization was carried out to yield a neohexane concentrate, the leaded product was almost equivalent in antiknock quality to leaded aviation alkylate.

In the event of another major war, it is probable that all existing isomerization units would be reactivated and pushed to capacity. Although production of Grade 115/145 aviation fuel required by newer aircraft engines may place somewhat greater emphasis on aromatics, there would still be a demand for maximum alkylate production, and butane isomerization would again play an important role. Expansion of pentane and naphtha isomerization is somewhat less certain and would depend on future developments in aircraft fuels.

Under peacetime conditions, the rising costs of petroleum and the upward trends in motor-fuel quality are increasing the economic incentives for upgrading all gasoline components. Alkylation and polymerization convert excess light ends to high-octane blending stocks and improve the quality of heavy gasoline components, but isomerization offers by far the best route for increasing the octane ratings of the pentanes and hexanes. Such increases may become necessary as over-all octane numbers are raised.

At the present time, the national shortage of aromatics is also reviving interest in naphthene isomerization.

Wartime necessity brought about the commercial development of the isomerization processes well in advance of the time when they would be needed under a peacetime economy; but either renewed military activity or increased peacetime demands for aromatics or for fuels of higher octane number may again bring isomerization into prominence.

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Synthesis of Liquid Fuels from Natural Gas

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In the development of a commercial process to produce synthetic liquid fuels from natural gas, reliable large scale techniques were developed for the production of oxygen and synthesis gas. To convert synthesis gas to hydrocarbons, the use of iron catalysts in a fluidized bed was required; the method of preparation of the catalyst proved to be considerably less important than the conditions of its environment during synthesis. The resultant integrated process is striking in its simplicity and has added several new tools to the methodology of chemical engineering; it provides the foundation upon which an American synthetic fuels industry can be built using shale or coal as well as natural gas. From the indicated available supply of gas alone, the process can contribute an appreciable fraction of American liquid fuel requirements with large quantities of aliphatic oxygenated chemicals and, by utilizing still more recent developments, huge amounts of acetylene needed for synthetic fibers and plastics. Although such conceptions are on a sound economic basis, legislation is required to accelerate the growth of this natural gas to liquid fuels industry.

The mass of data and material published during the past twenty-five years on the general subject of the synthesis of hydrocarbons by the catalytic reduction of carbon monoxide with hydrogen has been reviewed adequately by others (*13*). The object of this paper is to describe the highlights of the development of the Fischer-Tropsch type synthesis, prior to World War II, which have contributed to the present synthesis of liquid fuels from natural gas process and to dwell at greater length on certain of the work done by Hydrocarbon Research, Inc., in this field since the war.

It is quite fitting that this review should coincide with the twenty-fifth anniversary of the first public announcement of the Fischer-Tropsch synthesis. Great interest in the potentialities of the catalytic reduction of carbon monoxide and hydrogen had already been aroused at the turn of the century when Sabatier and Senderens first synthesized methane. By 1923 Badische Anilin- & Soda-Fabrik had successfully applied this basic reaction to the synthesis of methanol, and Fischer and Tropsch had disclosed their "synthol" process—that is, the synthesis of a complex mixture of alcohols, aldehydes, ketones, and fatty acids. But it was just 25 years ago, the year 1926, when Fischer and Tropsch published the first account of their classical work on what they termed the "normal pressure" synthesis of hydrocarbons, the forerunner of all hydrocarbon synthesis processes that use as building blocks carbon monoxide and hydrogen. The Fischer-Tropsch synthesis, offering petroleum-poor Germany a source of liquid fuels from indigenous deposits of coal, became of great national interest and under the impetus of the desire for national self-sufficiency was perfected and applied commercially in the remarkably short period of 9 years. A few plants were also erected in France and Japan.

Prior to World War II other countries of Europe and the United States followed these developments with considerable interest. Exploratory work, including the operation of small pilot plants, was undertaken by a number of organizations. None of this earlier work gave real promise that synthetic fuels could be produced at a cost competitive with the products derived from natural petroleum.

Toward the end of World War II when the United States production of petroleum was at an all-time high and when the ability of this country to sustain such production beyond the immediate future first became questionable, national interest in synthetic fuels was intensified. Many private industrial organizations initiated research and development programs which, in the aggregate, constituted an expenditure in manpower and money that has seldom been equaled in any development. The national government, in an unprecedented step, dedicated substantial public funds for governmental research and development on the longer range potentialities of the industry. In 1947 a group of private interests joined for the purpose of erecting a full scale synthetic oil plant. The plant, designed by Hydrocarbon Research, Inc., is now operating at Brownsville, Tex. The process used may be conveniently divided into (1) oxygen separation, (2) synthesis gas generation, (3) hydrocarbon synthesis, and (4) conventional recovery, separation, and finishing operations. The development of each of the steps is described separately in the succeeding paragraphs. The integrated process is also described and certain of the commercial aspects of the production of liquid fuels from gas are summarized.

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Separation of Oxygen from Air

Small quantities of liquid oxygen had been prepared as early as 1877 by Cailletet in France and Pictet in Switzerland. In 1895 Carl von Linde developed the first cycle for continuously liquefying air and fractionating it into its major components, oxygen and nitrogen. Claude and Heylandt followed with comparable cycles. All involved a chemical pretreatment of the air to remove the last traces of carbon dioxide and water which would otherwise deposit in the heat exchangers and eventually block the air passages. All required the compression of the air to a relatively high pressure. All were designed to produce oxygen of high purity. In 1928 Mathias Fränkl developed what was later to become known as the Linde-Fränkl cycle. Appreciating that for many industrial uses high purity was unnecessary, Fränkl set out to develop a process to produce oxygen of 90 to 95% purity. By using a number of regenerators in parallel and passing air through half of them while oxygen and nitrogen flowed through the remainder and then reversing the streams every few minutes, Fränkl was able to eliminate the chemical pretreatment of the bulk of the air. Using efficient regenerators, he was also able to limit the compression of the bulk of the air stream to 6 to 7 atmospheres. The necessary refrigeration was supplied in part by an expansion engine discharging at essentially liquid air temperature and in part by the isenthalpic expansion of a small stream of high pressure (about 125 atmospheres) air which was first chemically treated for removal of water and carbon dioxide.

The rapid development of low pressure oxygen separation plants in Germany was spurred chiefly by the need for a continuous method of producing hydrogen for coal hydrogenation and by the need for high heating value gas derived from coal and lignite without the use of oil. No parallel development was in progress in this country prior to World War II, and the oxygen plants erected here were small and limited to the production of oxygen for welding and cutting. However, during the war the development of small mobile plants for military use became the object of intensive development by several industrial organizations and university research groups, and a number of such plants were designed and built. One important development of this program was the reversing heat exchanger designed by S. C. Collins of the Massachusetts Institute of Technology. By switching air and nitrogen only in a countercurrent flow exchanger, and allowing oxygen to flow continuously in a separate pass of the same exchanger, Collins was able to produce oxygen of high purity, while continuously clearing the exchanger of water and carbon dioxide deposits. Moreover, the oxygen flow from the reversing exchanger was free of the pressure surges characteristic of the Fränkl cold accumulators.

Subsequent to World War II a number of American industrial organizations engaged in the development of low pressure oxygen separation cycles for a variety of services including the synthesis of hydrocarbons. One of the first demonstration units to be built was a 10-ton-per-day pilot plant designed and erected by Hydrocarbon Research, Inc., at its Olean, N. Y., laboratory. The cycle proved at Olean was later applied successfully in the first tonnage oxygen plant to go on stream in this country, a 200-ton-per-day unit erected in 1948 as part of a petrochemical plant at Winnie, Tex. A similar cycle was also used for the first synthetic oil from natural gas plant at Brownsville, Tex. Other low pressure cycles developed in this country since the war are also being applied commercially in the chemical and steel industries. Indeed, the production of tonnage oxygen has been fully as important a development as the synthetic fuel industry. Plants erected since the war or now being erected have a capacity of 4000 tons per day or twice this country's prewar capacity.

Generation of Synthesis Gas

For years mixtures of hydrogen and carbon monoxide have been prepared from natural gas and steam using nickel catalysts. The net reactions may be represented by the equations:

$$CH_4 + H_2O = CO + 3H_2 \quad (1)$$

$$CH_4 + 2O_2 \text{ (air)} = CO_2 + 2H_2O \quad (2)$$

The first equation applies to the preparation of the synthesis gas in the catalyst tubes and the second to the external heating of the catalyst tubes by burning of methane with air. An early application of the steam-methane process in this country was the manufacture of hydrogen for the hydrogenation of iso-octene to iso-octane. A subsequent application was the manufacture of hydrogen for ammonia synthesis. Technically this process could be used to generate gas for hydrocarbon synthesis. However, it has several undesirable features: The catalyst tubes are quite large in volume; the gas must be generated at low pressure; and the ratio of hydrogen to carbon monoxide in the product is about 3:1. As will become apparent later a hydrogen to carbon monoxide ratio of 3:1 in the synthesis gas results in an inefficient utilization of carbon in the synthesis step. To reduce this ratio to the desired value of about 2:1 would require the recovery of the carbon dioxide generated by Equation 2 and its return to the catalyst tubes so that the net reaction in the tubes would be represented by the equation:

$$3CH_4 + 2H_2O + CO_2 = 4CO + 8H_2 \quad (3)$$

A study made by Hydrocarbon Research, Inc., of this process and other possible methods of generating synthesis gas from methane, including partial combustion with oxygen, indicated that the partial combustion process was so much more economical than other methods that work was started on its development. At the time, the results of a number of earlier investigations of the partial oxidation of methane and other low molecular weight hydrocarbons had already been published. However, all such work was limited to small scale catalytically promoted experiments at low pressure, and whereas the reports were of considerable interest, there was little pertinent to the problem of generating synthesis gas by partial combustion under pressure in semicommercial or full scale equipment. Early in 1944 a pilot plant was erected at the Olean laboratory. During the exploratory work almost every conceivable type of system was tried, such as upshot generators, downshot generators, generators packed with catalyst, generators packed with refractory, generators without packing, premix burners, nonpremix burners, burners insulated with refractory, burners with water-cooled jackets, burners with water-cooled tips, preheated natural gas and oxygen, cold natural gas and oxygen, generators with firebrick linings, generators with Inconel linings, and generators with zircon lining. The most consistent troubles in the earlier work were excessive soot formation and lack of temper-

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ature control. After 8 months of research, the equipment and techniques were developed to such a degree that synthesis gas was produced at high pressure without catalyst, for long periods of time. Subsequent to the successful operation of the Olean pilot plant, similar units were operated at the laboratories of The Texas Co. at Montebello, Calif., and the Stanolind Oil and Gas Co. at Tulsa, Okla. These latter operations extended the range of the process variables first explored at Olean. A more complete description of the effect of some of the operating variables of the partial combustion process has been presented in a description of work done by the Stanolind Oil and Gas Co. (*8*).

The stoichiometry of the partial combustion of methane with oxygen can be expressed as the sum of four reactions:

$$CH_4 + {}^1/_2O_2 = CO + 2H_2 \tag{4}$$

$$CO + {}^1/_2O_2 = CO_2 \tag{5}$$

$$H_2 + {}^1/_2O_2 = H_2O \tag{6}$$

$$CH_4 = C + 2H_2 \tag{7}$$

However, the mechanism is far more complicated than indicated by these simple equations. The reaction takes place in two distinct phases—a phase of very short duration when reactions involving oxygen are completed and a relatively longer phase in which the products of oxidation undergo further reaction. Considerable heat is liberated in the first phase carrying the temperature of the flame burst well above the terminal temperature (the temperature of the gas leaving the combustion zone). The high flame burst temperature results when some of the early product hydrogen and carbon monoxide molecules collide with activated oxygen atoms or the equivalent—for example, hydroxyl fragments—and are further oxidized in preference to methane. The result is an initial overburning of part of the methane, a reaction which is far more endothermic than the partial combustion reaction represented by Equation 4. As the consumption of oxygen nears completion, reforming of the residual methane becomes the dominant reaction as its molecules collide with oxygen-rich fragments of high energy level. The reforming reaction is extremely rapid at the flame burst temperature, but it absorbs heat as it proceeds and slows down as the temperature level of the gas and the concentration of residual methane fall. As a result the reforming reaction never proceeds to equilibrium but continues at a low but finite rate until the gases are finally cooled by extraction of sensible heat.

The first phase described occurs very close to the burner tip, and it has not been possible either to sample the gas accurately or measure the temperature at this point. However, indirect measurements, with well designed burners, have indicated a flame burst temperature in the range of 3200° to 3600° F. with roughly 40% of the methane unconverted when oxygen consumption is complete. With poorly designed burners, the overburning in the first phase can, of course, become intolerable; the worst conceivable case is the complete combustion of approximately one fourth of the methane.

The oxygen consumption in the partial combustion process is a function of the preheat temperatures of the gas and oxygen, the heat leak from the combustion zone, and the efficiency of the burner which is measured by the terminal temperature required for a given conversion of methane. Pressure and space velocity are also important variables but their effect can easily be obscured by small changes in burner performance or terminal temperature.

Hydrocarbon Synthesis

Prewar Development of Synthesis Operation in Germany. The production of significant quantities of liquid hydrocarbons from synthesis gas over a cobalt catalyst was first reported by Fischer and Tropsch (*6*) in 1926. In 1932 a catalyst, useful for commercial operations, was described by Fischer and Koch (*4*), and in 1935 Ruhrchemie built the first full scale synthesis plant, which operated at atmospheric pressure. In 1936, the process was modified by the work of Fischer and Pichler (*5*) to operate at 5 to 15

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atmospheres, employing a similar cobalt catalyst. The product obtained from the cobalt synthesis resembled a light and very paraffinic crude oil. The octane number of the gasoline was too low for use directly as a motor fuel, and most German production was either reformed or was blended off with higher octane motor fuels.

Fischer and Pichler (*16*) in 1937 performed the first successful hydrocarbon synthesis experiments using an iron catalyst rather than the more expensive cobalt catalyst. These investigators operated, using a precipitated catalyst and a pressure of 15 atmospheres, for a sufficient period of time to demonstrate that if the heat of reaction was removed in a manner to limit the catalyst temperature, carbonization of the catalyst would not be a severe problem. To accomplish this, the catalyst was placed in an annulus formed by two concentric tubes with 10 mm. between tubes. Both walls of the annulus were cooled, and the rate of charge of the reactants was limited. The gasoline produced over the iron catalyst had a much higher olefin content than that produced over cobalt and by appropriate treatment could readily be isomerized to high octane gasoline. Also the yield of gasoline relative to the higher boiling compounds was greater. In 1938 Michael of I. G. Farbenindustrie (*17*) passed synthesis gas over an iron base synthetic ammonia catalyst with about 100 parts of recycle gas to control the catalyst temperature. Michael employed a temperature of about 600° F., considerably higher than used by Fischer and Pichler, operated at higher space velocities, and produced a gasoline product of essentially the same quality. Simultaneously Winkler and Duftschmid of I. G. Farbenindustrie (*1*) obtained results, similar to Fischer and Michael, when operating at 25 atmospheres with an ammonia catalyst and controlling the reaction temperature by circulating oil through the reactor to a cooler and back to the reactor.

The chief disadvantage of all the German processes was the low productivity per unit of reactor volume. In every process the limitation on capacity was imposed by the inability to remove heat and achieve adequate temperature control simultaneously.

Postwar Development in United States. During the latter part of World War II when experimental work on the Fischer type synthesis was accelerated in this country, the main effort was naturally directed toward increased reactor capacity. Those methods, developed by the Germans, that looked most promising received first consideration—that is, the high gas recycle operation, the oil circulation process, and a modification of the oil circulation process in which cooling was effected by evaporation rather than liquid circulation. Among others, Hydrocarbon Research, Inc., built pilot plants which utilized the latter two cooling means. However, a new technique, which appeared more promising than any of the German schemes, had been developed in this country during the war. It was the fluidized catalyst bed.

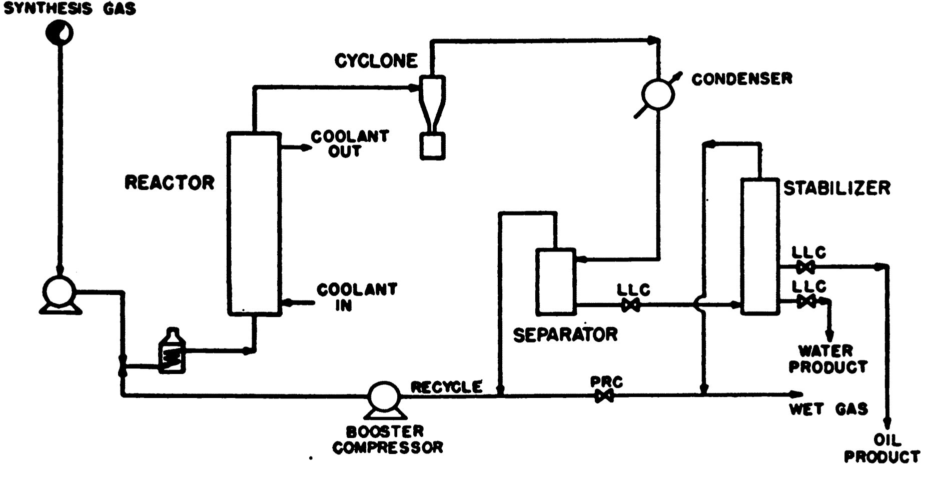

Figure 1. Schematic Flow Sheet of Hydrocol Pilot Plant

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In 1944 a fluid catalyst pilot plant was erected and operated at the Olean laboratory. A schematic flow diagram of the unit is shown in Figure 1. The unit operated well from the beginning. The conversion of reactants exceeded that achieved by the Germans even at space velocities 10 to 20 times those used in Europe. Also, iron catalysts were developed which gave oil yields comparable with those obtained by fixed-bed operations. Typical results from these early experiments are shown in Table I. A discussion of the conditions for the different runs is given in subsequent paragraphs.

Table I. Data for Hydrocol Pilot Plant Operation

	Experiment		
	A	B	C
Reaction temp., ° F.	650	590	665
Reaction pressure, lb./sq. inch gage	230	260	405
Reaction space velocity, vol./hour/vol.	650	600	1200
Recycle to synthesis gas ratio	1.1	1.81	1.4
Catalyst density (initial), lb./cu. ft.	58	46	82
Catalyst density (final), lb./cu. ft.	42	47	79
Carbon on catalyst (initial), %	24	13	17
Carbon on catalyst (final), %	38	13	18
Conversion of CO + H_2 in synthesis gas, %	95	91	98
CO in synthesis gas, %			
Converted to CO_2	13	13	14
C_2H_6 + lighter HC	7	15	16
C_3H_6 + heavier HC	74	66	63
Water-dissolved chemicals	6	6	7
Carbon on catalyst	0.69	0.02	0.04
H_2:CO ratio			
Fresh feed	1.9	1.9	1.9
Reactor feed	2.8	3.1	2.8
Partial pressure of hydrogen, lb./sq. inch			
Reactor feed	110	108	185
Reactor product	68	68	108
CO_2, %			
Fresh feed	4.2	5.7	0.0
Reactor feed	20	27	13
Reactor effluent	28.5	34.0	20.0

A comparison of the type product produced by the German fixed-bed process and the fluid process is shown in Figure 2. The amount of light fuel gas is the same for the two processes, and there is little difference in yield of the chemicals dissolved in the water product. However, the propylene-butylene and gasoline fractions are almost 50% greater for the fluid process. Also the corresponding fractions from the fluid operation are more unsaturated as shown in Figure 3. An advantage in reactor capacity or space velocity of five- to tenfold for the fluid process is also shown in Figure 3.

General Characteristics of Synthesis Reaction. The mechanism of the catalytic reduction of carbon monoxide with hydrogen is not clearly understood. The product under most conditions is a complex mixture of hydrocarbons and oxygenated compounds. The two exceptions to this general rule are the synthesis of methane and the synthesis of methanol. Under conditions that permit carbon-to-carbon linkage to occur, the product invariably contains a large number of different size molecules. By varying catalyst and/or operating conditions it is possible to control the average size and, to a degree, the type of molecule, but the product always contains many different compounds.

Complicated as the product may be, it is possible to illustrate its formation by three equations:

$$n\mathrm{CO} + 2n\mathrm{H_2} = (\mathrm{CH_2})_n + n\mathrm{H_2O} \tag{8}$$

$$2n\mathrm{CO} + 2n\mathrm{H_2} = (\mathrm{CH_2})_n + n\mathrm{CO_2} \tag{9}$$

$$n\mathrm{CO} + 2n\mathrm{H_2} = (\mathrm{CH_2})_n\mathrm{HOH} + (n - 1)\mathrm{H_2O} \tag{10}$$

Water, carbon dioxide, olefin hydrocarbons, and alcohols are shown as products. It is obvious that other equations could be written showing the formation of hydrocarbons of other types—that is CH_4, C_2H_6—and of the other oxygenates produced in this synthesis. Although Equations 8, 9, and 10 do not represent the reaction mechanism but simply express the stoichiometry of the system, they do indicate certain fundamental actions that

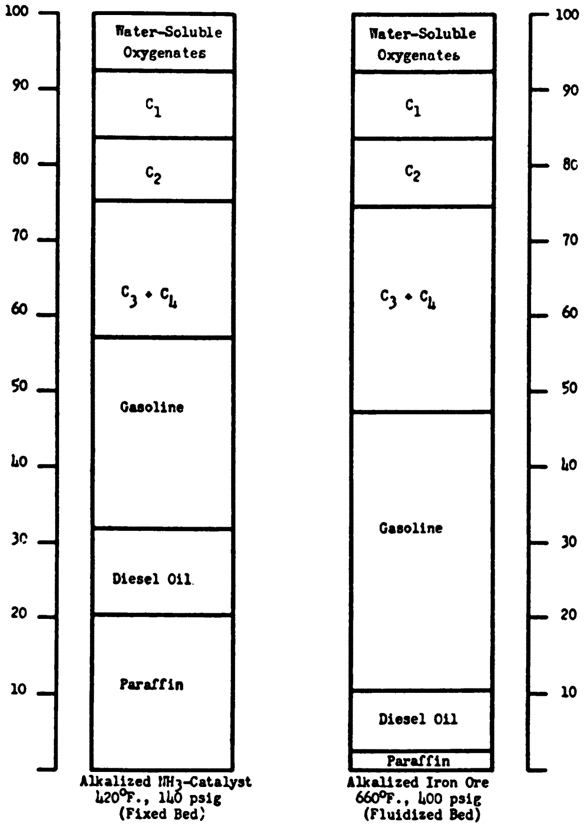

Figure 2. Product Distribution of Synthesis with Fixed and Fluidized Catalyst

must occur directly or through intermediates. These are the rupture of the carbon-oxygen bond of at least some of the carbon monoxide present and the forming of carbon-to-hydrogen and carbon-to-carbon linkages. Analysis of the products shows that these basic actions are accompanied by secondary molecular transformations equivalent to dehydration, polymerization, alkylation, isomerization, cyclization, and possibly rupture of carbon-to-carbon bonds of large molecules.

By proper selection of catalyst and operating conditions the relative extent to which these several actions proceed can be controlled. Indeed this is the basis for the seven different syntheses shown in Figure 4. Certain generalizations are evident from Figure 4: By operating at intermediate temperatures (470° to 650° F.) and atmospheric pressure with bulk nickel and cobalt catalysts, Sabatier produced methane as the chief product. When an active form of iron, nickel, or cobalt deposited on kieselguhr is used at low temperatures (300° to 450° F.), in the Fischer-Tropsch type synthesis, higher hydrocarbons predominate. The hydrocarbons are almost wholly aliphatic and predominantly saturated. By increasing the pressure to 75 to 400 pounds per square inch gage and using cobalt on kieselguhr, higher hydrocarbons including some solid paraffins are obtained; when iron is used at somewhat higher temperature, olefins and paraffins are obtained and significant amounts of oxygenated compounds (particularly at higher pressures and intermediate temperatures, Figure 4). By increasing the temperature further to 575° to 675° F. and the pressure to 225 to 600 pounds per square inch gage, the iron catalyst of the Hydrocol synthesis can be made to yield a liquid hydrocarbon fraction, which is chiefly olefinic and which boils predominantly in the gasoline range. This synthesis also yields a significant fraction of oxygenates. By increasing the pressure to 1500 to 15,000 pounds per square inch gage, lowering the temperature to 300° to 480° F., and using ruthenium as the catalyst, high molecular weight compounds are formed [paraffin wax synthesis of Fischer and Pichler (*9*)]. In the same pressure range but at somewhat higher temperature and with an oxide catalyst—for example, zinc oxide—methanol is the sole product (I. G. Farbenindustrie methanol synthesis). At still higher temperatures with thorium oxide as the catalyst, isoparaffins are formed [Fischer-Pichler-Ziesecke synthesis (*12*)].

Synthesis Reaction in Fluid Bed

In commercial operation, the liquid fuels synthesis reaction must be carried out at a high conversion level and with high selectivity because of the large volume of synthesis gas which must be prepared and handled relative to the amount of liquid produced. To do this it is necessary first to have a catalyst of proper activity and selectivity and secondly, and equally important, to control the composition of the atmosphere or environment throughout the reactor in order to maintain high catalyst activity and selectivity for extended periods of time. The catalysts are not stable in all atmospheres.

Three terms frequently used in the discussion of the synthesis reaction are "conversion," "selectivity," and "yield." As used in this article they have the following arbitrary definitions:

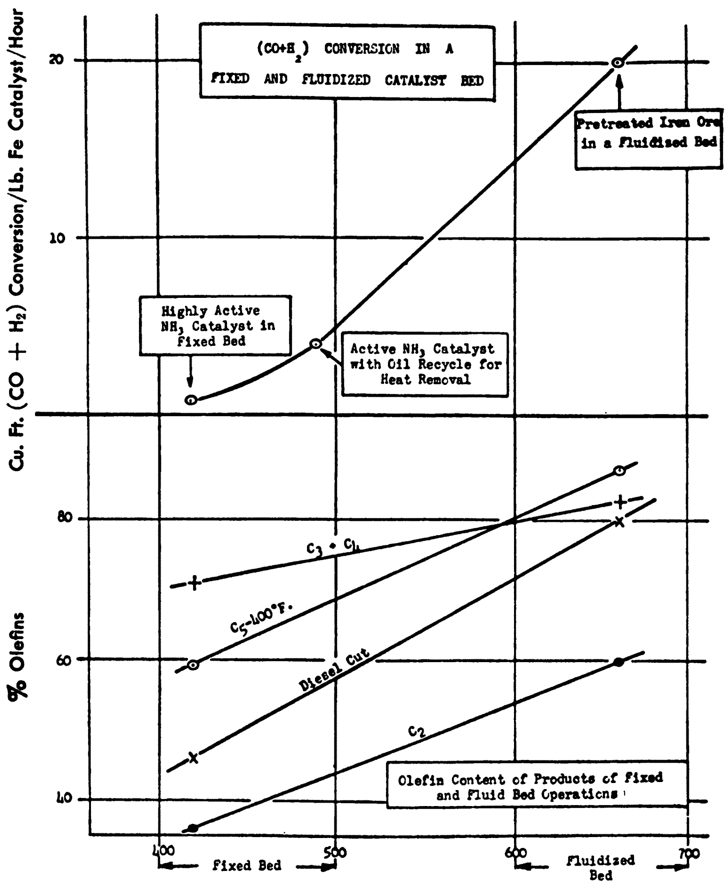

Figure 3. Carbon Monoxide plus Hydrogen Conversion in a Fixed and Fluidized Catalyst Bed

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Conversion is the fraction of reactant carbon monoxide and/or hydrogen converted to other compounds. It is generally expressed in terms of the fresh feed components, but sometimes in terms of the total feed components for recycle operation.

Selectivity is the ratio of the reactant carbon monoxide converted to propylene and higher hydrocarbons and all oxygenates (alcohols, aldehydes, and acids) to the reactant carbon monoxide converted to all hydrocarbons plus oxygenates. A selectivity of 100% indicates the production of propylene and heavier hydrocarbons plus oxygenates but no methane, ethylene, or ethane, and a selectivity of 0% indicates the production of methane, ethylene, and ethane but no higher hydrocarbons or oxygenates. Theoretically selectivity can range between 0 and 100% independent of conversion or carbon dioxide production.

Yield is the per cent of carbon monoxide in the net feed converted to a particular product.

Catalyst. The major components of the catalyst base are iron oxide and an alkali promoter such as potassium hydroxide. It is not necessary to utilize an iron oxide of high porosity; an extended surface of 5 to 20 square meters per gram is generally sufficient compared with 100 to 500 for cracking catalysts. Apparently more important is the pore size and geometry, although as yet little is known about the actual range of sizes and arrangements which constitute the active centers of the catalyst.

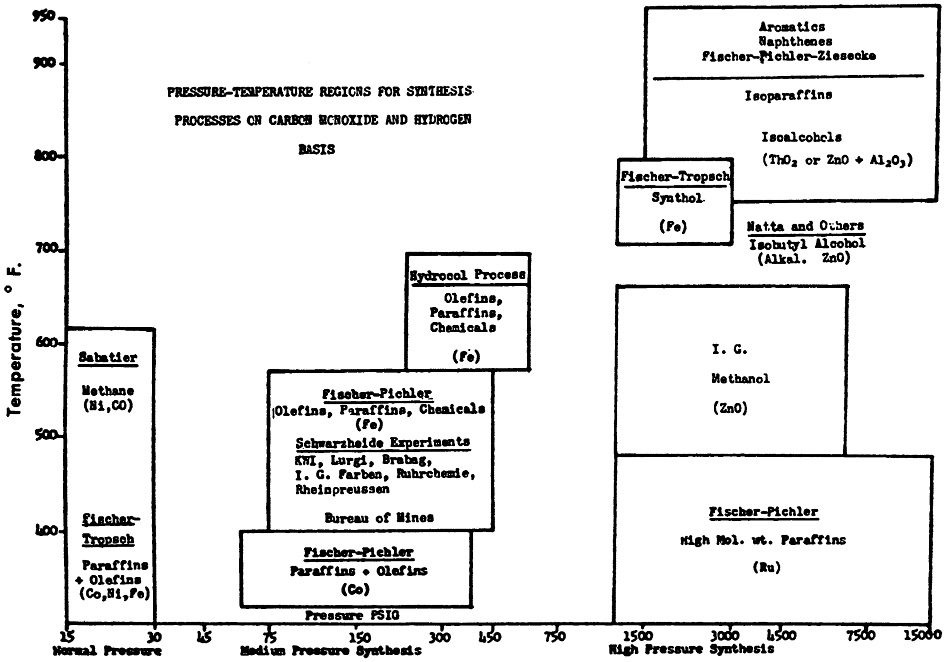

Figure 4. Pressure-Temperature Regions for Synthesis Processes on Carbon Monoxide and Hydrogen Basis

The selection of raw materials and the method of preparation of the catalyst base are important in determining the final quality of the catalyst. Impregnating almost any iron oxide with potassium hydroxide and drying it will yield a catalyst of some activity, but care must be exercised both in selecting the raw materials and in the method of preparation, if a superior catalyst is to be obtained. Generally, the purer the components the better the catalyst, but substantial quantities of impurities such as silicon dioxide, aluminum oxide, and carbon can be tolerated. Suitable raw materials are obtainable at low cost, and satisfactory methods of preparation are simple and inexpensive.

The use of the catalyst base as such in a fluid bed generally results in an initial period

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of low activity and low selectivity, and even after long exposure to reactor conditions, the catalyst is neither highly active nor selective. To shorten the induction period and to achieve ultimately a more satisfactory catalyst, the catalyst base is normally preconditioned. The first step of preconditioning is generally the reduction of the iron oxide with hydrogen. Usually, the higher the degree of reduction, the higher will be the activity of the final catalyst. However, the reduction itself is not enough. Whereas the reduced base appears to be highly active and is probably highly selective, it is not stable in the environment of the fluid bed changing rapidly to a mixture of oxide and carbide. If this change is allowed to proceed uncontrolled, the catalyst produced is generally high in oxide content and not of the highest activity or selectivity.

The reduced catalyst is thus further conditioned by exposing it to an environment which favors carbide formation relative to oxide formation. This can be done in a number of ways. For example, it was common practice for the Germans to treat their reduced catalyst with carbon monoxide at low pressures (*10*). When the catalyst is preconditioned and is maintained in a proper environment, it changes composition only slowly with time and retains its activity and selectivity at a high level. The freshly conditioned catalyst is chiefly a mixture of iron carbides and iron oxide, with a relatively small amount of reduced iron. As synthesis proceeds the catalyst accumulates a carbonaceous deposit which, in amounts up to 50% by weight of the catalyst, does not seem to affect significantly its catalytic powers.

There has been considerable speculation concerning the role of carbide in the iron base catalyst. The carbide was originally depicted as an intermediate in the reaction (*7*), but more recent work indicates the contrary (*3*). It now appears more probable that the lattice between carbide crystals or between groupings of carbide and relatively fewer oxide or even free iron crystals offers the form of pore structure required for both high activity and selectivity.

The role of the promoter in the catalyst is to increase the average molecular weight of the hydrocarbon product. Within limits, the higher the alkali concentration, the higher will be the average molecular weight of the product. Further, the promoter facilitates the formation of iron carbide (*11*). The promoter also has the effect of increasing the activity of a catalyst of low activity level, but no similar effect has been obvious with catalysts of high activity.

Proper Catalyst Environment. As already mentioned, the performance of the catalyst is highly dependent on its environment—that is, the composition, temperature, pressure, and relative rate of flow of the gas to which it is exposed. To maintain a high level of activity of the catalyst, it is necessary to operate under conditions which retard its reversion to the oxide. Thus the concentrations of oxidizing gases, such as water and carbon dioxide, must be limited. Obviously both water and carbon dioxide are products of the synthesis reaction, and so these compounds cannot be entirely eliminated. However, the rates of oxidation of the catalyst by these gases is relatively slow and the degree of oxidation obtained is markedly influenced by the relative concentration of such reducing gases as hydrogen and carbon monoxide. It is thus fortunate that there are certain tolerances, with respect to both water and carbon dioxide, which permit the retention of catalyst activity. Nevertheless these tolerances must be respected. The need for high catalyst activity in a recycle operation might be questioned. However, there is one important reason, independent of the cost of the recycling of reactants, which makes high activity mandatory. All iron catalysts that are active in promoting the synthesis reaction are also active in promoting the water gas reaction, and the product gas is never far from equilibrium in this latter reaction. Thus any carbon monoxide not converted to hydrocarbons will be largely converted to carbon dioxide. Since the carbon dioxide, unlike the water, remains in the product gas on cooling, increasing the quantity of recycle to offset low conversion per pass results in markedly increasing the oxidizing components of the catalyst environment. As a result, a relatively inactive catalyst loses activity quite rapidly, whereas, with proper control, a highly active catalyst remains active for long periods.

Certain of the specifications for the environment necessary to maintain catalyst selectivity are different from those essential to the maintenance of catalyst activity, and they are not strictly compatible. A control of selectivity (independent of the environment), which can be employed within limits but only within limits, is the previously mentioned adjustment of the alkali content of the catalyst. Additional requirements for high selectivity are the control of the relative concentration of hydrogen and carbon monoxide and the concentration of carbon dioxide relative to hydrogen and carbon monoxide in the reactor feed. If the concentration of hydrogen relative to carbon monoxide is too high, the tendency is to produce low molecular weight hydrocarbons. The control of the carbon dioxide concentration relative to that of the hydrogen and carbon monoxide in the catalyst environment is necessary for maintenance of selectivity, because of the water gas reaction as stated. If the carbon dioxide concentration is too low, then the mass action effect is to increase the net yield of carbon dioxide and hydrogen at the expense of water, thus raising the effective ratio of hydrogen to carbon monoxide and adversely affecting selectivity.

To achieve high yields of useful products it is obviously necessary to limit the yield of carbon dioxide as well as to operate at high levels of conversion and selectivity. As stated in the preceding paragraphs the yield of carbon dioxide can effectively be limited first by operating with high conversion of carbon monoxide and secondly by providing a reactor feed high in carbon dioxide content. But again there must be a compromise between the limiting of the carbon dioxide yield and the satisfying of the other conditions of the environment.

The environment of the catalyst must be controlled in another respect if the performance of the catalyst is to be sustained, and again the controls are not wholly compatible with those for maintenance of catalyst activity, selectivity, and yield. When too high a percentage of the compounds synthesized have long carbon-to-carbon chains, carbonaceous material rapidly accumulates within the porous structure of the catalyst causing its disintegration. Since selectivity is an expression of the relative number of molecules having long carbon-to-carbon chains, those factors that control selectivity contribute to the extent of disintegration of the catalyst.

Control of Catalyst Environment. There are four general controls of the environment of the catalyst:

1. The catalyst itself, as determined by the source materials, method of preparation, method of preconditioning, and its particle size and fluidized density
2. The composition of the synthesis gas
3. The composition and relative quantity of any part of the product stream returned to the reactor in admixture with the synthesis gas
4. The three operating variables—reaction pressure, reaction temperature, and reaction time or space velocity.

The effect of the catalyst itself, as measured by conversion, on the catalyst environment is clearly shown in Figure 5. The left half of the figure illustrates the concentration

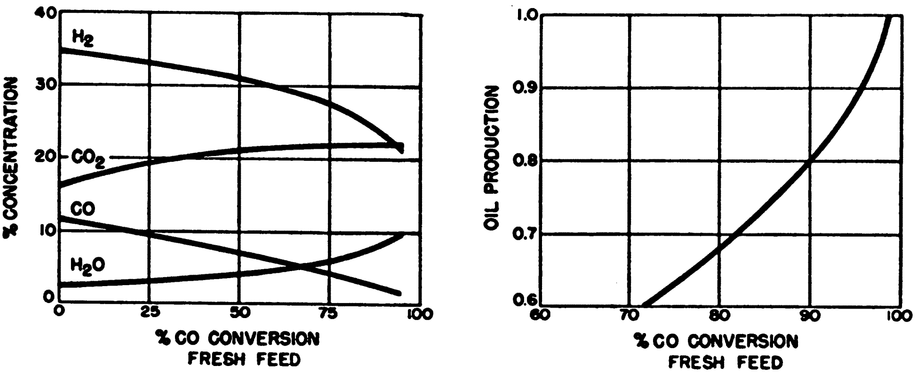

Figure 5. Effect of Conversion on Catalyst Environment and Ultimate Oil Yields

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of the water gas components in the reactor as a function of carbon monoxide conversion. The right half of the figure shows the oil production as a function of carbon monoxide conversion on an arbitrary oil scale, with one unit equivalent to the oil produced by a good catalyst—that is, a carbon monoxide conversion of 98% and selectivity of 80%—with a recycle ratio of 2. Oil production increases rapidly in the range of high conversions of carbon monoxide. Obviously it is in this range that the better catalysts operate. The curves of Figure 5 also show that in this range the ratio of hydrogen to carbon dioxide and carbon monoxide in the product gas, and hence in the gas available for recycling to the reactor, changes most rapidly. Other conditions being equal the concentration of hydrogen in the recycle gas is lower, the more active the catalyst.

The composition of the synthesis gas, particularly the concentrations of hydrogen, carbon monoxide, and carbon dioxide, affects the atmosphere throughout the reactor directly, and also indirectly by its effect on the composition of the recycle gas. Synthesis gas, prepared by partial combustion of methane or some less hydrogen-rich carbonaceous material, lacks sufficient hydrogen for the conversion of all the carbon monoxide to hydrocarbons, and in this sense the synthesis gas is deficient in hydrogen. Stoichiometrically methane has sufficient hydrogen to convert all its carbon to olefins by the two-step process:

$$CH_4 + {}^1/{}_2O_2 = CO + 2H_2 \tag{4}$$

$$nCO + 2nH_2 = (CH_2)_n + nH_2O \tag{8}$$

However, hydrogen is in effect wasted in both the gas generation and synthesis steps—in the former by combustion to water and in the latter by production of compounds of higher average hydrogen to carbon ratio than olefins and by loss of hydrogen gas in the reactor effluent. It is therefore necessary to provide additional hydrogen from some source; this source is the equivalent of the water gas reaction:

$$CO + H_2O = CO_2 + H_2 \tag{11}$$

As selectivity decreases, the hydrogen to carbon ratio in the hydrocarbon product increases, principally because of the increased formation of methane and ethane. Thus, a catalyst of high activity but low selectivity demands an environment which allows the water gas reaction to proceed to a greater extent than required by a catalyst of higher selectivity. Hence, conditions must be selected to yield a significant quantity of carbon dioxide. This relationship is clearly indicated by the curve of Figure 6. The yield of carbon dioxide required to maintain a concentration of hydrogen in the effluent gas of 35% is plotted against selectivity. The correlation of selectivity with hydrogen to carbon ratio of the hydrocarbon product, on which the curve of Figure 6 is based, was derived from the data of approximately eighty pilot plant operations.

The necessity of controlling the relative concentrations of hydrogen and carbon monoxide in the reactor feed to achieve high selectivity is illustrated by Figure 7. The single curve correlates the datum points for selectivity as a function of the molal ratio of hydrogen to carbon monoxide in the mixed feed—that is, the mixture of synthesis gas and recycle. The useful portion of the hydrocarbon product increases from 70 to 85% as the hydrogen to carbon monoxide ratio is decreased from 5 to 2, and the increase in oil yield is proportionately greater because of the lower yield of carbon dioxide coincidental to the higher selectivity as described above.

Catalysts operating at low selectivity level, for any one of the reasons already enumterated, generally disintegrate less rapidly than catalysts of higher selectivity operating at the same temperature. Likewise, catalysts of low activity tend to disintegrate moer slowly than catalysts of high activity. One variable which has a pronounced effect on carbon formation and resultant disintegration of the catalyst is the hydrogen content of the catalyst environment. This effect is demonstrated by Figure 8 where the rate of carbonization of the catalyst is shown as a function of the hydrogen partial pressure. There are certainly other variables operative in the correlation of Figure 8 such as hydrogen concentration, carbon dioxide concentration to the extent it affects hydrogen concentration in the environment of the catalyst, the relative concentrations of hydrogen and carbon monoxide, and variations in catalysts.

Generally, in the range 550° to 700° F., decreasing reaction temperature increases selectivity and decreases conversion. However, highly active catalysts can be operated at lower temperatures with higher total oil yields. There are two other important effects of temperature. At the upper limit of the temperature range quoted, the rate of disintegration of the catalyst is accelerated, and at the lower limit, catalysts of high activity and selectivity tend to accumulate wax with a resultant loss in fluidity of the catalyst bed.

Increased reaction pressure in the range 200 to 600 pounds per square inch gage appears to increase oil yields and decrease the rate of disintegration of the catalyst. However, the effects are not large, and simultaneous changes in velocity and solid-to-gas contact within the reactor tend to obscure the true effect of pressure per se.

In the range 500 to 3000 volumes of synthesis gas per hour per volume of fluidized catalyst, increasing space velocity decreases conversion, the decrease being more pronounced with catalysts of lower activity.

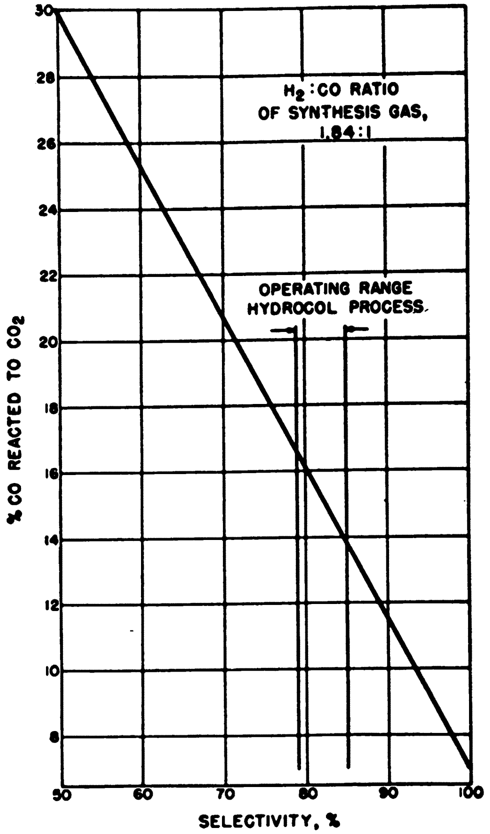

Figure 6. Minimum Carbon Dioxide Yield for Stoichiometric Requirements vs. Selectivity

To recapitulate, the synthesis reaction in the fluid bed is quite complex. For successful operation it is necessary to provide a satisfactory catalyst and environment. This in turn requires care in the selection of raw materials for the catalyst, in its preparation and preconditioning, and in the control of the reactor feed. A combination which led to an intolerable rate of disintegration of the catalyst is shown in the first column of Table I. The results of two experiments at a lower level of selectivity which proved operable are shown in the second and third columns. The difference in operability of experiments A and B seems to stem from a variation in catalyst selectivity per se, whereas the difference between A and C appears in part to be a difference in catalyst environment. Compared with A, the reaction pressure of experiment C was 405 versus 260 pounds per square inch gage, and the reactor inlet hydrogen partial pressure 185 versus 110 pounds per square inch. The difference between the operable and inoperable conditions of the experiments of Table I represents about 20% in oil production. This difference has naturally led to work aimed at establishing conditions for catalyst preparation and control of catalyst environment which will allow operation nearer to the level of selectivity of experiment A. The results of this work are not ready for publication at this time.

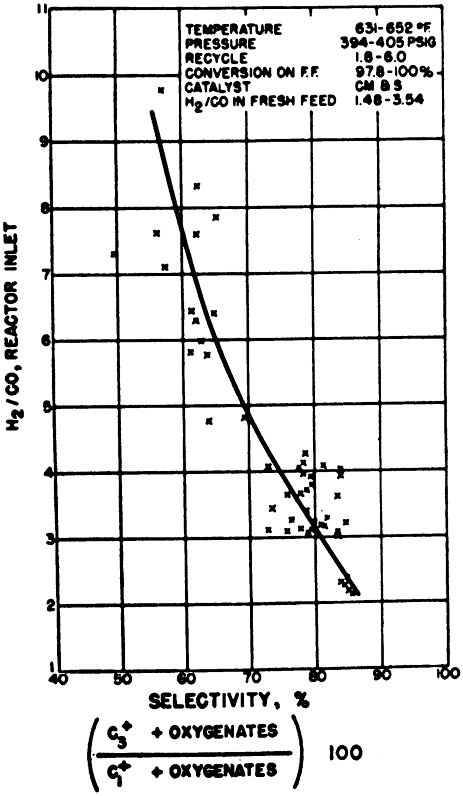

Figure 7. Effect of Total Feed Composition on Selectivity

Catalyst Poisons. Synthesis gas prepared by the partial combustion of sweet natural gas can be charged to the reactors directly without purification. However, synthesis gas containing more than 0.1 grain of sulfur per 100 cubic feet must be purified before use over fluidized iron catalysts. Other catalyst poisons are known, such as chlorine (*14*), but they are not likely to be encountered in the natural gas to gasoline process.

Recovery, Separation, and Finishing Operations

The propylene-butylene fraction constitutes a large part of the useful hydrocarbons produced by synthesis. It differs from similar fractions derived from petroleum refining in its high olefin (over 80%) and low isobutylene content, but this is no handicap in converting it to high octane gasoline by polymerization or by alkylation, if isobutane is available from another source. Polymerization is effected readily over a phosphoric acid on quartz catalyst with high conversion of propylene as well as butylene. The polymer

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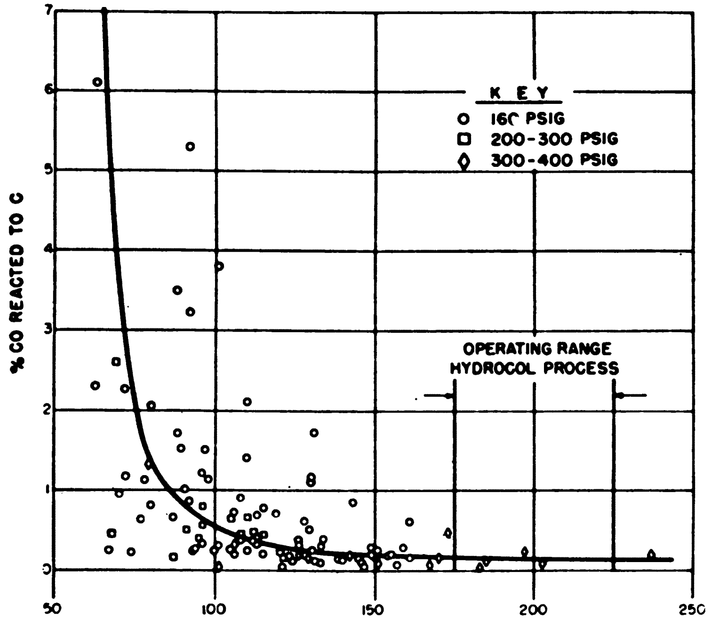

Figure 8. Reactor Inlet Hydrogen Partial Pressure vs. Per Cent Carbon Monoxide Reacted to Carbon

gasoline is indistinguishable from the high octane polymer gasolines produced in the modern petroleum refinery. The vapor pressure of the pool gasoline is controlled by the degree of polymerization of butylene. The synthesis process produces no excess butanes.

The liquid hydrocarbon product from the synthesis reactor distills primarily in the gasoline range, with relatively minor quantities distilling in the light gas oil and fuel oil ranges. The raw synthesis gasoline contains dissolved alcohols, aldehydes, ketones, acids, and other oxygen-bearing compounds. The hydrocarbon fraction is predominantly α-mono-olefins. To produce a salable high octane gasoline, it is necessary to eliminate the dissolved oxygenates and to isomerize the α-olefins. This is readily accomplished by passing the mixture over bauxite or other isomerization catalysts at 750° to 850° F., simultaneously isomerizing the olefins and converting the oxygenates to hydrocarbons. The product is then a stable highly olefinic gasoline of 90 CFRR clear octane number. The treating can be accomplished with only minor losses to gas and carbon. The raw synthesis gas oil has the same general chemical structure as the gasoline, and it can be either deoxidized to produce distillate fuel or cracked to gasoline. It can be used also as a source of straight-chain olefins for special purposes, such as the manufacture of detergents.

The relatively low molecular weight alcohols, aldehydes, ketones, and acids dissolved in the water stream condensed from the synthesis products can be separated into specification chemicals. Details concerning the production of these highly valuable by-products of the process have been given in recent publications (*2*, *15*).

Commercial Plant Design

The developments previously described have been integrated into the design of the first commercial Hydrocol plant. The plant is now producing oxygen on a large scale, producing synthesis gas under pressure by partial combustion, synthesizing chemicals and oil, and recovering, polymerizing, and treating the various fractions. Specific operational data are not yet available for publication. It is hoped that such data with a description of the plant can be the subject of another paper within a reasonably short time.

To illustrate generically the integrated Hydrocol process, Figure 9 has been included.

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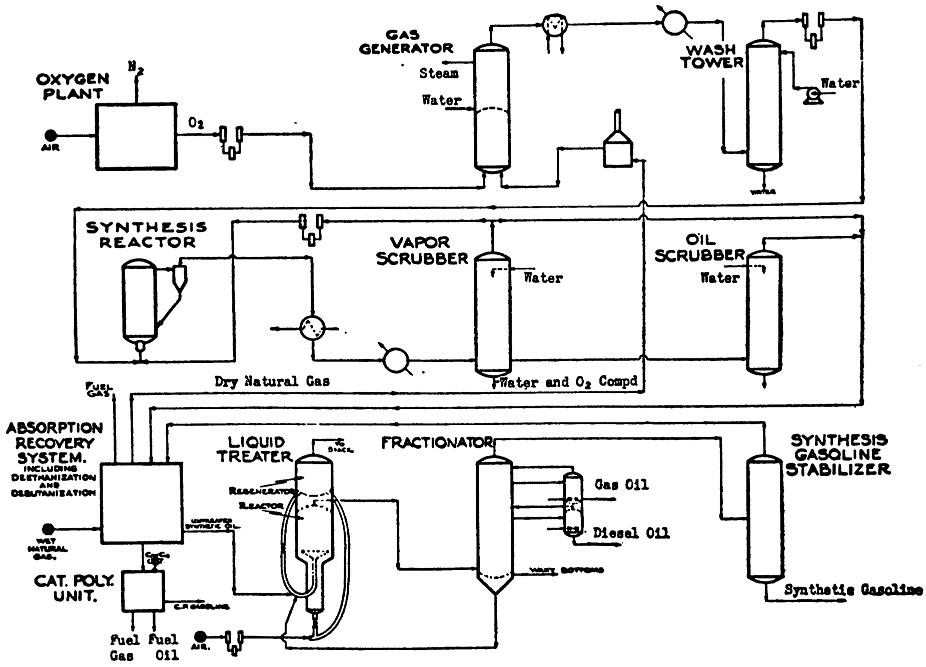

Figure 9. Simplified Flow Sheet of Hydrocol Plant

This flow sheet illustrates that a commercial plant is not complex. Process and design calculations have been made for a number of plant sizes and it is of interest to enumerate the more important figures for a 7700-barrel-per-day plant. Such a plant consuming 100,000,000 cubic feet of natural gas per day (which includes all fuel for processing both the oil and the chemicals) requires 62,000,000 cubic feet of oxygen per day (2600 tons). This oxygen would be produced in two units. There would be two synthesis gas generators, operating at 425 pounds per square inch gage to produce 280,000,000 cubic feet of synthesis gas per day. The synthesis step would be conducted in three reactors, each containing approximately 200 tons of catalyst. From the synthesis gas there would be produced 6500 barrels of gasoline per day having a clear CFRR octane number of 90, 1090 barrels of gas oil per day with a cetane number of 52, and 115 barrels of fuel oil per day. The water-soluble chemical production would amount to 460,000 pounds per day and 140,000 pounds of ethylene per day could be recovered from the tail gas. The gasoline would be highly unsaturated, containing about 86% of mono-olefins. If desired, certain fractions of this gasoline could be separated and used in the manufacture of detergents, synthetic lubricating oils, and other special products.

The operation of the first commercial Hydrocol plant will give added impetus to the American synthetic oil development whether the raw starting material be shale, coal, or gas. New fields in the chemical industry will be opened, and several new and important chemical engineering techniques will have been proved. Among these are the production of tonnage oxygen, the generation under pressure of mixtures of carbon monoxide and hydrogen from either natural gas, refinery gas, or liquid fuels, and a technique for conducting highly exothermic chemical reactions under controlled temperature conditions while utilizing the heat of reaction to produce high pressure steam.

Availability of Natural Gas for Hydrocarbon Synthesis

There are sufficient gas reserves presently proved, with the prospect of additional reserves to permit the utilization of as much as 2 trillion cubic feet of natural gas annually for the production of synthetic fuels. This quantity of gas is available in addition to that

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Table II. Natural Gas Utilization and Reserves[a]

Year	Natural Gas, Trillion Cubic Feet			
	Total production	Utility sales	Nonutility sales	Estimated proved reserves at end of year
1945	..	2.2	..	147.8
1946	4.9	2.2	2.7	160.6
1947	5.6	2.6	3.0	165.9
1948	6.0	2.9	3.1	173.9
1949	6.2	3.1	3.1	180.4
1950	6.9	3.7	3.2	185.6
1954	(8.9)	(5.2)	(3.7)	(209)
1958	(10.9)	(6.7)	(4.2)	(225)

[a] Report of the American Gas Association, "Proved Reserves of Crude Oil, Natural Gas Liquids, and Natural Gas," Dec. 31, 1950 [*Oil Gas J.*, **49**, No. 38, 213 (1951)].

necessary to satisfy current and projected utility demands. The expenditure of $2,500,000,000 by gas pipeline companies during the years 1946 to 1950 increased the annual pipeline take by approximately 1.5 trillion cubic feet. During this same period the annual nonutility consumption increased more slowly at a rate slightly in excess of 0.5 trillion cubic feet. These figures are shown in Table II. The forecasted expenditure of $2,750,000,000 for pipeline facilities during the period 1950 to 1954, although possibly increasing annual gas production to almost 9 trillion cubic feet, will probably be concomitant with an increase in proved reserves to over 209 trillion cubic feet. A further extrapolation indicates a total gas production approaching 11 trillion cubic feet and a proved reserve of 225 trillion cubic feet in 1958. The above figures would safely allow an annual increase in production of two trillion cubic feet for synthesis, while maintaining an adequate reserve behind all gas users and a ratio of production to reserves less than that prevailing for crude oil. Hence there is no immediate evidence of a shortage of natural gas for synthesis. The utilization of 500 billion cubic feet per year, for example, would add 100,000 barrels of liquid fuels per day to supplies.

Chemical Production

The approximate production of water-soluble chemicals from a single 7000-barrel-per-day synthesis plant is shown in Table III. The Stanolind Oil and Gas Co. has at Brownsville, Tex., a chemical plant to separate and purify the water-soluble chemicals made from the first commercial Hydrocol plant. The oil-soluble chemicals (not listed in Table III) vary in quantity from 50 to 100% of the water-soluble chemicals and are composed of alcohols, aldehydes, ketones, and acids of average molecular weight distinctly higher than the average molecular weight of the water-soluble chemicals. Currently these oil-soluble chemicals are converted to hydrocarbons, but additional development work will surely result in processes for their recovery. They will then constitute a new and important source of higher alcohols and organic acids.

Table III. Oxygenated Chemicals Production from Various Quantities of Natural Gas Compared with 1948 Production Statistics

	Oxygenated Chemicals, Million Lb./Year		
	Production from one Hydrocol plant	Production from 500 billion cu. ft. natural gas/year	Estimated production, 1948
Methanol	0.5	7	1060
Ethanol	61.2	838	980[a]
Isopropanol	1.3	18	840[b]
n-Propanol	19.6	268	..
Higher alcohols	8.5	117	..
Acetaldehyde	11.2	154	440[c]
Higher aldehydes	4.4	60	..
Acetone	17.9	245	480
Methyl ethyl ketone	3.6	49	..
Higher ketones	2.0	27	..
Acetic acid	25.2	346	420
Higher acids	11.0	151	..

[a] 37% used to manufacture acetaldehyde.
[b] 60% used to manufacture acetone.
[c] 75% used to manufacture acetic acid and acetic anhydride.

The production of water-soluble chemicals from several plants should not burden the market although it would be necessary to develop outlets for certain of the chemicals which are not now available in commercial quantities—for example, *n*-propyl alcohol and the higher molecular weight aldehydes, ketones, and acids.

The approximate production of chemicals from a synthesis capacity equivalent to an annual processing of 500 billion cubic feet of natural gas is also shown in Table III and is there compared with the estimated production of the same chemicals in 1948. Even with such a large output, some of the chemicals now in high demand would be salable with only slight dislocations for marginal producers. Others would, of course, have a serious impact on present markets until substantial new outlets were developed. It seems reasonable to expect, however, that with new synthetic products being developed continually, all the chemicals could, in time, be marketed profitably.

Currently it appears that the revenue from the sale of the water-soluble chemicals will contribute approximately 25% to the gross income of the process. When it becomes possible to purify and dispose of the oil-soluble chemicals, the revenue from chemical sales should amount to 40 to 50% of the total.

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Liquid Fuels from Coal and Oil Shale

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The desirability of long-range development work on synthetic liquid fuel processes is discussed. Procedures for mining and chemical processing of coal and oil shale for the manufacture of liquid fuels are outlined. The basic chemical and engineering problems involved in coal gasification, coal hydrogenation, hydrogenation of carbon monoxide, retorting of oil shale, and refining of shale oil are presented. Current development work is included to indicate foreseeable improvements. Brief mention is made of critical economic factors of the various processes.

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Most analysts agree that imports of petroleum now are needed to supplement our domestic production and will be necessary in increasing amounts in the coming years. Although continued research and development on synthetic liquid fuel processes during the next few decades are advised by everybody concerned, opinions differ about preparation for an emergency, such as war, during this period. Some (*27*) think we should start building synthetic liquid fuel plants at once. Others (*35*) conclude that reasonable stockpiling of steel for drilling new wells and fabricating pipelines, a high inventory of alkylate, and strict rationing of gasoline will suffice.

Of greater significance than the extent of our domestic petroleum resources and their maximum rate of efficient utilization is the sharp increase in the cost of discovery of new petroleum fields.

This cost increased about sixfold during the period 1937–47. Despite vastly improved technology in procedures for locating new oil deposits, the amount of oil discovered per well drilled is now only about half of that in 1937. In addition to increases in cost of labor and materials, the average depth of the wells has increased markedly. Because of the increased cost due to greater difficulty in finding new oil and to the necessity for much deeper wells, and because of recent progress in the mechanized mining of coal and oil shale, the cost of production of these latter two raw materials probably will decrease relative to that of petroleum. Perhaps the most important reason for maintaining our interest in processes for producing liquid fuels from coal and oil shale is to provide a price "ceiling" for liquid fuels from petroleum. There are special economic and geographic factors that may make profitable, in the near future, the manufacture of high-B.t.u. gas and fuel oil from coal and oil shale.

Coal is our major source of fossil fuel, being about 87% of the total. Oil shale is 9%, petroleum is 2.5%, and natural gas is 1.5%. These estimates are based on the probable yield of liquid fuel. They are, at best, only very approximate (*1, 9, 11*). Thus, if all of the known oil-shale deposits in the United States were included, the probable yield of liquid fuel would be about 50% of the total since the 9% estimate excludes shale assaying less than 10 gallons per ton. Similarly, in estimating the probable yield of liquid fuel from coal, somewhat arbitrary assumptions must be made concerning the feasibility of mining thin seams.

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Mining of Coal

In recent years developments in mechanized mining and loading of coal in the United States have been accelerated by the construction and testing of the Joy continuous miner, constructed by the Joy Manufacturing Co. of Franklin, Pa.; the Colmol, produced by the Jeffry Manufacturing Co. of Columbus, Ohio; a machine manufactured by Crawford-Oliphant, Inc., of Vincennes, Ind.; and one designed by the Mine Development Committee of Bituminous Coal Research, Inc. A completely mechanized mine produces 10 to 12 tons of coal per man per shift as compared with an average of 5 to 6 tons for all coal mines in the United States. The resultant decrease in cost per ton of coal, at the mine, would be about $2.00, which would lower the cost of synthetic gasoline from coal by about 2 cents per gallon. Coal mining procedures based on disintegration of the coal bed by sonic vibrations may further reduce the cost of mining. An alternate procedure, which avoids mining of coal, is underground gasification. However, the engineering problems in controlling the burning of an underground bed of fuel so as to produce gas of uniform composition have not yet been solved.

Mining of Oil Shale

Because our economically important oil shale deposits have an average of only 10 to 15% of organic matter from which oil may be obtained by thermal decomposition, it would seem, upon first consideration, that it should be more economic to mine and process bituminous coal which contains 80 to 90% of organic matter. However, both mining and primary processing or retorting of oil shale, demonstrated on a large scale by the Bureau of Mines at Rifle, Colo., have been shown to be relatively cheaper than similar operations for coal. Because the oil shale mined at Rifle, Colo., is a tough marlstone rock, a type of highly mechanized quarrying operation has been developed which makes possible production of about 116 tons per man per shift. This figure is based on the total labor, including direct supervision, engineering, and all maintenance personnel. An estimate (*28*) for a mine producing 19,200 tons of oil shale per day was 42.6 cents per ton. This included costs of management, depreciation, taxes, and insurance but did not provide for depletion, interest on investment, profit, or expenditures for off-site facilities.

Primary Processing (Retorting) of Oil Shale

Several types of continuously operating, internally heated oil shale retorts have been developed and tested in large scale pilot plants (*24, 27, 28*). The most promising of these appear to be the Union Oil Co. upflow shale retort (*24*) and the Bureau of Mines gas combustion retort (*28*). In the former, crushed shale is fed into the bottom of a vertical retort. Air is blown in at the top of the retort and a combustion zone of burning organic matter exists just below the top of the retort. The crude shale oil distills ahead of this combustion zone, and the vapors flow downward and condense on the cold upflowing oil shale. The spent shale is discharged at a high temperature by rabble arms at the top of the retort.

The Bureau of Mines gas combustion retort also is vertical, but with downflow of shale and upflow of air and gas. The shale enters the top of the retort through a gas seal and flows through the retort by gravity. The retorted shale is discharged at the bottom by a rotating disk and leaves the retort through a gas seal. Cold product gas is introduced into the bottom of the retort, where it is heated by the descending, hot, spent shale. About one third the way up the retort, there is a vertical gas-mixing tube, open at both ends but shielded by a conical section to prevent shale from entering. The gas-mixing tube is about one fifth the height of the retort and one fourth its diameter. The descending shale flows in the annulus between this tube and the wall of the retort. The preheated gas is mixed with air in this tube, and the mixture passes up into the combustion zone, where the gas and some of the organic residue in the spent shale are burned. The hot flue gas heats the shale and pyrolyzes the organic matter in it, thus producing shale-oil vapors, product gas, and spent shale. Near the top of the retort, the oil vapors are condensed by the cold incoming shale.

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Refining of Shale Oil

Both of the retorting procedures described above have the advantage of avoiding the use of water for cooling the spent shale or for condensing the shale oil. The regions containing our largest deposits of oil-rich shale are arid and sparsely populated, and for these reasons it may be desirable to refine the crude shale oil elsewhere. After a viscosity-breaking operation (mild thermal cracking) to reduce the pour point, the shale oil could be transported by pipeline to Los Angeles or Chicago for sale as fuel oil or for refining to produce motor fuel. Table I compares the characteristics of the crude and viscosity-broken shale oil. The amount of coke and gas produced in the viscosity-breaking operation is 2 to 4% of the feed.

Table I. Characteristics of Crude and Viscosity-Broken Shale Oil

	Crude Shale Oil	Viscosity-Broken Shale Oil
Gravity, ° API	19.7	21.4
Pour point, ° F.	85	15
Gasoline, vol. %	5	15
Gas oil, vol. %	15	28
No. 6 fuel oil, vol. %	80	57

Viscosity-broken shale oil is suitable for use as No. 5 or No. 6 fuel oil. Hydrogenation at high pressures (200 to 700 atmospheres) of the crude or viscosity-broken shale oil, or preparation of "coker distillate," followed by hydroforming the $<200°$ C. (392° F.) fraction, hydrogenation of the heavier fraction at relatively low pressure (100 atmospheres), and catalytic cracking of the hydrogenation product are necessary for the production of a major portion of gasoline. The latter alternative, suggested by the Union Oil Co., has been tested recently in a pilot plant operation by the Bureau of Mines (*4*). Oil yield in the coking step was 80 volume % and 77 weight % of the crude shale oil. The yield of jet fuel and Diesel oil in the hydrogenation step was nearly 100 volume %. In the hydrogenation step, 1200 to 1400 cubic feet of hydrogen per barrel of coker-distillate feed were consumed. The yield of gaseous hydrocarbons was sufficient to produce, upon reforming, all of the hydrogen used in the process. The Diesel oil is of premium grade, and the jet fuel meets military specifications and can be catalytically cracked to produce a high grade gasoline. Coking of the shale oil in the Bureau of Mines tests was more drastic than is considered necessary for the Union Oil Co. process; and a yield of 85 to 87 volume % (rather than 80%) is expected to be consistent with ease of hydrogenation of the $>200°$ C. (392° F.) fraction of the coker distillate.

Primary Chemical Processing of Coal

Coal Gasification. All procedures for producing liquid fuel from coal include the manufacture of hydrogen or mixtures of hydrogen and carbon monoxide. In fact, of the total cost of synthetic liquid fuel, 40 to 50% is expended for compressed hydrogen in the coal-hydrogenation process and about 60% for synthesis gas (hydrogen–carbon monoxide mixture) in the Fischer-Tropsch process. Of the cost of gasification, 20 to 30% is for mining the coal and 70 to 80% for the subsequent mechanical handling and chemical processing.

The conventional "blue" water-gas process has been used to a large extent in Germany and the United States to obtain a mixture of about equal volumes of hydrogen and carbon monoxide. The ratio of hydrogen to carbon monoxide in this gas usually is 0.9 to 1.2, and it can be "shifted" by means of the water-gas shift ($CO + H_2O = CO_2 + H_2$) and subsequent scrubbing to remove the carbon dioxide to yield mixtures richer in hydrogen or pure hydrogen. The conventional water-gas process consists in heating a bed of lumps of high-temperature coke to just below the ash-fusion temperature by blowing preheated air through the bed. Combustion gas is purged to the atmosphere. After the maximum temperature has been reached, the air blast is cut off and replaced by one of steam, and the gas resulting from the reaction $C + H_2O = CO + H_2$ is collected. This process is an expensive one, because high grade coke with ash of high melting point is needed.

Processes and equipment for the gasification of inferior coke and chars from low-temperature carbonization of subbituminous and lignitic coals were developed in Germany (*13*), where the relatively large yield of low-temperature tar was welcomed as raw material for hydrogenation processes. The market for low-temperature tar in the United States has been too small and the selling price too low to encourage the use of low-temperature chars for gas production.

A few processes for complete gasification of coal were developed in Germany (*13*). Probably the most efficient of these is the Lurgi-Drawe (*13, 18, 32*) process, in which noncoking subbituminous coal, lignite, anthracite, or semicoke is reacted with a mixture of steam and oxygen at 20 atmospheres pressure and at a temperature as low (usually 900° to 1000° C., 1652° to 1832° F.) as is consistent with the reactivity of the fuel. For use in synthetic liquid fuel production, this gasification process has one outstanding advantage—that the gas is produced at 20 atmospheres and can be purified and "shifted" under pressure, and thus the first stage of compression of hydrogen or synthesis gas is accomplished in the gasification procedure. Its disadvantages are the necessity for sized coal which does not coke or spall, the energy lost in the "lock-hopper" systems of introducing the coal and of discharging the ash, and the limited capacity of the generator, caused by the necessity of keeping the reaction temperature below the fusion point of the ash.

The most widely used commercial process in Germany for the complete gasification of brown coal and brown coal char is the Winkler (*13, 32*). Fuel as 5- to 50-mesh coal or char particles is gasified in fluidized suspension in a mixture of steam and oxygen. Largely because of carry-over of fines containing a large percentage of carbon, this process is not so efficient as the Lurgi; but, because the Winkler process can use brown coal, which cannot be coked (without prior briquetting) or readily gasified by any other existing commercial process, it is used extensively in Germany for the production of Fischer-Tropsch synthesis gas and of mixtures of hydrogen and nitrogen for ammonia synthesis.

A modification of the Winkler process, known as the Flesch-Winkler (*8*), was developed to overcome the difficulties in gasification of coking coals and to provide an effective means of removing fly ash from the gas. The Flesch-Winkler producer is cylindrical with about 7 square feet of grate area. About 13 feet high, it is operated with a fuel bed about 3 feet deep. The operation alternates between down run and up run, about 85% of the operating time being in down run. During the down run, the gasification zone moves downward, leaving a layer of slowly solidifying clinker in the upper part of the bed, which serves as a preheater for the steam-oxygen (or air if producer gas is being made). The gas leaves the producer at 400° to 500° C. (750° to 930° F.). At the end of the down-run period, a relatively short up-run period occurs, using only enough steam-oxygen (or air) to maintain the bed in an expanded state and permit the coarser lumps of clinker to settle to the grate, from which they are discharged into an ash pit by means of a rotating arm. During the up run, the coal feed, which is introduced just above the grate, is preheated by the combustion of some gas, which is introduced with the steam-oxygen mixture. Operating data for this process are insufficient to permit evaluation of its efficiency.

Much effort and ingenuity were expended in Germany to develop continuously operating gasification processes without oxygen. In these processes (*13, 32*), such as the Pintch-Hillebrand and the Bubiag-Didier, brown coal briquets, or sized, noncoking subbituminous or bituminous coal, were passed through a drying zone, a carbonization zone, and a gasification zone, all contained in a type of vertical retort. Gasification was done with preheated steam.

In Great Britain, the Imperial Chemical Industries, Ltd., has developed a fluidized coal gasification process (*32*) using combustion of part of the fuel with air to supply the heat necessary for the endothermic steam-carbon reaction. This procedure is divided into three steps: carbonization, air-blowing, and steam-blowing. The first and third steps operate with fluidized beds, and the second with a dilute suspension. Powdered coal is fed into the carbonization vessel, where it is heated by combustion of some of the carbonization gases. The powdered char is blown into a feed hopper connected with the air-

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blow vessel, in which the temperature of the char is raised to just below the ash-fusion temperature. The heated char is then blown into the steam-blow vessel, where gasification occurs. In this process, the tar can be recovered if desired. As virtually no operating data have been published, this process cannot be appraised critically. It is apparent, however, that transport of large amounts of hot solids will present major engineering problems.

In the United States, research and development work on gasification of coal have been confined largely to the use of powdered coal, oxygen, and steam. During the past few years, large pilot plants have been operated by fuel companies to obtain engineering data applicable in designing plants of commercial size. At atmospheric pressure, fluidized beds of powdered coal using oxygen-steam mixtures have been found operable, even with bituminous coal. Although it is feasible to gasify coal efficiently by this process, the gasification rate is limited by the ash-fusion temperature and, for coking coals, also by the necessity of maintaining a large (about 10 times the fresh coal feed) rate of recycle of coke and ash to the reactor. The extension to pressure operation has not yet been made in fluidized coal gasification. Another procedure reported as being tested in a pilot plant of adequate size consists in pumping a slurry of powdered coal and water through a preheater into a pressure vessel into which oxygen under pressure (several hundred pounds per square inch) also is introduced. The ash is discharged as liquid slag. No data have been published on the performance of these two industrial pilot plant operations.

As part of its work on synthetic liquid fuel processes, the Bureau of Mines has operated three types of powdered coal gasification pilot plants. In Louisiana, Mo., in the synthetic liquid fuels demonstration plant, a Koppers coal dust gasification (*26*) pilot plant was built and tested. Powdered coal and oxygen at about atmospheric pressure were fed into two burners, one in each end of a cylindrical refractory-lined reactor, 6.5 feet in inside diameter and 9 feet long. Steam also was introduced at each end in a fashion designed to form a sheath or envelope of steam around the combustion zones emanating from the burners. Ash was removed largely in suspension in the product gas and partly by settling in ash pits attached to the reactor. The results of tests in this pilot plant indicate that further development work and changes in reactor design are necessary.

In Morgantown, W. Va., the Synthesis-Gas Production Branch of the Bureau of Mines has operated a pilot plant for the gasification of powdered bituminous coal entrained in oxygen–superheated steam mixture (*31*). The reactants are introduced through an inlet at the bottom of, and tangential to, the cylindrical reactor which is about 3 feet in inside diameter and 21 feet high. The efficiency of this process is good. The operations reported have been for only short periods, and the engineering difficulties involved in discharge of molten ash have not yet been overcome.

The conditions used in most nonfluidized, coal dust suspension gasifiers constitute a special case of a more general procedure described in 1938 by the British Fuel Research Board (*2*) and subsequently studied in the United States by Yellott and Kottcamp (*37*), Von Fredersdorff (*33*), and Perry, Corey, and Elliott (*23*). This general procedure is the gasification of powdered coal by the vortex principle. By tangential injection of all or part of the reactants into a cylindrical reactor, the reacting mixture is conducted along a spiral path. Because the particle size of the coal is continuously decreased during the gasification, individual particles move in spiral paths of continuously decreasing diameter until the discharge port in the center of one end of the cylinder is reached. Relative motion of the solid particles with respect to the stream of gaseous reactants and products occurs. The capacity of such equipment per unit volume of reactor is higher than in other types such as, for example, the fluidized reactor. The available data for vortex gasification show that such processes with downflow of all reactants can be readily operated. Recent unpublished reports on pilot plant experiments by Perry, Corey, and Elliott show that 90% of the carbon was gasified when 0.88 pound of oxygen per pound of coal was used.

It is probable that development of satisfactory processes for gasification of pulverized coal with oxygen-steam mixtures would be expedited by additional laboratory research on the kinetics of the steam-carbon reaction (*20*) at temperatures between 1000° to

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1500° C. (1832° to 2732° F.). The reaction between powdered carbon and oxygen is reported to be immeasurably rapid at these temperatures, and the rate-determining step of these gasification processes is that of the steam-carbon reaction.

Experiments on underground gasification of coal are in progress at Gorgas, Ala. (*27*). Although it is anticipated that such gasification may be of practical importance for the manufacture of electric power, the production of hydrogen–carbon monoxide mixtures for synthetic liquid fuel processes will involve solution of a number of engineering problems before full evaluation of this procedure can be made.

Fuel Oil and Gas Oil from Hydrogenation of Coal

Coal can be hydrogenated directly to yield oil. In the first stage of coal hydrogenation by the Bergius–I.G. Farbenindustrie process (*13, 29*), the coal is converted chiefly to a middle oil whose boiling range is 200° to 325° C. (392° to 617° F.). Powdered coal (about minus 80-mesh) is mixed with somewhat more than its weight of a recycle heavy oil from the process and a small percentage of catalyst powder. For German brown coal, about 4% (based on the dry coal) of red mud from bauxite purification is employed as catalyst, and for bituminous coal, about 0.1% of tin oxalate (oxide or sulfide also may be used) plus about 1% of ammonium chloride. The brown coal is dried to about 5% moisture content, and the bituminous coal is washed to decrease its ash content and then dried. The pastes of coal, oil, and catalyst have the compositions shown in Table II.

Table II. Composition of Coal-Oil-Catalyst Paste for Coal Hydrogenation, Weight %

	Brown Coal	Bituminous Coal
Dry coal[a]	44.1	45.9
Catalyst	4.0	1.4
Solids in recycle oil	1.1	4.6
Water	2.4	1.0
Recycle oil	48.4	47.1

[a] Dry brown contains 12%, and dry bituminous, 4.5% of ash.

The coal-oil-catalyst paste and an excess of hydrogen (300 to 500 cubic meters per ton of brown coal paste, 500 to 1000 cubic meters per ton of bituminous coal paste) are pumped at 250 to 300 atmospheres pressure through a heat exchanger and a gas-fired preheater into the reactors. The reactants enter the first of three or four converters at about 430° C. (806° F.) and are rapidly heated to 470° to 490° C. (878° to 915° F.) by the exothermic heat of the hydrogenation reaction. The temperature in the reactors is kept in the range 470° to 490° C. (878° to 915° F.) by injection of about 1000 cubic meters of cold hydrogen per ton of coal paste.

The coal hydrogenation reactors are about 1.2 meters in inside diameter and 18 meters high. The pressure retaining wall is kept relatively cool by insertion of a layer of insulation between it and the reaction vessel, on both sides of which the same pressure is maintained. The throughput is about 0.45 ton of ash- and moisture-free brown coal and about 0.25 ton of ash- and moisture-free bituminous coal per hour per cubic meter of reactor volume, the corresponding contact times being about 1 and 2 hours, respectively. Upon leaving the last reactor, the products pass to a hot catchpot operating at about 440° C. (824° F.) and under the same pressure as in the reactors. The liquid separated in the hot catchpot contains in suspension the ash of the coal, the catalyst, and any unreacted portions of the coal such as "fusain" (or mineral charcoal) which is not converted to oil or oil-soluble material. This heavy oil slurry is cooled and discharged at atmospheric pressure. About two thirds of it is then mixed with about 75% of its weight of distillate heavy oil obtained by topping the cold catchpot product, and the mixture is centrifuged. The centrifuge residue is mixed with the remaining third of the heavy oil slurry from the hot catchpot, and the mixture is coked in a rotating kiln. The heavy oil obtained by condensation of the kiln vapors is mixed with the liquid product from the centrifuge and the mixture recycled as pasting oil. The light oil obtained from condensation of the kiln vapors is mixed with the cold catchpot oil.

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Gases and vapors from the hot catchpot are cooled and passed to a cold catchpot. The condensate is discharged at atmospheric pressure and topped to provide middle oil for the second stage of hydrogenation and distillate heavy oil, which is recycled for dilution of the heavy oil slurry and for paste preparation.

Hydrogenation of bituminous coal was found more difficult than that of brown coal, chiefly because the primary products of hydrogenation of bituminous coal have a higher percentage of asphaltenes (material soluble in benzene but insoluble in *n*-hexane). The slower rate of destructive hydrogenation of asphaltenes is reflected in the much lower throughput of bituminous coal per unit volume of reactor.

The amounts of the products of the first stage of the Bergius-I.G. Farbenindustrie coal-hydrogenation process are shown in Table III. For bituminous coal, the total of carbon monoxide, carbon dioxide, and water produced is much smaller than for brown coal. The total of all of the entries in Table III, excluding the hydrogen consumed, is 107% for the brown coal and 104% for the bituminous. It should be above 100% by the amount of hydrogen that reacted with the coal. The 7% excess for brown coal agrees well with the 6.7% hydrogen consumed. The smaller excess of 4% for bituminous coal is due largely to the lower oxygen content of that coal. These excess figures are differences between relatively large numbers and probably contain an appreciable cumulative error.

Table III. Products of First Stage of Coal Hydrogenation

(In % of ash- and moisture-free coal)

	Brown Coal	Bituminous Coal
Gasoline plus middle oil	50	66
Hydrocarbon gas	15	29
$CO + CO_2$	11	
$H_2O + H_2S + NH_3$	21	
Unconverted coal	1.5	4
Oil lost in carbonization of centrifuge residue	8.5	5
H_2, consumed	6.7[a]	9.5[b]

[a] Not including H_2 dissolved in liquid products.
[b] Including H_2 dissolved in liquid products.

Some data on the chemical composition of gasoline and middle oil from the first stage of coal hydrogenation are available from a Bureau of Mines survey of the amenability to hydrogenation of a number of United States coals (*12*, *14–16*). Some of the data, shown in Table IV, indicate that the total oil yield is greatest for coals containing 82 to 84% carbon, and that coals of higher and of lower carbon content yield smaller amounts of oil. Gasoline content of the oil is in the range 20 to 30%. Aromaticity of the total neutral (after removal of tar acids and tar bases) oil increases with increasing carbon content of the coal. Additional data (not shown in Table IV) show that the gasoline (20° to 200° C., 68° to 392° F.) fractions contain 50 to 70% saturates, about half of which are paraffins and the other half naphthenes. The fraction of saturates in the remainder of the oil (>200° C.; 392° F.) decreases with increasing boiling point. Olefin and aromatic contents increase with increasing boiling point. Saturates and olefins in the oil boiling above 200° C. are largely cyclic.

Table IV shows that the total tar acid yield increases with decreasing carbon content of the coal. Of the total tar acids for all the coals of Table IV, except the Pittsburgh bed coal, about 50% distill below 235° C. (458° F.) at atmospheric pressure. About 70% of the total tar acids from Pittsburgh bed coal distill below 235° C. (458° F.). These lower boiling tar acids are chiefly phenol, cresols, and xylenols, and they are present in the proportion 1 to 4 to 5, respectively. This proportion does not vary much with the carbon content of the coal. Data (*36*) on the character of the tar acids boiling above 235° (458° F.) show that ethylphenols and indanols are present in amounts of the same order of magnitude as that of the phenol in the >235° C. (458° F.) fraction.

Concerning the tar bases, data are available (*19*) which show that the fraction of the total oil boiling below 250° C. (482° F.) at atmospheric pressure contains about 1% of pyridine bases and about 0.5% of each of aniline and the toluidines.

Recent experimental work in the Bureau of Mines (*27*) has indicated the following possible improvements in the first stage of coal hydrogenation:

It has been shown by operation in a continuously operating experimental plant that bituminous coal can be hydrogenated at relatively low pressures (about 1500 pounds per square inch) to produce a heavy fuel oil (*3, 10*). Although now not competitive with such fuel oil from petroleum, the process may be important in remote areas where coal but no petroleum is available.

A study of catalysts for the first stage of coal hydrogenation has disclosed conditions for efficient liquefaction using cheap and readily available catalysts (*27, 34*).

A feasible procedure for the recovery of oil from the residual solids in the first stage of coal hydrogenation consists in treating the heavy oil slurry from the hot catchpot with superheated steam (*25*). At short contact times of a spray of heavy oil slurry with superheated steam, a high recovery of oil, with little or no coking or secondary asphaltene production, was achieved.

The work of the Bureau of Mines Demonstration Plant Branch at Louisiana, Mo., has resulted in improvements in high pressure instrumentation, welded construction, and development of simplified pumps and compressors (*26–28*).

Hydrorefining Gas Oil from Coal Hydrogenation

The second stage of the coal hydrogenation process (*13*) is the hydrogenolysis of the gas oil (or middle oil) produced in the first stage. The products of this second or vapor-phase stage are chiefly gasoline and C_1 to C_4 hydrocarbons. The oil feed and hydrogen at 250 to 300 atmospheres are preheated to 400° C. (752° F.) and passed through a bed of catalyst granules, which are either tungsten disulfide or 25% tungsten disulfide plus 3% nickel sulfide on activated alumina. The hydrogen to oil ratio is high enough (usually about 2000 cubic meters per ton of oil) to ensure complete vaporization of the oil in the preheater. The reactants flow downward through the converters, which are of about the same dimensions as those in the first or liquid-phase stage of coal hydrogenation. The catalyst is disposed in four or five baskets with gas-mixing chambers between the baskets. Cold hydrogen is introduced into the mixing chambers to keep the reaction temperature in the range 400° to 410° C. (752° to 770° F.). The oil throughput varies from 0.6 to 1.5 ton per hour per cubic meter of catalyst, depending upon the chemical composition of the oil feed; a higher throughput is possible with more paraffinic oils. During this first (saturation) step of the vapor-phase hydrogenation, virtually all of the oxygen and nitrogen of the feed is eliminated as water and ammonia; relatively little reduction in molecular weight occurs.

In the second (splitting) step of the vapor-phase hydrogenation, the products of the saturation step are passed through a bed of catalyst granules which are usually 90% hydrofluoric acid–treated clay plus 10% hydrogenating component such as ferrous, tungsten, or molybdenum sulfide. The throughput in the splitting step is 0.8 to 1.0 ton per hour of oil per cubic meter of catalyst. Temperature is maintained in the range 425° to 450° C. (797° to 842° F.), and the total pressure is the same as in the saturation step. The liquid product, which contains 50 to 70% of gasoline, is fractionated, and the oil boiling above the end point of the gasoline fraction is recycled through the splitting catalyst. When the vapor-phase stage of coal hydrogenation is operated at 700 atmospheres, the saturation and splitting steps can be achieved in one reactor.

In the saturation step, 2 to 3% by weight of the feed is converted to C_1 to C_4 hydrocarbons. In the splitting step, 15 to 20% of the make-up feed appears as C_1 to C_4 hydrocarbons in the products. The motor gasoline yield is 92 to 95%, and the aviation gasoline yield is 80 to 83% by weight of the feed to the vapor-phase stage. Less of the butanes can be included in the aviation than in the motor gasoline. The hydrogen consumed varies greatly with the chemical composition of the oil feed. Highly paraffinic feed consumes as little as 3% of its weight of hydrogen, whereas a highly aromatic oil will require as much as 9% of its weight of hydrogen.

Liquid Fuels from Hydrogenation of Carbon Monoxide

In the Fischer-Tropsch process, as developed commercially by the Ruhrchemie A.G. in Germany (*30*) in 1935–40, synthesis gas containing 2 volumes of hydrogen per volume of carbon monoxide was compressed to about 7 atmospheres and passed through a granular

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bed of cobalt catalyst at 185° to 205° C. (365° to 401° F.). Major products of the synthesis were wax, oil, water, gaseous hydrocarbons, and a minor amount of carbon dioxide. The hydrocarbons were largely straight-chain paraffins. The olefin content varied with pressure contact time and temperature. Improved modifications of the Ruhrchemie process involved recycling of exit gases from the reactor, use of iron instead of cobalt catalysts, and more efficient and cheaper designs of heat-transfer surfaces in the reactors. These changes increased the olefin content of the product and the flexibility of the process, particularly in the control of the proportions of gasoline, Diesel oil, and alcohols.

Application of fluidized catalyst techniques to the Fischer-Tropsch synthesis (*30*) has yielded a process that produces chiefly (about 70%) motor gasoline, with minor amounts (about 30%) of fuel oil and oxygenated compounds. The fluidized iron catalyst process is outstanding because of its very high space-time yield and because it may be competitive with existing petroleum production and refining processes, if natural gas at 10 cents or less per 1000 cubic feet is available as the raw material for synthesis gas production.

In another recently developed process (*7*, *30*), a cooling oil is circulated through a bed of granular fron catalyst at a rate sufficient to expand the bed and keep the catalyst particles in a state of constant agitation. This process produces a somewhat lower proportion of motor gasoline and correspondingly larger proportions of Diesel oil, fuel oil, and wax than is produced by the fluidized catalyst process. Although the space-time yield of the oil circulation process is only about half of that of the fluidized process, much less methane and ethane are produced. When coal is used as raw material for synthesis gas production, a low $C_1 + C_2$ yield is essential because of the relatively high cost of the synthesis gas.

Important criteria for comparison of different processes for Fischer-Tropsch synthesis are: operability, yield of industrially valuable products per unit volume of synthesis gas, and yield per hour per unit volume of reactor. Operability is difficult to define and measure on a pilot plant scale. The basic requirement for satisfactory operability isthat a steady state be reached within a relatively short time after starting the plant or after introduction of fresh catalyst in an operating plant. This steady state should persist with little, if any, change in operating conditions and character of product for a long enough period to keep operating and maintenance costs sufficiently low to provide an economically feasible process. In much of the pilot plant work done in Germany (*30*) on the hot-gas recycle, the powdered catalyst–oil slurry, and the oil circula-

Table IV. Yield and Characterization of Oil from First Stage of Hydrogenation of Coals of Various Rank

Rank of Coal	Name of Coal Bed	Location of Coal Mine			Moisture, Weight % of Coal	Ash, Weight % of Coal	Carbon Content, Weight % of M.A.F.[a] Coal	Oil Yield, Weight % of M.A.F.[a] Coal	Boiling Range of Oil, ° C., Vol. %		
		State	County	Name of mine					20–200	200–330	Over 330
Bituminous high-volatile A	Mary Lee	Ala.	Jefferson	Sayreton	4.2	9.8	86.9	62	21	64	15
	Pittsburgh	Pa.	Allegheny	Bruceton[b]	1.6	6.3	84.2	72	25	63	12
Bituminous high-volatile B	Illinois No. 6	Ill.	Franklin	Orient No. 2	7.8	6.5	80.6	71	20	52	28
Bituminous high-volatile C	McKay	Wash.	King	Strain-Upper Diamond	9.6	3.7	78.6	70	23	69	8
Subbituminous B	Rosebud	Mont.	Rosebud	Colstrip	25.1	7.6	76.7	63	30	59	11
	...	Colo.	Weld	Puritan	24.1	4.1	76.6	63	24	69	7
	Monarch	Wyo.	Sheridan	Monarch No. 45	23.2	3.9	75.6	66	27	57	16
Lignite	Ft. Union	N. D.	Mercer	Beulah[b]	34.9	8.0	73.0	54	32	63.5	4.5
	Coteau	N. D.	Ward	Velva[b]	39.5	4.5	72.0	55	27	69	4

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Rank of Coal	Name of Coal Bed	Location of Coal Mine			Tar Acids		Tar Bases		Volume % of Neutral Oil		
		State	County	Name of mine	Vol. % of oil	Weight % of m.a.f.[a] coal	Vol. % of oil	Weight % of m.a.f.[a] coal	Olefins	Aromatics	Saturates
Bituminous high-volatile A	Mary Lee	Ala.	Jefferson	Sayreton	12.8	8	4.3	2.5	8.0	65	27
	Pittsburgh	Pa.	Allegheny	Bruceton[b]	17.5	11	3.5	2.8	8.2	67	24.8
Bituminous high-volatile B	Illinois No. 6	Ill.	Franklin	Orient No. 2	21.5	15	2.3	1.7	8.5	58.5	33
Bituminous high-volatile C	McKay	Wash.	King	Strain-Upper Diamond	20.5	15	5.5	3.7	12.5	48	39.5
Subbituminous B	Rosebud	Mont.	Rosebud	Colstrip	22	14	3.8	2.1	10.0	45.5	44.5
	. . .	Colo.	Weld	Puritan	20	13	4.0	2.8	11	56	33
	Monarch	Wyo.	Sheridan	Monarch No. 45	25	16	4.5	3.1	13	46	41
Lignite	Ft. Union	N. D.	Mercer	Beulah[b]	22.5	12	2.8	1.6	11.5	50.5	38
	Coteau	N. D.	Ward	Velva[b]	29	15	3.0	1.6	11	53	36

[a] Moisture- and ash-free.
[b] Name of town.

tion processes, a steady state was not reached, and operability of the processes was not demonstrated. In the United States, the fluidized iron catalyst and the oil-circulation processes only recently reached satisfactory levels of operability.

The durability of the steady state in the Ruhrchemie process (granular catalyst bed, externally cooled) was 150 to 200 days. In the fluidized iron process, it is about 20 days, and in the oil circulation process it is 100 to 200 days. The high space-time yield of the fluidized iron catalyst process compensates for the relatively short life of the steady state. Thus, the total weight of oil synthesized per pound of catalyst during the life of the steady state is approximately the same for the fluidized iron catalyst and the oil circulation processes.

Table V shows the salient features of several Fischer-Tropsch processes. Two of these—the powdered catalyst–oil slurry and the granular catalyst–hot gas recycle—have not been developed to a satisfactory level of operability. They are included to indicate the progress that has been made in process development. Such progress has been quite marked in increase of space-time yield (kilograms of C_3+ per cubic meter of reaction space per hour) and concomitant simplification of reactor design. The increase in specific yield (grams of C_3+ per cubic meter of inert-free synthesis gas) has been less striking, as only one operable process—the granular catalyst–internally cooled (by oil circulation) process—has exceeded the best specific yield of the Ruhrchemie cobalt catalyst, end-gas recycle process. The importance of a high specific yield when coal is used as raw material for synthesis-gas production is shown by the estimate that 60 to 70% of the total cost of the product is the cost of purified synthesis gas.

Foreseeable improvements that will increase operability and decrease operating costs of Fischer-Tropsch processes are: the development for the fluidized-iron process of a catalyst that will not accelerate the reaction $2CO = CO_2 + C$ and will not be appreciably oxidized during the steady-state life of the catalyst; and the development of a more active and mechanically stable catalyst for the oil-circulation process so as further to reduce $C_1 + C_2$ production. The hot-gas recycle process could be made operable by use of a catalyst that will be less active but more resistant to thermal shock which occurs during regeneration to remove carbon deposits, and during operation at lower end-gas recycle rates. The powdered catalyst–oil slurry process recently has been satisfactorily operated in a pilot plant by Kölbel and Ackerman (*21*). Although the space-time yield in this operation was low (10 to 20 kg. of C_3+ per cubic meter of slurry per hour), the $C_1 + C_2$ production was less than one third of that

Table V. Characteristics of Various Fischer-Tropsch Processes

Catalyst	Temp., ° C.	Pressure, Atm.	$C_1 + C_2$, G./Cu. M.	C_3+ G./Cu. M.	C_3+[a], Kg./Cu. M./Hr.	% by Weight of Total Oil + Oxygenated Compounds: Gasoline	Diesel	Heavy oil plus wax	Water-soluble chemicals	Steel[b], Ton/Bbl./Day	Motor Octane No.	Cetane No.
					Granular Catalyst, Externally Cooled, No Gas Recycle							
Co	175–200	1	20	140	8	56	33	11	[c]	2.7	50	100
Co	175–200	10	20	150	10	35	35	30	[c]	2.4	25	100
Fe	200–225	10	..	125	10	32	18	35	15	2.5	..	...
					Granular Catalyst, Externally Cooled, Gas Recycle							
Co	190–224	10	15	160	13	50	22	22	6	1.9	..	...
Fe	230	20	20	145	14	19	19	56	6	2.1	..	...
Fe	275	20	30	145	14	68	19	8	5	2.2	..	...
					Powdered Catalyst—Oil Slurry, Gas Recycle							
Fe	250–275	20	10	170	20	25	30	51	4	1.2	..	...
					Granular Catalyst, Internally Cooled (by Oil Circulation), Gas Recycle							
Fe	240–280	20	20	170	58	58	10	24	8	0.7	74[d]	78
					Granular Catalyst, Hot-Gas Recycle							
Fe	300–320	20	35	140	32	70	17	1	12	0.7	75[d]	50
					Fluidized Catalyst, Gas Recycle							
Fe	300–320	20	35	150	115	73	7	3	17	0.6	76[d]	...

[a] Kilogram of total product, excluding water, carbon dioxide, methane, ethane, and ethylene per volume of reactor per unit time. [b] In converter and its accessories only. [c] Very small, less than 1%. [d] Bauxite treated, but no tetraethyllead added.

of the fluidized-iron catalyst process, and the operation (90 to 95% conversion of carbon monoxide in one stage) was quite steady for 5 months. The data presented are incomplete, no description of catalyst preparation and pretreatment being included.

Use of Hydrocarbonization of Coal in Synthetic Liquid Fuel Processes

Recent laboratory-scale experiments (*5*, *6*) on the partial hydrogenation and carbonization of bituminous and lower-rank coal in a fluidized bed at hydrogen pressures of 1000 pounds per square inch or less have indicated that:

The products are 20 to 30% (of the dry coal) of an aromatic oil, about an equal amount of C_1 to C_4 hydrocarbon gas, and 40 to 60% of char.

The effective contact time at 550° to 600° C. (1023° to 1112° F.) is of the order of a few minutes.

When the powdered coal is mixed intimately with a catalyst such as 1% (of the dry coal) of ferrous sulfate or 0.2% of ammonium molybdate, the oil yield is increased, and its asphaltene content is reduced.

It is feasible to operate with coking coals when a relative high burden of char is maintained in the reaction zone.

The char contains no organic sulfur compounds, although some inorganic sulfur (probably FeS_2) is present.

About 50% of the oil product can be obtained as distillate at 200° C. (392° F.) and 2 mm. of mercury pressure.

The yield of gaseous hydrocarbons can be varied from 15 to 30% with only minor change in the amount and quality of the oil product.

A possible process for liquid fuel production based on the above indications would include the following steps:

Partial hydrogenation of the powdered coal in a fluidized bed at 500 to 1000 pounds per square inch pressure of hydrogen and 550° to 600° C. (1023° to 112° F.).

Distillation (topping) of the oil product and recycling the residual oil boiling above about 350° C. (662° F.) to the hydrocarbonization reactor. The oil boiling below 350° C. (662° F.) would be washed with aqueous alkali to remove tar acids and subsequently blended with the Diesel oil from the Fischer-Tropsch synthesis.

The char would be gasified under pressure with steam and oxygen, and the resulting gas after hydrogen sulfide removal would be used as raw material for the Fischer-Tropsch synthesis.

The production of gaseous hydrocarbons can be controlled so as to supply just enough raw material for hydrogen production by reforming under pressure with steam and oxygen. If, however, a market exists for high B.t.u. (1000 B.t.u. or higher per 1000 cubic feet) gas at about 60 cents per 1000 cubic feet, it probably would be profitable in areas relatively close to the Atlantic seaboard to produce an excess of gaseous hydrocarbons.

This speculative procedure has some very attractive advantages, such as: The total pressure is relatively low, the coal throughput per unit of reactor volume is high, no high pressure hydrorefining of oil is necessary, the yield of motor gasoline and Diesel oil is as high as in either the coal-hydrogenation or in a conventional Fischer-Tropsch process, and the cost of synthesis gas purification is greatly reduced by elimination of organic sulfur in the hydrocarbonization step.

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Cost Estimates for Synthetic Liquid Fuel Processes

Only the Bergius–I.G. Farbenindustrie coal-hydrogenation process and the Ruhrchemie Fischer-Tropsch process using cobalt catalyst have been operated on a commercial scale. Although accurate cost data are available (*13*) for these processes, such data are of no direct, immediate importance to the current situation on synthetic liquid fuels in the United States because of differences in cost of raw materials and in view of improvements and radically new process designs made in the past few years. No full scale plant data are available for accurate cost calculations of these new and improved processes. Approximate estimates have been published (*17*, *22*, *27*), and these indicate that synthetic motor gasoline from oil shale will be competitive with that from petroleum, whereas that from coal with no separation of chemicals such as phenols, benzene (from coal hydrogenation), or of alcohols and fatty acids (from hydrogenation of carbon monoxide) will cost several cents per gallon more than motor gasoline manufactured from petroleum. When chemicals are separated and credited and the gasoline is sold at current prices, the over-all operation would be profitable. Most of the published approximate estimates fail to take account of the sharp differences in the amounts of engineering and large pilot plant data upon which the different estimates are based. The current highly fluid state of development of coal gasification and of the Fischer-Tropsch processes is such that, although comparative cost estimates are of value for administrative purposes in research and development, they can be critically appraised only with adequate knowledge of the type and amount of data available for each process.

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Desulfurization and Sweetening

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The paper presents a general picture both on a geographical and on a product basis of the distribution of sulfur in petroleum. Early processes for desulfurization and sweetening are briefly reviewed and process developments are discussed on the basis of a simple division of petroleum products into gases, light distillates, and middle distillates and fuel oils. Future needs of the industry are discussed, and the ways in which research is likely to be applied.

Sulfur is present in one form or another in every crude oil which contributes significantly to total world production. A simple picture of its distribution on a geographical basis is given in Table I.

Distinction between so-called sulfurous and nonsulfurous crudes is indefinite, but if an arbitrary value of 1% by weight of sulfur content is selected the production figures shown in Table II are obtained.

Of the North American total, about 1,100,000 barrels per day came from Texas, 420,000 from California, 170,000 from Mexico, and the remainder largely from Arkansas, Mississippi, and New Mexico. The sulfurous Venezuelan crudes come from the Lake Maracaibo area and these, like the Mexican crudes, give relatively low yields of naphtha and middle distillates, thus differing from the Middle East crudes. Only small amounts of crude oil with sulfur contents greater than 1% by weight exist in U.S.S.R., Europe, and the Far East.

Although sulfur compounds in crude oil have always created problems for the refiner, the information available today is meager on the form in which the sulfur is actually present in crude oil. One reason is because refining treatments are generally a last step in a sequence of processing operations and because the sulfur contents of individual distillate fractions bear little relation to those of the crudes from which they are prepared. Tables III and IV illustrate this. They refer to products from conventional refinery distillation which neglect hydrogen sulfide liberated during distillation.

The problems created by sulfur have changed as the industry progressed; just over twenty-five years ago the main problems were to make straight-run gasoline and kerosene without offensive odor and of suitably low sulfur content. Since then the complexities

Table I. World Crude Oil Production—1949 *(14, 20)*

Area	Approximate Production, M Bbl./Day	Average Sulfur Content % Wt. *(4, 16, 19, 22, 28, 34, 35, 38, 39, 40)*
North America, including U. S., Mexico, and Canada	5270	1.0
South America including Trinidad	1570	1.8
Near and Middle East, including Persia, Saudi Arabia, Kuwait, Iraq, Bahrein, and Egypt	1430	1.6
U.S.S.R. and Eastern Europe	810	Less than 0.4
Far East, India, Pakistan, and Burma	200	Less than 0.2
Western Europe	30	Less than 1.0
Total	9310	

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Table II. Production of Crude Oils Containing More Than 1.0% by Weight of Sulfur

	M Bbl./Day	Range of Sulfur Content, Wt. %	% of Total Production in Area
North America	1800	1-5.5	34
South America	1100	1-2.5	70
Middle East	1400	1-2.6	98

have increased largely through the introduction of more complicated processes. The consumers of petroleum products have naturally exercised an influence toward the manufacture of sweet smelling and lower sulfur content products but developments have occurred largely through the desire of refiners for more efficient refining procedures for established finished products. In certain cases the refiner has been assisted by the fact that desulfurization leads to recovery of commercially valuable sulfur or sulfur compounds, but on the whole this has not been a driving force.

Processes and Products

In this part of the paper, development of processes is summarized on the following simple classification of products:

Gases
Light distillates
Middle distillates and fuel oils

Gases (*2*, *3*, *18*). The sulfur present in natural gas or in refinery cracked gases is predominantly hydrogen sulfide, though quantities of organic sulfur compounds may occur. The hydrogen sulfide content may range from virtually zero to about 15 volume % but the content of organic sulfur compounds is always small; thus, desulfurization of petroleum gases is largely a question of hydrogen sulfide removal.

For the principal use of natural gas as a domestic and industrial fuel, the total sulfur content is frequently regulated by law to a maximum of 15 grains per hundred cubic feet. Sometimes it is specified that the hydrogen sulfide content shall be substantially zero. Similar requirements with respect to total sulfur and hydrogen sulfide apply to liquefied petroleum gas. In other uses of natural gas—for example, carbon black manufacture—the limitations about sulfur content are less severe but a relatively low hydrogen sulfide content is preferred. Probably the most stringent requirement is in gas for conversion to synthesis gas; here hydrogen sulfide must be absent and the total sulfur content is limited to 2 p.p.m. with 0.2 p.p.m. preferred. In the polymerization of refinery cracked gases, it is rare that the allowable sulfur content—mainly hydrogen sulfide—is limited by the sulfur tolerance of the catalyst used; the desired quality of the finished polymer is more usually the controlling factor.

The early processes tended to be of a chemical nature and examples of these are the Seaboard (*21*) process using sodium carbonate solution as absorbent; the Thylox (*15*) process using sodium thioarsenate; and the early iron oxide process, which is still in common use for removal of traces of hydrogen sulfide. Although there have been improvements in processes of the above type, for example the recovery of hydrogen sulfide by the vacuum carbonate (*29*, *32*) process, the main trend in hydrogen sulfide removal has been toward the use of liquid absorbents which can be regenerated with recovery of hydrogen sulfide for sulfur or sulfuric acid manufacture. These processes can usually be applied equally to natural and refinery gases. In recent years the Girbotol (*10*) process has been widely used with an ethanolamine absorbent, usually monoethanolamine, but triethanolamine is used in particular cases. Another development is the glycol-amine (*12*) process which accomplishes dehydration of natural gas at the same time as desulfurization. Other hydrogen sulfide removing processes of this type are the phosphate (*27*) process employing tripotassium phosphate and the alkacid (*5*) process using the potassium or sodium salt of an amino acid.

In these developments an important feature has been the recovery of sulfur in one form or another for further use. Usually this recovery has been associated with the

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sweetening of gas for sale as fuel or refinery processing, but in some circumstances the recovery of sulfur has become an economic proposition even where the gases are flared. In such cases, a less complete removal of hydrogen sulfide can be tolerated.

Light Distillates (*6*). The main products in this category are gasolines and kerosenes. As far as sulfur is concerned in these products, in most countries there is now a fair agreement with regard to quality requirements. Both products are expected to have no objectionable smell, to pass a corrosion test, and to have sulfur content below 0.25% by weight.

Types of sulfur compounds fall into two main classes, the acidic compounds such as hydrogen sulfide and mercaptans, and the neutral compounds which include sulfides both alkyl and cyclic, thiophenes, and disulfides.

The acidic bodies are objectionable because of their smell and corrosive nature and are responsible for a crude oil or a distillate being given the term "sour." Their conversion by refining is normally termed sweetening. Refiners were chiefly concerned with sweetening, before many of the less desirable properties now known to characterize sulfurous distillates were appreciated.

Table III. Sulfur Contents of Products of Distillation

(% wt.)

T.B.P. Boiling Range, ° F.	Crude Oil	Gasoline and Naphtha Boiling below 300		Kerosene 300–450		Gas Oil 450–650		Residue Boiling above
Sulfur	Total	Mercaptan	Total	Mercaptan	Total	Mercaptan	Total	650°
Far East	0.15	<0.003	0.003	<0.003	0.01	<0.003	0.15	0.3
East Texas	0.36	<0.003	0.012	0.003	0.03	<0.003	0.28	0.78
East Venezuela	0.55	<0.003	0.011	<0.003	0.05	<0.003	0.35	1.2
Iranian	1.4	0.063	0.087	0.008	0.15	0.004	0.90	2.3
West Texas	2.0	0.14	0.17	0.09	0.62	0.05	1.6	3.2
West Venezuela	2.2	<0.003	0.023	<0.003	0.20	<0.003	1.0	2.7
Kuwait	2.45	0.010	0.015	0.004	0.16	0.003	1.30	3.8

Apart from liquid phase adsorption on a solid adsorbent such as bauxite, the early processes for sweetening and desulfurization were of a chemical nature. Some are in operation today in substantially their original forms, some have been greatly improved, and new processes performing similar functions have been developed. It is beyond the scope of this paper to cover them all, even in outline, therefore a comparative selection has been made to illustrate the advances achieved. The division, which is on a rather arbitrary basis, is given in Table V.

Table IV. Sulfur Distribution in Products of Distillation

Crude	Sulfur Content of Crude, % Wt.	Sulfur in Product, Lb./100 Lb. Sulfur in Crude: Gasoline and naphtha	Kerosene	Gas oil	Residue
Far East	0.15	0.3	3.6	38.6	57.5
East Texas	0.36	0.9	1.3	15.4	82.4
East Venezuela	0.55	0.5	1.7	15.5	82.3
Iranian	1.4	1.1	1.5	12.6	84.8
West Texas	2.0	1.8	4.2	14.8	79.2
West Venezuela	2.2	0.05	0.55	6.6	92.8
Kuwait	2.45	0.1	0.8	9.5	89.6

Plumbite, Hypochlorite, and Copper Chloride Processes. The plumbite (*7*) process used sodium plumbite and sulfur as the reagents and its initial advantages, which to some extent still hold today, were cheapness of reagent, simplicity of plant, and ease of operation. It depended on the conversion of lead mercaptides to the corresponding disulfides, the lead being converted to lead sulfide by the sulfur. A subsequent development was the partial replacement of reagent sulfur by air, used either internally or externally for the regeneration of lead sulfide. A major disadvantage of the process is the fact that the sweetened product generally has a higher sulfur content than the unrefined material. With the advent of tetraethyllead as a means of increasing octane number, this disadvantage became emphasized because polysulfides, which are frequently formed in the plumbite process, have a serious effect on lead response. It may also cause difficulty with kerosenes because the residual sulfur compounds are often present in a form which tends to increase char value.

Early attempts to use sodium hypochlorite (*8*) as a sweetening reagent were largely unsuccessful, owing to instability of the reagent and chlorination of the product, but this difficulty was overcome by maintaining a slight excess of free alkali. The hypochlorite process also accomplishes desulfurization to a certain extent because sulfides and disulfides are partially converted to sulfones and sulfonic acids which are appreciably soluble in the spent reagent. Traces of acid chlorides soluble in the hydrocarbon layer are also produced and they make necessary a further alkali wash. This disadvantage together with the cost of chlorine, has reacted against the hypochlorite process and today it finds only limited applications, such as sweetening natural gasoline and solvent naphthas and as a final treatment for the removal of traces of residual mercaptan in cracked gasolines.

Table V. Sweetening and Desulfurization Processes

Older Processes	Newer Processes
Plumbite and hypochlorite	Copper chloride
Caustic soda	Aqueous methanol and solutizer
Sulfuric acid	Hydrogen fluoride
Bauxite	High temperature catalytic desulfurization

In the past fifteen years the use of copper salts (*33*) as sweetening agents has become widely adopted. The reagent is used either in aqueous solution, or supported on a fixed bed of inert carrier, or as a slurry on inert carrier. But the same essential step in each variation of the process is the oxidation of mercaptans to disulfides by cupric salts which are reduced to cuprous salts. Regeneration of the reagent is brought about by oxidation, and here again there are a number of process variations such as use of oxygen or air, and internal or external regeneration. The advantages of the copper chloride processes are low chemical consumption, simplicity of operation, and most important of all, no loss in octane rating or lead response of finished gasolines. It is, however, not without disadvantages, as faults in operation may lead to development of color and loss of inhibitor response due to traces of residual copper. These either have to be removed or their effect nullified by the addition of copper "deactivators."

Caustic Soda and Aqueous Methanol Processes. Caustic soda has been used for the removal of acidic compounds, including mercaptans, since the petroleum industry started. The reaction between mercaptans and caustic soda is reversible and equilibrium is set up between mercaptan in the aqueous and hydrocarbon phases (*26*). The lower boiling mercaptans are fairly strongly acidic and consequently are removed largely by caustic soda solution. But, as the molecular weight increases, the acidity decreases and the solubility of mercaptan in the aqueous phase is considerably reduced. Thus, aqueous caustic soda solution is effective only with low boiling distillates and although with heavier naphthas and kerosenes it will still function as a partial desulfurization agent, it leaves behind higher boiling mercaptans.

Developments of the caustic soda process which now have wide application involve the use of methanolic alkali or the addition of solubilizers such as fatty acids, phenols, and naphthenic acids (*24*, *30*, *41*, *42*). These addition agents operate differently but they all have the same over-all effect of partitioning a substantially increased proportion of the mercaptan into the aqueous phase. This results in an increased degree of sweetening and desulfurization. The products, however, are seldom doctor-negative. The spent reagent can usually be regenerated either by steam stripping or by external oxidation, sometimes in the presence of a catalyst such as tannic acid, or by electrolytic means.

Sulfuric Acid and Hydrogen Fluoride Processes. Although sulfuric acid (*9*) has also been used as a sweetening and desulfurizing reagent since the early days of the industry, it is not generally appreciated that its desulfurizing action is largely due to preferential solvent action on the alkyl sulfides and disulfides. Mercaptans are oxidized to disulfides by acid of the concentration normally used in the treatments of gasolines and kerosenes, so that the acid can behave both as a sweetening and desulfurization reagent. Where redistillation of the acid treated product is carried out, a further degree of desulfurization is achieved because the higher boiling disulfides remain in the distillation residue.

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The disadvantages of sulfuric acid are: its cost, its tendency to cause high processing losses, and the necessity for redistillation in many cases.

The temperature of treatment with sulfuric acid has an important effect on the quality and yield of the product. By the use of low temperature and proper conditions of contact, it is possible to cut down the polymerizing effect of acid on olefins, thus reducing losses without impairing its solvent power for sulfur compounds.

Recently it has been shown that anhydrous hydrogen fluoride exerts a selective solvent action on sulfur compounds and can be used satisfactorily for the desulfurization of kerosenes. In some respects it behaves similarly to sulfuric acid. Points of difference, however, are that it does not oxidize mercaptans to disulfides and that it can be used over a wide temperature range, 30° to 150° F., without affecting results. Hydrogen fluoride does not yet seem to have been used in full scale commercial units.

Bauxite and High Temperature Catalytic Processes. During the past ten years there has been an intensified full scale application of high temperature desulfurization processes over catalysts such as bauxite and clay (*31*). They provide an alternative method for the production of low sulfur content gasolines and kerosenes. They are most effective with straight-run materials boiling up to 300° to 400° F. In many cases they are installed not because desulfurization is essential, but because the saving in tetraethyllead required to reach a given octane number offsets the processing cost.

Middle Distillates and Fuel Oils

The sulfur compounds in Diesel oils, heater oils, etc., frequently make some form of refining treatment necessary. While many straight-run products are of adequate quality without treatment, some of high mercaptan content require sweetening. Cracked materials may contain sulfur compounds in a form which makes treatments necessary for mercaptan removal, stability improvement, or reduction of deposit formation in engines and equipment. Comparatively little has yet been done in the full scale application of processes specific for reducing sulfur content, because there has been no general need and necessary demands have been met by supplies from low sulfur crudes. A further reason is that processes applied solely for desulfurizing feed stocks in this boiling range are relatively costly. This would make it difficult to compete with natural low sulfur products, especially as the refiner does not make a simultaneous economy as in the case of gasoline when tetraethyllead response is improved.

When sweetening is applied to this class of products conventional processes (including sulfuric acid, plumbite, copper chloride, methanolic caustic, and solutizer) may be used, but they give greater trouble than when applied to light distillates. With sulfuric acid, disadvantages are: loss of yield, difficult neutralization of separated hydrocarbon layer, and sludge disposal. With plumbite, deleterious high boiling polysulfides are formed and sweetening may not be complete. With copper chloride, the general presence of nitrogen bases is harmful, color stability is difficult to achieve, and loss of copper may be high.

There has been no general adoption of desulfurization, but several established processes

Table VI. Desulfurization of Gas Oil

Method of Treatment	Oleum	Sulfur Dioxide[a] Extraction	Furfural Extraction	HF[b] Extraction	Catalytic	Hydrocatalytic
Product of 0.5% sulfur content						
Yield, vol. %	97	88	82	91	Not possible	100
Pour point, ° F.	15	20	20	20		15
Diesel index	58	68	66	64		58
Treatment, vol. %	1.8	60	70	8		Above 20 v./v./hr.
Product of 0.2% sulfur content						
Yield, vol. %	Not possible	80	Not possible	Not possible	Not possible	100
Pour point, ° F		20				15
Diesel index		75				58
Treatment, vol. %		125				About 20 v./v./hr.

[a] 4-stage countercurrent extraction at 30° F.
[b] Single-stage batch extraction.

are available including sulfuric acid, solvent extraction, and high temperature catalytic treatment. Sulfur dioxide (*17*, *36*) and furfural (*27*, *39*) are solvents in present use while hydrogen fluoride (*1*, *11*, *23*) has passed the pilot plant stage. High temperature catalytic desulfurization employs either clay or bauxite as catalyst and sulfur reduction is achieved mainly by removal of mercaptan sulfur, the other sulfur compounds being less affected. Comparisons of these desulfurization processes are shown in Table VI for a Middle East straight-run Diesel oil of approximately 1% by weight of sulfur content, 15° F. pour point, and 54 Diesel index. Table VI also includes hydrocatalytic desulfurization which has been available for many years as a technical process using a variety of catalysts but which is not widely applied.

The general advantage of the solvent extraction process is that, where desirable, a simultaneous increase in Diesel index may be achieved. Yields are moderate but the highly sulfurous extract may present a disposal problem because heavy fuel oils from crudes, for which middle distillate fractions have to be treated for sulfur reduction, are already of high sulfur content. Furfural requires special mention because of its successful application to cracked feed stocks. The advantages of the hydrocatalytic process are the high yield and elimination of sulfur as hydrogen sulfide but full scale application is retarded by the high cost of hydrogen.

The sweetening or desulfurization of residual fuel oils is not being practiced commercially to any significant extent.

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Discussion

Although there is a range of processes in operation for the removal of hydrogen sulfide from petroleum products, it is likely that research will be carried out for improvements. These may include new absorbents to give more effective extraction or to reduce corrosion difficulties which now involve special materials of construction or cause high maintenance charges. It is also likely that new processes will be sought for recovery of sulfur. The existing way of doing this generally consists of absorption of hydrogen sulfide followed by separate oxidation of the regenerated hydrogen sulfide stream, but there is no theoretical reason why it should not be accomplished in a single step with elimination of the absorption process. A development on these or other lines leading to reduction in the cost of sulfur recovery would probably be adopted widely.

The review of processes and developments in connection with liquid products brings out the point that it is the products of lowest sulfur content—i.e., gasolines and kerosenes —that have had the most work done on them. Reasons for this include:

In bulk they represent a high proportion of total products.

As their conditions of use demand freedom from odor it has been imperative to install processes for handling the relatively high mercaptan contents.

They are high priced products relatively able to carry the cost of refining treatments.

In the case of gasoline the cost of sulfur removal has been partially offset by economy in tetraethyllead.

The chemistry of their treatment is reasonably well understood.

Specification clauses demanding freedom from offensive odor cannot reasonably be made more rigorous (although certain countries demand doctor-negative products) and there is no evidence to show that existing limits for total sulfur in aviation and motor gasolines, kerosenes and aviation gas turbine fuels should be reduced, although most refiners already work well within them. Quality requirements of these products will not act as a spur for research for process improvements, but it is likely that most refiners will continue with research either to reduce costs or to eliminate the disadvantages of existing processes. It seems probable that advances are more likely to be made with sweetening or mercaptan removal than with general desulfurization.

It is in the field of middle distillates and fuel oils that sulfur may confront some refiners with major problems that will grow as the production of higher sulfur crudes increases. It may be worth while to consider in some detail the case of high speed Diesel oil, for which discussion about sulfur content is controversial. Curiously enough it is in the United States, where low-sulfur material has been in relatively plentiful supply, that

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the scare seems greatest and where most laboratory data have been published to focus attention on the effect of sulfur on wear and deposits.

It is well known that if engines are run with water jackets at unnecessarily low temperatures there will be corrosive wear, but this can be minimized by good design coupled with jacket temperature control. It is also known that unduly high piston temperatures can lead to excessive deposit formation, to which sulfur compounds may contribute. But here again good design ensuring adequate and even piston cooling, with due attention to the conditions under which the engine will operate, can do much to lessen the trouble. A valuable paper, read by Dicksee (*13*) before the Society of Automotive Engineers in January 1951, pointed out that in prewar years high speed Diesel oils in the United Kingdom had an average sulfur content of just over 0.6% by weight and that, although it is now above 0.8% by weight, operators have not observed any increase in wear, lacquering, or ring sticking. These statements are most important as they represent the unbiased judgment of a considerable section of commercial Diesel engine operators. They assist the refiner of high sulfur crudes in forming an appraisal of the real need for installing desulfurization processes which, in their present state of development, are costly. It may be that certain engines designed for arduous duties over a wide range of operating conditions demand a high additive content lubricant to combat difficulties to which sulfur compounds contribute. If so, these needs should be met. But care should be taken to ensure that false prominence is not given to an aspect of fuel quality which need not give rise to general difficulties.

Time will show if there is need for desulfurization of high speed Diesel fuels. There is no doubt that many companies are actively studying desulfurization processes so as to be in a position to make the best choice. Of those for which published information is available for full scale operation, the most attractive seemed to be sulfur dioxide and furfural extraction, the latter having merit because it has successfully handled high sulfur catalytically cracked recycle stocks. The previously mentioned extraction process using anhydrous hydrogen fluoride also seems attractive because of the low treatment and high yield of refined product, but, until the results of commercial operation are fully known its merits cannot be established.

Research is likely to continue with a view to improving methods of sweetening and removing mercaptans from all middle distillates including heater oil. It is doubtful, however, that much effort will be applied specifically toward desulfurization of heater oils except in cases where fuel instability and poor performance of equipment are due to sulfur compounds or where the treatment for stability improvement simultaneously lowers sulfur content.

It is also doubtful that the industry will be in a position for many years to come to undertake sulfur removal from residual fuels solely to improve product quality. A number of consumer industries demand low sulfur fuel oils, but these special requirements can at present be met more appropriately by selection of crude rather than by adoption of desulfurization processes. In general industrial use, it is corrosion and atmospheric pollution that are the main disadvantages of high sulfur content. But there is no sign yet of the development of a cheap desulfurization process, the cost of which can be substantially offset by the gain in efficiency resulting from permissible lower stack temperatures or by the elimination of flue gas scrubbing equipment previously necessary for reduction of sulfur dioxide content.

In all products the presence of sulfur is undesirable and in some degree harmful.

Table VII. Tonnage of Sulfur in Crude Petroleum

Area	Millions of Long Tons per Year
North America, including U. S., Mexico, and Canada	2.6
South America, including Trinidad	1.4
Near and Middle East, including Persia, Saudi Arabia, Kuwait, Iraq, Bahrein, Egypt	1.1
U.S.S.R. and Eastern Europe	0.2
Far East, India, Pakistan, Burma	<0.1
Western Europe	<0.1
Approx.	5.3

It is therefore certain that research to find improved methods of sulfur removal will continue, with emphasis being given to those products for which consumer interests are most pressing. Recent evidence of diminution of sulfur supplies in the United States, as well as the desire of other countries to minimize purchase of dollar sulfur, may add impetus to the search for new methods of sulfur removal and recovery. The tonnages of sulfur in present production of crude petroleum, excluding natural gas, are given in Table VII. It shows that the potential availability is very high.

Of existing methods, some form of hydrocatalytic process effects the greatest degree of desulfurization and achieves most sulfur recovery. Such processes will probably be examined in great detail with the hope that the more favorable product distributions resulting from hydrogenation will at least partially offset the high hydrogen cost. There will probably also be an increase in the work being done to find the form in which sulfur is present in crude oils and at the same time the bacteriological work of Zobell will continue to be of great interest because it can conceivably produce startling developments.

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Dewaxing and Deasphalting

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Waxes of both crystalline and microcrystalline types occurring naturally in lubricating oil fractions derived from crude petroleum are undesirable components of the finished oils. Refiners of petroleum have devoted considerable effort, money, and time to the development of methods for the economical removal of these waxes from petroleum fractions. Advances during the past 25 years have resulted in the extensive use of solvents for dewaxing. The major present-day problems confronting the refiner and the trends in research designed to solve these problems are stated briefly. The asphaltic materials—resins and asphaltenes—contained in petroleum, because of their instability and excessive carbon-forming tendency, are undesirable components of finished lubricating oils. The problem of obtaining the ultimate separation between the valuable oil fractions and the asphaltic materials has confronted the refiner since the beginning of petroleum processing. Prior to 1925, the principal methods employed for this purpose were distillation, chemical treatment, and adsorption. Because these methods were deficient in many respects, improved methods were sought. With the introduction of high vacuum distillation and the selective precipitation of the asphaltic materials with propane, increased recovery of the valuable high viscosity oil fractions has been realized. These processes are the principal ones in commercial use today for deasphalting of petroleum.

Petroleum crude oils, which are divided for the purposes of conventional classification into three main types—asphalt (or naphthenic)-base, paraffin-base, and mixed-base—contain varying amounts of hydrocarbons which readily solidify and are identified as wax. The asphalt-base crudes may contain only a trace of wax, while the wax content of the paraffin-base crudes and the mixed-base crudes may be as high as 15% or higher (*73*). Crude oils with a wax content as high as 35% are known.

Dewaxing

The wax content of crude petroleum in itself is of no immediate concern to the refiner, although it may be a major problem to the producer because of "waxing up" of well casing and sucker rods. It may cause difficulty in transportation of the raw crude oil, and wax settling out in tanks may also become troublesome. The refiner, however, is concerned with wax occurring in the oils to be processed and in the finished oils. The major portion of waxes present in crude petroleum boil in the same range as the lubricating oils produced from the crude oil, so that the wax and oil cannot be separated by distillation. Waxes are therefore present in the distilled unrefined lubricating oils as well as in the residue remaining from the distillation of the crude oil. The waxes generally crystallize from the oil at ordinary temperatures or below and thus rob the oils of their fluidity, preventing their free circulation in service at normal or lower than normal operating temperatures. This is especially true of the fractions from paraffin and mixed-base crudes. In fractions derived from asphalt-base crudes, however, the wax content is often so small that its presence has no effect on the fluidity of the oil even at reduced temperatures, although it may result in an undesirable wax cloud formation.

Because the paraffin and mixed-base crudes yield lubricating oil fractions of high quality, means had to be devised in the early days of the petroleum industry to separate the wax from the oil. The removal of wax from petroleum fractions is one of the most important phases in the production of lubricating oils and fuel oils of low pour point, and has received the attention of many investigators.

Methods for Separation of Wax from Oil

In all the methods commercially practiced to date for removal of wax from petroleum fractions, other than by destructive cracking, crystallization by cooling has been involved. The earliest of such methods of dewaxing petroleum oils was an act of nature. Crude oil chilled in tanks through the winter months with subsequent crystallization of wax, which settled to the bottom of the tank. An upper layer of relatively wax-free oil could then be decanted or withdrawn. As a further development of this method, topped crude or residuum was diluted with a low boiling naphtha and chilled by natural or artificial means or by a combination of both; the wax material settled (*6*). After almost 100 years of petroleum refining, a few refiners still practice this method of "cold settling." The method is time-consuming and intermittent in operation, requires extensive tankage, and is inefficient with respect to obtaining high yields of dewaxed oil. Furthermore, the degree to which the pour point of the oil can be reduced is limited by the available temperature to which the oil can be chilled and by other factors influencing settling of the wax.

Cold Pressing and Centrifuge Methods

When topped crude—i.e., crude oil from which the gasoline, kerosene, and light gas oil fractions have been removed—was subjected to further distillation, it was found that the wax present in the lower boiling point fractions was highly crystalline; the crystals would not settle and therefore the wax could not be removed by the cold settling method. Consequently, a different method had to be found for removing wax from these lubricating oil fractions. By a long-known method of the shale oil industry the paraffin was crystallized and then separated from the liquid oil by pressing it in filter bags or filtering through cloth under pressure. This method was adopted by the petroleum refining industry to remove paraffin wax from the so-called "paraffin distillate" which contained filterable, large wax crystals. Later, the pressing operation was improved by adopting filter presses of the plate-and-frame type, similar to those used in the shale oil industry (*69*). This method is conventionally called "cold pressing."

In early practice the paraffin distillate generally was prepared under distilling conditions that permitted mild cracking (*63*), which was believed to be required in order to produce a fraction with good pressing or filtering qualities. Following the introduction of efficient fractionation equipment, it was realized that cracking was not necessary. The primary requisite is good fractionation with elimination of entrainment of oil of high viscosity and residual-type materials which affect crystal growth adversely.

For successful pressing, the paraffin distillate must be of sufficiently low viscosity, normally 70 to 100 S.S.U. at 100° F. (*27*), and the wax present must be of the large crystal type and of such a nature that when the distillate is chilled to about 0° F., a fairly well-defined, sufficiently rigid crystal is formed to permit filtration under pressure. The filter normally employed for this operation is of the plate-and-frame type (*28*). In some cases, wax may be removed from paraffin distillates of somewhat higher viscosity, in the range of 100 to 200 S.S.U. at 100° F., by diluting the distillate to lower the viscosity with a petroleum naphtha prior to chilling and then crystallizing the wax (*45*).

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The waxes present in the oils boiling at a higher temperature than the paraffin distillate do not crystallize in a form which permits cold pressing, even though naphtha dilution is used. Therefore only the lubricating oils of lower viscosity could be removed from the topped crude and dewaxed by the cold pressing method. The balance of the lubricating oil had to be left in the undistilled portion of the crude or long residue and this residue subjected to dewaxing by the cold settling method, by diluting it with a petroleum naphtha, chilling relatively slowly, and allowing the wax to settle.

As these two methods for dewaxing petroleum oils became more widely used, many improvements were made. Instead of chilling in tanks or vessels operated batchwise, continuous methods of chilling were developed. Instead of the cold settling type of operation, centrifuges were employed (*42*) to increase the effect of gravity manifold, improve the degree of separation between oil and wax, and convert the process to a continuous rather than a batch method. These improvements did not, however, overcome the major disadvantages of these two methods of dewaxing. It was still necessary to prepare carefully selected fractions from the crude oil in order to separate the waxes from each fraction by one of the two dewaxing procedures. Dewaxing temperatures far below the desired pour point of the dewaxed oil were used and considerable oil in the wax concentrates was lost.

Furthermore, with the wide variation in the crystalline nature of the waxes present in the long residuum, impractical settling rates frequently existed in the cold settling operation, and sometimes the wax could not be discharged from the centrifuge bowl. These difficulties may be ascribed to crystallization of the wax in a wide range of crystal sizes and the presence of materials influencing the crystal nature of the wax in the long residuum.

The removal of a portion of the residue as an intermediate or "slop cut" distillate prior to dewaxing resulted in a marked improvement in the cold settling and centrifuge operations. This practice was followed for many years, but with the demand for greater quantities of distillate lubricating oils, the refiner was faced with the problem of dewaxing the intermediate or slop fractions boiling between the paraffin distillate and the residue in order to meet his lubricating oil requirements. Because the waxes present in the intermediate fraction crystallized in very small crystals, which did not have sufficient rigidity to allow filter pressing or sufficient density to cause them to settle or permit removal by centrifuging, it was impractical to dewax these fractions by existing conventional methods. These valuable lubricating oil fractions, therefore, had to be burned as fuel or used as charge stocks to cracking units.

This was the status of dewaxing 25 years ago. About this time, there developed a sharp increase in the demand for motor oils of lower average viscosity and the refiner was called upon to produce large quantities of distillate lubricating oils from the crude. To accomplish this, crude stilling was increased to obtain added quantities of the paraffin distillate which could be dewaxed by the existing cold pressing method. Because the supply of high viscosity lubricating oil was also increased by processing larger quantities of crude, there soon was an oversupply of heavy grades of motor oil. Lubricating oil refiners, in order more nearly to balance the production of oils of low and high viscosity, needed a dewaxing method that would remove wax from the entire range of wax-bearing oils.

Filter-Aid Dewaxing Process

The problem received concentrated attention. One method (*87*) introduced used naphtha as a diluent, with an inert material, such as diatomaceous earth, to build up the wax crystal structure artificially, so that relatively good filtration rates were obtained and a wash could be applied to the wax cake on the filter to displace the retained oil. This method was identified as the Weir process or filter-aid dewaxing process and was placed in commercial operation about 1928 (*30*). It was the first commercial process capable of successfully dewaxing the intermediate distillates, as well as paraffin distillates of lowest viscosity and residual stocks of highest viscosity.

In operation of the filter-aid dewaxing process, the waxy stock is diluted with naphtha, the mixture is chilled to the dewaxing temperature, and cooled filter aid, wet with naphtha, is added.

The chilled oil-naphtha solution containing crystallized wax and the filter aid is then filtered by means of a continuous vacuum filter or an intermittent pressure leaf filter. Increased dewaxed oil yields are realized by applying a cold naphtha displacement wash to the wax cake on the filter. The pour point of the dewaxed oil is usually 25° to 35° F. higher than the filtering temperature.

The naphtha is recovered from the dewaxed oil solution in conventional distillation equipment. The wax cake containing the filter aid is discharged from the dewaxing filter into a heated vessel, where the wax is taken into solution and the inert filter aid settles to the bottom in the form of a concentrated slurry. The aid separated from the wax solution is slurried with kerosene and this slurry is filtered on a continuous filter at a temperature sufficiently high to flash off water adsorbed on the aid. The dried and recovered aid on the filter is subjected to a chilled naphtha wash to displace the kerosene and cool the aid, which is then recycled to the chilled oil-naphtha mixture. Recovery of the aid in this manner permits its re-use indefinitely.

The advent of this process removed the limitation of dewaxing only paraffin distillates of low viscosity and undistilled residua, as it was capable of separating the waxes irrespective of crystal size and type from the lowest to the highest viscosity oil. However, the costs of operation were high because of the expense of handling and recovering the filter aid. The process was not widely adopted by the petroleum industry and was soon supplanted by one of the modern dewaxing processes, employing special solvents which were being developed about the same time.

The use of the filter-aid dewaxing process was limited to three commercial installations.

Use of Solvents in Dewaxing

The possibility of using special organic solvents other than petroleum naphtha in dewaxing apparently was considered prior to 1925, as a number of investigators reported the solubility of petroleum wax in solvents readily available in the laboratory—for example, chloroform and benzene (*83*) and amyl acetate and alcohol (*1*). A number of solvents and solvent combinations were proposed for dewaxing operations—for example, aliphatic esters (*49*), benzene plus halogenated hydrocarbons (*80*), and sulfur dioxide plus aromatics (*25*). The solvents investigated were for the most part not readily available and the use of special solvents for large scale dewaxing therefore was delayed. However, about 1925 a number of organic solvents became available in increasing commercial quantities and efforts were renewed in the development of a process employing special solvents for dewaxing. The investigations led to the proposal of a very large variety of organic solvents, a number of which have been discussed adequately in the literature (*44*).

The first commercial installation employing special organic solvents in dewaxing was made by the Indian Refining Co. in 1927 (*32*). The process as originally used employed a mixture of acetone and benzene as the special solvents, based on the inventions of F. X. Govers. The process as further developed employs a mixture of methyl ethyl ketone and aromatic solvents such as benzene and toluene. It is known as the solvent dewaxing process.

As a result of this successful demonstration, numerous other solvents were tried by a large number of investigators in an attempt to find the ideal solvent (*67*) which possessed good solubility characteristics—i.e., substantially complete solvent action on the wax-bearing oil at approximately 100° F., and at a temperature of about 0° F. complete solvent action on the normally liquid components present in the waxy oil, but substantially no solvent power for the wax precipitated at this temperature. Besides having desirable solubility, the solvent must be available, be of low cost, and have a boiling point that permits ready recovery from the oil and wax by distillation. It must also be chemically stable, noncorrosive to ordinary materials for plant construction, and not highly toxic. Because the last traces of solvent are most easily removed from the components of the charge stock by steaming, the solvent must be unaffected by and easily separated from water (*79*). The latent heat of vaporization and specific heat of the solvent should be of such magnitudes as to avoid excessive refrigeration and heat loads. Many of the solvents

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investigated do not meet these requirements in a number of respects and consequently have not been accepted in commercial operation.

A number of solvents such as propane, trichloroethylene, and methyl *n*-propyl ketone, although not fully meeting requirements, come sufficiently close to make their use attractive. Acetone, methyl ethyl ketone, sulfur dioxide, and ethylene dichloride, although they have a low solubility for wax, do not possess an adequate solubility for oil at the dewaxing temperature. However, by blending such solvents with a solvent for oil—for example, aromatic solvents—complete miscibility with the oil can be obtained at low temperatures (*36*). Whereas the oil solvents may have some solubility for wax, the solvent mixture may be adjusted to obtain a balanced mixture approaching the characteristics of an ideal dewaxing solvent and be capable of producing a dewaxed oil of a pour point very close to the dewaxing temperature.

In commercial operation, the physical characteristics of the wax crystallized on chilling permit easy removal by filtration in the case of some solvents. With other solvents, the wax mass may best be removed by centrifuging.

The ease with which wax may be removed from oil-solvent mixtures depends to a large extent upon its crystal structure. The waxes present in the lower viscosity distillates tend to crystallize from oil-solvent solutions in very large crystals, while those in the higher viscosity distillates and residua form relatively small crystals. The size of crystal depends not only upon the nature of the oil fractions (*34*) but also upon the viscosity of the solution from which it crystallizes (*41*), and the manner in which the chilling is conducted. The character of the fraction may be controlled to some extent during the distillation process, and the viscosity of the medium from which the wax crystallizes may be regulated by addition of the solvent. Thus, the size of the crystal may be regulated to permit efficient separation of the wax from the oil-solvent solution.

The structure of the wax crystal may also be controlled to some extent by the addition of substances to the oil, either before dilution with solvent or before the oil-solvent mixture is cooled. A number of materials, including aluminum stearate (*9*), colloidal substances of the type of bitumen (*52*), and highly polymerized or condensed high molecular weight paraffins (*10*), have been proposed as wax crystal regulators. Obviously the use of such materials will be an added expense (and will require equipment for their application). Unless a major improvement is realized, their use is not warranted; however, in some cases, regulation of the crystal may be required and the use of wax crystal regulators may be justified.

Instead of filtration or centrifuging as a means of separating the crystallized wax from oil, an electrical precipitation method has been proposed, similar to that employed in desalting of crude or removal of entrained solids from gases.

The wax-bearing stock is diluted with propane, naphtha, or other solvents and the mixture is chilled to crystallize the wax. This mixture is then introduced into a cooled vessel containing, for example, a rotating cathode and a stationary anode. An electrical charge is impressed upon the solid wax particles by the action of a high potential current and these particles are collected on the rotary oppositely charged electrode. The wax deposited on the electrode may then be washed with cold solvent to remove adhering and occluded oil, and the wax removed.

The separation of the wax from petroleum oils by this method is substantially independent of the physical condition of the wax, so long as it is in the solid form. Thus, control of the size and form of the crystal is not required to obtain high rates of separation of the wax from the oil solution. A series of patents (*46*) has been issued, but there is no record that the process has been applied on a commercial scale.

As a result of the search for solvents and the investigation of methods for their application in dewaxing, five commercial processes came into being. These are discussed below, in the order of the number of commercial installations made.

Solvent Dewaxing Process

This process is sometimes referred to as the acetone-benzene (A-B) process or MEK (methyl ethyl ketone) process.

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Basically, the process employs a selective solvent or mixture of solvents which have adequate oil solubility to permit operation at reduced temperatures without the separation of a second liquid or oil phase and in which the wax solubility is so low that the resulting dewaxed oil pour point is substantially the same as or within a few degrees of the dewaxing temperature. Generally, the solvent employed is a mixture of an aromatic solvent to obtain the required oil solubility and a polar solvent—for example, a ketone—to produce highly crystalline, easily filterable wax.

The solvent employed in the first commercial installation, of the Indian Refining Co., was a mixture of acetone and benzene (90% grade). In the subsequent development of the process by The Texas Co., a large number of solvents were found to be satisfactory. At present, the process normally employs a mixture of methyl ethyl ketone and industrial grade benzene, which have been found to be admirably suitable and provide a relatively low cost solvent. Toluene is substituted for all or part of the benzene when low chilling temperatures are required to obtain oils of very low pour point, as benzene may crystallize out from the mixture at these lower temperatures.

The process is capable of dewaxing any type of wax-bearing oil from the lowest viscosity distillate to the highest viscosity residual stocks, regardless of the wax content or type of wax present. The oil may be unrefined or refined to any degree prior to dewaxing. No conditioning agent need be added to obtain good results.

The outstanding characteristics of the process are its simplicity of operation, great flexibility, and ability to produce high yields of dewaxed oils with pour points equal to or within a few degrees of the dewaxing temperature. No special equipment, special alloys, high pressures, or excessively low operating temperatures are required.

In commercial operation (*31*, *60*), the waxy stock oil is mixed with the solvent and charged to conventional double-pipe, scraped-surface exchangers and chillers. Approximately two thirds of the chilling of the charge mix is obtained by exchange with dewaxed oil solution and the remaining one third by use of indirect refrigeration with ammonia or any other refrigerant in the outer pipes of the chillers. The chilled mix is discharged from the chillers into a filter-feed tank from which it flows by gravity to totally enclosed continuous, drum-type vacuum filters for separation of the wax from the oil-solvent solution. Vacuum is applied to a filtrate-receiving system by means of an ordinary vacuum pump, and the oil solution is pumped from the filtrate receivers to the solvent recovery equipment where the solvent is distilled from the oil by either direct or indirect heat. Steam is used to remove the last traces of solvent in stripping equipment.

The wax cake is washed continuously and automatically on the filter with cold solvent to displace any retained oil solution. By control of the conditions of solvent composition, dilution, and the manner in which the cake is deposited on the filter, the displacement wash becomes very effective in producing wax of very low oil content.

The wax cake containing some solvent is discharged from the filter and pumped through exchange and heating equipment to a wax-mix surge tank held at a temperature of about 130° F. Water inadvertently entering the system freezes into ice particles during the chilling process and is separated with the wax on the filter. Under the conditions of temperature maintained in the wax-mix surge tank, the water separates from the wax mix. This water contains a small percentage of ketone which is removed by distillation in a fractionation tower; solvent-free water is discharged from the system at the bottom of this tower. The solution of wax and solvent is pumped directly from the storage vessel to solvent-evaporating and stripping systems where the last trace of solvent is removed.

This process is the most widely used dewaxing process in the petroleum industry today. Sixty-one units have been installed throughout the world.

Propane Dewaxing Process

Liquid propane is employed as the solvent in this process. The use of a petroleum fraction as a solvent for dewaxing is desirable from the standpoint of the availability and cost of solvent, and the higher boiling hydrocarbon fraction has been employed many years for dewaxing of residual stocks.

The results of work (*74*, *86*) showed that the solubility of wax increases as the molecular weight of the hydrocarbon solvent decreases. This fact no doubt excluded from consideration for some time the use of the liquefied normally gaseous hydrocarbons as solvents for dewaxing. However, because these low molecular weight fractions offered an advantage over naphtha with respect to viscosity at low temperatures, their use appeared attractive. Investigations revealed that the solubility of wax was lower in the normally gaseous petroleum hydrocarbons than would be predicted on the basis of the available data for pentane and hydrocarbons of higher molecular weight. The solubility of wax is lowest in liquid propane (*3*). It also was demonstrated in these investigations that direct evaporative cooling could be employed to crystallize the wax in a form which permitted ready separation from the oil-solvent mixture by filtration. The applicability of this method of dewaxing was confirmed and the process carried to full scale plant operation about 1932 by the Standard Oil Co. (Indiana) at Wood River, Ill. The Standard Oil Co. (New Jersey), Union Oil Co. of California, and The M. W. Kellogg Co. have also contributed to the development of this process.

In present-day commercial practice, waxy oil charge is blended with 1 to 3 volumes of liquid propane at a temperature sufficiently high (120° to 160° F.) to ensure complete solution of the wax. The mixture is first cooled by exchange with cold filtrate and then charged to a batch chilling vessel, in which temperature is reduced to that required to obtain the desired pour point of the dewaxed oil, by evaporation of propane from the solution. Cold propane is injected into the vessel in order to maintain the propane-oil ratio approximately constant. The crystallized wax is removed by filtration on a continuous rotary filter (*59*) under a pressure of about 4 to 8 pounds per square inch.

The wax cake is washed on the filter with cold propane to displace the oil-solvent solution trapped in the cake. The cake is discharged continuously from the filter drum and then is transferred from the filter by means of a screw conveyor. The propane is recovered from both the wax cake and oil solution by distillation and is recompressed for re-use. The last traces of propane are removed at atmospheric pressure and with steam.

The process is applicable to the full range of lubricating oil stocks, including distillate and residual fractions (*13*), and unrefined stocks as well as those which have received selective solvent treatment. In production of oils of 0° F. pour point, the difference between the temperature of filtration and the pour point is usually 30° to 40° F.

Propane is available in ample quantities and can be produced as a liquid in most refineries. Propane is a highly satisfactory refrigerant and in dewaxing the principle of direct evaporative cooling is employed advantageously. Propane also is cheap, stable, noncorrosive, and nontoxic.

Nine units have been installed using liquid propane as a dewaxing solvent.

Several continuous methods of chilling have been proposed to replace the batch chilling method normally employed in propane dewaxing.

In one continuous method (*17*), the waxy oil charge—for example, in the case of a topped crude—is diluted with an equal volume of propane and the mixture is chilled to about −25° F. by means of heat exchange with cold filtrate in double-pipe scraped-surface equipment. This chilled mixture is then mixed with propane which has been chilled by autorefrigeration to −45° F. to bring the ratio of propane to oil to about 5 to 1. Ninety per cent of the refrigeration required is accomplished in this manner; the remaining 10% is obtained by evaporating propane from the diluted mixture.

It is claimed that the chilling rate is rapid and that the wax is crystallized in a form which permits high rates of filtration. However, there is no record that this or other methods of continuous chilling propane-oil mixtures have been applied on a commercial scale.

Sulfur Dioxide–Benzene Dewaxing Process

This process, commercialized by Edeleanu Gesellschaft, m.b.H., employs a solvent mixture composed of benzene and liquid sulfur dioxide. The same solvents are used in the Edeleanu process for selective solvent refining. Generally, the volume ratio of the two solvents is 80 parts of benzene to 20 parts of sulfur dioxide for dewaxing (*58*). For selective solvent refining the solvents are blended in the proportion of about 75% sulfur dioxide and 25% benzene.

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This dewaxing process is always installed in combination with Edeleanu solvent extraction because recovery of the solvents from the preceding step is not required. For example, if dewaxing follows the refining operation, the raffinate solution is taken directly from the extraction unit and the solvent composition is adjusted to that used for dewaxing by the addition of a benzene-rich solvent which is readily recovered from the dewaxed oil solution because of the wide difference in boiling points of the solvents.

In commercial operations of the dewaxing step, the mixture of wax-bearing oil and solvent is heated to ensure complete solution of the wax and is then passed through exchangers and chillers to totally enclosed rotary drum filters at a temperature about 10° to 15° F. below the desired pour point of the dewaxed oil. Vacuum for filtration is applied to the filtrate receiving vessel. The wax cake on the filter is washed with cold solvent to remove the occluded oil-solvent solution. Sulfur dioxide superheated gas is used for stripping the solvent from the oil-solution and the wax phase, and the last traces of solvent are removed under vacuum.

Because extended corrosion has been experienced with sulfur dioxide when moisture is present, every precaution must be taken to eliminate water from the system. The use of the process is limited to three installations made in Europe.

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Bari-Sol Dewaxing Process

This process uses a solvent mixture composed of ethylene dichloride and benzene and a special type of totally enclosed centrifuge developed by the Sharples Specialty Co. and Max. B. Miller, Inc. The solvent is heavier than either the wax or oil to be processed, which permits discharge of the wax phase from the center of the centrifuge bowl without the use of a carrier liquid.

The solvent composition is adjusted to obtain complete solution of the oil at the dewaxing temperature, which normally is about 5° to 15° F. below the desired pour point of the oil. In practice (*2*), it has been found that a solvent composed of 78% ethylene dichloride and 22% benzene by volume is satisfactory for a wide range of stocks. Ethylene dichloride has some selective action on the oil components of the charge stock and the presence of benzene is required to avoid the formation of a second oil phase at low temperatures.

The process is reported capable of dewaxing any wax-bearing stock, either raw or after selective solvent refining, and waxes with a relatively low oil content may be obtained by a two-stage operation in which the wax from the primary stage is rerun after further dilution with cold solvent on a second battery of centrifuges.

In plant operation the waxy stock is blended with the discharged oil solution from the secondary centrifuges and sufficient recovered solvent is added to bring the dilution to about 3 parts of solvent to 1 of waxy oil. This mixture is heated to 110° F. with agitation to ensure a homogeneous solution and is then charged through exchange and chilling equipment directly to the primary centrifuges.

The dewaxed oil and wax phases discharged from the centrifuges are transferred through heat exchange equipment to individual solvent recovery units for continuous recovery of solvent.

Three commercial units have been installed in the United States.

Separator-Nobel Dewaxing Process

This process employs trichloroethylene as the solvent. The first unit was installed by Standard Franco Americaine de Raffinage, Port Jerome, France (*70*). The operation is similar to that of the Bari-Sol process. The mixture of solvent and waxy oil charge is chilled and the wax is separated from the chilled solution by means of a centrifuge developed by the Separator-Nobel (SN) Co., whence the process derives its name. On account of the high specific gravity of the solvent in which the oil is dissolved, the oil phase is heavier than the wax phase and, therefore, wax is discharged from the center of the centrifuge bowl. The wax phase then passes to a steam-heated receiver. The cold oil solution is discharged from the outside of the bowl.

It is reported that trichloroethylene does not hydrolyze and is stable if temperatures in the recovery system are held below about 265° F., and that under the proper conditions of distillation, there is no danger of corrosion. The solvent, however, may decompose on excessive heating or exposure to light if antioxidants are not used (*15*).

The process is capable of dewaxing distillate and residual oils with both low and high wax content, but it is particularly suited for processing stocks containing a small amount of wax. However, by two-stage operation, stocks of very high wax content also can be dewaxed. The dewaxing temperature required ranges from 7° to 35° F. below the desired pour point and depends upon the type of stock being processed (*26*).

The process has not been widely accepted and only two installations have been made in Europe.

Indicated Trends

The development of the solvent processes for dewaxing during the past 25 years has largely overcome the major disadvantages of the old cold pressing and cold settling or centrifuge processes. Any wax-bearing oil may now be dewaxed irrespective of its wax content, viscosity, and method of preparation. Dewaxing differentials have been reduced and the recovery of oil increased by the use of the solvent processes.

The principal dewaxing processes currently in commercial use, however, all employ solvents and all require refrigeration for crystallization of the wax. The provision of facilities for refrigeration and evaporation of the solvent represents a major portion of the total investment for a dewaxing unit. Furthermore, the cost of operating these facilities is a large part of the total operating expense of a unit. Reduction of investment costs and operating expense for the dewaxing of petroleum fractions is a problem confronting petroleum technologists.

These problems are receiving considerable attention—for example, a further examination has been made of the possibility of replacing the low temperature methods of dewaxing oil by a procedure involving liquid-liquid contact of the wax-bearing stock with a selective solvent, such as acetone and aniline, at operating temperatures above the melting point of the wax but below the critical solution temperature of wax and solvent (*40*). It is reported that this method is capable of bringing about a partial concentration of the wax in the insoluble portion of the charge stock, but with the solvents so far reported it would be uneconomical with respect to yields of dewaxed oil in comparison with the present low temperature methods for processing stocks containing a nominal content of wax.

It is reported (*40*) that the liquid-liquid process for separation of wax and oil is particularly suited for deoiling of waxes and that in some instances it is replacing the "sweating" process in Europe for the production of commercial waxes.

An interesting possibility is the application of the liquid-liquid separation method to the treatment of petroleum fractions containing a small percentage of wax for the production of oils substantially free from wax.

Discovery by Bengen (*7*) that urea forms addition compounds with the aliphatic straight-chain hydrocarbons has opened new possibilities for the removal and separation from petroleum of such materials as waxes which are preponderantly nonbranched. Urea-wax addition compounds are apparently formed readily at ordinary room temperatures, and as these compounds have very definitely defined crystal structure (*75*), their separation should be easily accomplished.

The addition compounds can be separated into the components by thermal decomposition involving heating to a moderately low temperature, by extraction with solvents which dissolve the organic component or by subjecting to the action of a urea solvent such as water (with the application of a very small amount of heat). The choice of the most appropriate conditions for the formation of addition compounds and the method of resolving these into the components is reported to depend to some degree upon the type of wax-bearing stock being processed (*75*). The process is stated to lend itself readily to continuous operation in which the urea is recirculated for further compound formation (*75*).

The method of adduct formation with urea is now being investigated (*5, 68, 90*)

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extensively and the process seems assured a permanent place in commercial application. The extent to which it may be utilized cannot be fully predicted at this moment.

Deoiling of Waxes

The petroleum waxes have many important industrial uses (*53, 64, 85*) and, because they are relatively pure compounds, they may be an excellent source of raw materials for the manufacture of chemicals. For maximum quality, the waxes should be practically oil-free (*8*). The waxes produced in the dewaxing of lubricating oil fractions generally contain appreciable quantities of oil and therefore are unsatisfactory for many uses. The amount of oil associated with the waxes depends largely upon the method employed in removing them from the charge stock, and may vary from a few per cent to as high as 35%. The higher quantities are found in waxes obtained by pressing and centrifuging with naphthas, while the smaller amounts are associated with waxes produced by the more efficient present-day dewaxing methods in which solvents other than naphthas are employed.

The removal of oil from both crystalline and microcrystalline waxes is an important phase in petroleum refining. In the early days of the industry, it was found that the "slack wax" produced in pressing operations could be deoiled by "sweating," which consists of solidifying the slack wax in large shallow pans and then gradually raising the temperature to separate fractionally first the oil, then intermediate fractions containing some oil and the low melting point waxes, and finally a fraction of a selected melting point which remains as a solid in the pan (*24, 29, 63*). Waxes of low oil content are produced by this method, but the yields of the desired fractions from the pressed wax are relatively low. The method is applicable only to the more highly crystalline type waxes.

Sweating could not be applied to waxes obtained in dewaxing residua and heavy distillate fractions, because these waxes do not form the large, well-defined crystals that are essential for sweating. Oil was removed by diluting these waxes with a solvent, such as naphtha, chilling to the temperature required to produce a wax of desired melting point, and cold settling or centrifuging the chilled solution.

With the advent of modern dewaxing methods sweating and naphtha deoiling are being rapidly replaced by the more versatile solvent-deoiling methods. The deoiling may be conducted independently of the dewaxing operation. However, as the same solvent or a mixture of the same solvents may be employed in both operations, the two processes can be operated concurrently in separate sections of a single plant.

Two solvent processes in use—namely, the wax fractionation process (*62*) and the wax manufacturing process (*61*)—have been described. These processes are capable of consistently producing high yields of waxes of very low oil content from a full range of charge stocks. The crystalline waxes produced by the wax manufacturing process show oil contents by ASTM analysis that are below 0.3%, and the process is stated to be highly economical in the use of solvent.

A nonsolvent process, based on the emulsification of the oily wax with water and cooling to crystallize the waxes, has been introduced for partial deoiling of crystalline waxes (*76*). The oil is removed by centrifuging the cooled emulsion in a specially designed centrifuge. The process is continuous and operating costs are reported to be low, as only exhaust steam is required for heating. Plant costs are also stated to be low, because no solvent recovery is involved. The process is capable of reducing the oil content of high oil "slack waxes" to less than 5% to produce semirefined grades of wax and is stated to be particularly suited as an adjunct to existing sweating equipment to increase capacity and improve the quality of sweated wax (*77*). However, its application is limited to the deoiling of crystalline wax, and other facilities would be required for deoiling microcrystalline waxes in a refinery where a full range of waxes is produced.

Summary of Dewaxing

Twenty-five years ago the dewaxing processes available to the refiner of lubricating oils were the cold pressing method applicable only to low viscosity distillates and the cold settling and centrifuge methods applicable to certain residual oils. A vast amount of work by many investigators led to development of a number of processes employing special solvents for dewaxing. Most of the lubricating oil dewaxed today is produced by the solvent dewaxing process using a solvent composed of a ketone and an aromatic hydrocarbon, and the propane dewaxing process employing liquid propane as a solvent. Several other processes, using special solvents, which also are adaptable to the dewaxing of the full range of lubricating oils, are in limited commercial operation.

Although the bulk of low oil content waxes, especially those having melting points below about 135° F., are produced today by sweating, solvent deoiling is fast becoming the more important method for the production of all waxes derived from petroleum.

Investigations of new methods are being continued. The trend is toward methods for removal of wax at normal or higher temperatures to avoid the necessity of employing refrigeration.

This review of progress in the development of methods for the removal of wax from petroleum oils is not purported to be complete with respect to all literature and patent references.

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Deasphalting

Most petroleum crude oils contain varying amounts of substances of high molecular weight, semisolid to solid noncrystalline, which are normally classified as resins and asphaltenes (*72*). Very little is known concerning the chemical structure of these substances. The resins are tacky or solid complex materials miscible with most liquid petroleum products. The asphaltenes are solid compounds of high molecular weight, which decompose rather than melt on heating to elevated temperatures. Both the resins and asphaltenes have a high ratio of carbon to hydrogen and an excessive carbon-forming tendency. Because of this characteristic, these asphaltic materials are undesirable constituents of lubricating oils and their removal is required for the production of oils of high quality. The asphaltic materials normally are very dark in color and impart dark colors to the oils. Although this color may not be deleterious, it must be removed to give the lubricating oils a desirable appearance with respect to marketing.

Distillation

The asphaltenes are nonvolatile and remain in the residue when the crude is subjected to distillation. The resins are partially volatile and therefore may be present in the lubricating oil fractions of higher boiling point as well as in the residue. Among the many methods employed for the separation of these materials from the oil fractions are distillation, adsorption, chemical treatment, and precipitation by special solvents.

It was recognized in the early days of the petroleum refining industry that the asphaltic materials could be separated from the lubricating oils by distilling the crude oil and leaving the asphaltic materials in the undistilled portion. Distillation may be considered the first deasphalting process applied commercially. Its principal disadvantage was the relatively large loss of the lubricating oil fractions of high molecular weight which, because of their low volatility, were retained in the asphaltic residue.

In order to increase the yields of good quality, high viscosity lubricating oils which were in demand at that time, the industry was faced with the problem of developing more efficient methods for separating the oil from the asphaltic materials in the residue. In many cases the residue represented a substantial proportion of the crude oil. Investigations undertaken included chemical treatment with sulfuric acid (*35*), removal of the asphaltic materials with metallic chlorides (*50, 66*), and adsorption on clay (*56*). Solvent precipitation of the asphalts also was studied (*11, 18, 19, 38, 78*).

Treatment with Sulfuric Acid

The selection of sulfuric acid for removal of asphaltic materials from residual stocks was logically the first choice, because many refiners had used this acid for treating lubricating oil distillates to improve quality. This method of deasphalting was adopted early.

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The conventional method of carrying out the operation consisted briefly of agitating the stock to be treated with acid by blowing with air in a vessel, allowing the heavy sludge formed to settle by gravity, and separately withdrawing the sludge and treated oil. The process was a time-consuming, batchwise operation, and frequently difficulty was experienced in disposing of the hard, viscous sludge formed. There also was a substantial loss of oil to the sludge, which became excessive in the case of the heavy residual stocks where the sludge would not readily settle because of the high viscosity of the oil. These difficulties were partially overcome by diluting the charge stock with a petroleum naphtha prior to treating, but additional improvements were sought because the naphtha had to be recovered by distillation, and this added greatly to the cost of the operation. Furthermore, some darkening of the color was invariably experienced in removing the naphtha.

A further improvement in the process was made about 1925, when introduction of centrifugal separators for the separation of the acid sludge permitted the process to be placed on a continuous basis and eliminated the use of naphtha (*43*, *84*). In this operation, the raw oil and acid streams are accurately controlled through proportioning equipment and flow into a mixing vessel where the treating is completed in a relatively short time. The mixture then flows to a centrifuge which separates the sludge from the oil.

The conversion of the process from batch treating to continuous centrifuging effected a marked improvement in the economy of the operation. The time of treatment and the quantity of acid required for treating were substantially reduced. The loss of oil to sludge was decreased and the sludge was less viscous than that obtained in batch operation and could be disposed of with less difficulty.

These improvements, however, did not prevent degradation of a considerable portion of the oil to an acid sludge which is of little value. Furthermore, the process is not applicable to certain types of oils which contain some resins and very small amounts of asphalt.

Although the process using sulfuric acid may be deficient in some respects, it was applied extensively and is still in use today in a number of refineries.

Adsorption on Clay

Asphaltic materials may be separated from the residue by adsorption on clay. The oil is percolated through a relatively tall column of comparatively coarse clay or mixed with a selected clay of fine mesh at relatively high temperatures, and the spent clay is removed by filtration.

The percolation method has been applied particularly to stocks which contain low concentrations of asphalts, but in which the resin content may be high.

Obviously to remove large amounts of asphaltic materials, substantial quantities of clay would be required in both the percolation and hot contacting methods, and the adsorption process then may become uneconomical in the treating of raw residua. With the exception of residual oils containing low concentrations of asphalts, oils to be treated with clay generally receive some pretreatment—for example, with sulfuric acid followed by neutralization of the acid oil, or selective solvent extraction.

Treatment with Metallic Chlorides

Metallic chlorides are effective in removing asphaltic materials, and one plant was installed about 1934 for treatment of lubricating oils by the Alchlor process using aluminum chloride (*51*). It is reported that after such treatment, residual oils are free from resinous and asphaltic materials. Although aluminum chloride treating of lubricating oils is in commercial operation, the process apparently has not been extended beyond the one installation.

Deasphalting with Alcohols

Early investigations dealing with solvents showed that alcohols, alcohol-ether mixtures, ketones, and petroleum naphthas were effective to some extent in removing asphaltic materials from petroleum fractions. The alcohols appeared to be the most promising, but at the relatively low temperatures required (about 35° F.) the viscosity of the alcohol-oil mixture is usually too high to permit rapid settling of the precipitated materials. Wax crystallization also may occur simultaneously and interfere with settling. When wax is absent, hard asphalts may be precipitated with the alcohols, but the degree to which the carbon residue of the residual stock may be reduced appears to be limited. There is no record that alcohols have been applied commercially.

Vacuum Distillation

With the introduction of distillation and fractionation under high vacuum in the presence of steam, it was possible to effect a relatively efficient separation of oil from the asphalts. However, in the case of the more highly "paraffinic" crudes, a complete separation between oil and asphaltic materials could not be made, because the high viscosity oil fractions which have very low vapor pressures are thermally decomposed at the relatively high temperatures required in the distillation.

The development of modern fractionating equipment, in which a minimum pressure drop exists across the bubble trays, brought about a further improvement in the efficiency of the separation of oils from the asphaltic materials. Modern vacuum distillation is widely used at the present time for the production of oils of low asphaltic material content.

A number of special vacuum distillation processes have been developed, whereby thermal decomposition of the oil is kept to a minimum. One of these employs thin film vaporization, in which mercury vapor is employed as an indirect heating medium (*39*, *71*). Another employs a carrier other than steam—for example, kerosene—in the vaporization of the heavy lubricating oil fractions (*16*). These processes are being operated on a commercial scale, but apparently because of their special nature they have not been widely adopted by the petroleum industry.

The demand for larger quantities of high viscosity lubricating oils, and the desirability from the standpoint of economy of deriving maximum yields of valuable oils from the crude oil, led a number of companies to investigate further the problem of increasing the recovery of high molecular weight lubricating oil fractions present in asphaltic residua.

Propane Deasphalting Process

The most outstanding development resulting from these investigations is the use of liquid propane for the selective precipitation of resins and asphalts. The development of the propane deasphalting process is a very important contribution to petroleum technology in the refining of residual oils and provides a method for substantially complete separation of lubricating oils from the asphaltic materials contained in the residua derived from any crude source.

Propane is a unique solvent, in that its solvent power for oil is reversed over the range of about 110° to 200° F., exhibiting less solvent power as the temperature is increased. This is in contrast to the action of ordinary selective solvents, which exhibit increased oil solvent power as the temperature is raised. By taking advantage of this property of propane and by controlling the temperature and propane ratio, very efficient separation of the asphaltic materials can be attained.

The theoretical aspects and operating features of the propane deasphalting process have been described fully (*12*, *14*, *89*).

Generally, the heavy materials removed in the process included both resins and asphalts, but by operating in two or more stages, these materials can be segregated. This may often be desirable, as both products then may be obtained in a relatively pure state and thus they become of greater commercial importance. Deresining of heavy distillate fractions also is possible, and the process may be operated for the separation of special resin fractions (*33*), which may be of value in the manufacture of specialty products.

In the first installation of the propane process made in 1934, the operation was conducted in stage equipment, but after a few units had been constructed, a countercurrent tower was used.

In the tower operation, the asphalt-bearing stock is introduced close to the top of

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the tower and the precipitated asphalt is washed free of oil by a countercurrent or rising stream of liquid propane introduced near the bottom of the tower (*20, 23*). The quantity of propane required depends to some extent upon the type of charge stock and the temperature conditions employed.

In practice, propane ratios of about 4 to 9 volumes to 1 of charge stock are adequate. The use of a temperature gradient in the tower increases efficiency (*22*). The temperatures range from about 100° to 130° F. and 150° to 180° F. at the bottom and top of the tower, respectively. The asphalt-solvent phase contains approximately equal proportions of asphalt and propane, is liquid at the temperature of operation, and readily flows from the tower. The remainder of the propane is associated with the deasphalted oil. The phases are discharged from the tower through exchange equipment to separate solvent recovery units, where the propane is evaporated. The last traces of propane are removed by steaming. The recovered propane is compressed and liquefied for re-use. Obviously, if propane dewaxing is to follow the deasphalting step, the propane contained in the deasphalted oil-propane solution need not be removed, as it could be used as a refrigerant and as diluent and subsequently recovered from the products obtained in the dewaxing step.

Propane deasphalting is used extensively in the production of lubricating oils from residual stocks, and is almost always applied prior to selective solvent refining, where a single extraction solvent such as phenol or furfural is used.

Within the past five years, the propane deasphalting process has found a place in the recovery of high boiling, desirable catalytic cracking feed stocks with a relatively low carbon content from petroleum residua (*57*).

Although the use of pressure equipment is required, the operating pressures involved generally do not exceed a gage pressure of 500 pounds per square inch. As corrosion is not experienced, ordinary construction metals may be used.

To date, twenty-six commercial units have been installed to deasphalt residual oils for the production of lubricating oils and three units to deasphalt (decarbonize) heavy reduced crudes for preparation of catalytic cracking feed stocks.

Recently, the use of organic carbonates—for example, diethyl carbonate to modify the action of propane as a deasphalting agent—has been disclosed (*55*). It is stated that the use of a modifier of this type permits recovery of the high viscosity oil which is normally discarded with the asphalt. There is no record that the modifier has been employed in commercial operations.

Processes that have been combined with propane deasphalting include acid treating, "cold" fractionation of heavy lubricating oils, and selective solvent refining.

Combination of Processes

The combination of deasphalting and sulfuric acid treating is suitable for the production of bright stocks of conventional viscosity index from heavy petroleum residua.

In commercial installation, the acid is applied to the deasphalted oil in propane solution and the sludge is removed by continuous settling. The acidic oil-propane solution is neutralized continuously with a solution of caustic and water-washed for removal of the last traces of caustic. The oil after removal of propane may be finished by conventional percolation through clay to produce a "green cast" finished bright stock (*4*).

The settling of the acid sludge in the presence of propane is said to be sufficiently complete to allow neutralization with a small amount of fine-meshed clay, which is introduced into the acid oil-propane solution and passes with the oil through the propane recovery unit. The clay is removed from the oil by conventional filtration to produce a finished bright stock with a good color (*48*).

The advantages claimed for the process are reduced acid requirements, lower sludge loss, and lower clay requirements for finishing, as compared to the conventional method of acid-treating residual stocks in naphtha solution. This process of combined deasphalting and acid treating has been installed in two refineries.

It is reported that the use of propane as a diluent makes acid treating of Pennsylvania residual stocks commercially feasible (*88*), but no references to the commercial application of this method of treating Pennsylvania oils have been found.

Propane fractionation of heavy lubricating oil combined with propane deasphalting permits the separation of the charge stock into a series of fractions of different viscosity and a deasphalted bright stock, simultaneously (*21*)—for example, a reduced crude containing the SAE 30 and heavier grades of lubricating oil charged to a countercurrent propane fractionating tower may be separated into fractions equivalent to SAE 30 and SAE 50 grade oils and a deasphalted bright stock by withdrawing products from the system at one or more intermediate points.

A commercial unit recently has been installed employing this combined process (*47*, *65*). Two propane-treating columns rather than a single column are employed in this unit for the production of an SAE 50 oil and a bright stock. The reduced crude is charged to the first column and the SAE 50 oil is taken overhead, the bottoms being split into a bright stock and asphalt in the second column. By varying processing conditions, the viscosities of the fractions taken from the two columns may be altered as desired.

Asphalts are removed from residual stocks by the Duo-Sol process of selective solvent refining (*81*, *82*), in which two solvents, propane and Selecto (a mixture of phenol and cresol), which have relatively low mutual solubilities, are used. The propane acts as a deasphalting agent and as a solvent for the paraffinic oil, while the asphaltic materials together with the nonparaffinic oil present in the residuum are taken into solution in the Selecto. The Duo-Sol process combines deasphalting and selective refining. However, it generally is regarded as a solvent refining process and is therefore not discussed here.

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Hydrogenation

High pressure liquid phase hydrogenation provides a means of eliminating asphaltic materials from heavy petroleum residua (*37*). The first commercial unit for hydrogenation of petroleum was installed in the United States about 1929. Conversion of the high viscosity charging stock into a liquid product of a more highly paraffinic nature is possible, but with an appreciable loss in viscosity level. Some gasoline and gas oil are produced, but the quantity of these fractions may be controlled to some extent by selection of the proper operating conditions. During the liquid phase hydrogenation, the asphalt present in the charge stock may be completely converted to liquid products—aromatic, naphthenic, and paraffinic materials (*54*).

This process, while capable of eliminating the asphaltic materials present in heavy stocks, has not been applied solely for this purpose on a commercial scale. Possibly with an increasing scarcity of crude petroleum, this type of hydrogenation will be incorporated into refining operations in future to convert asphaltic materials to more useful products.

Principal Commercial Processes

Vacuum distillation and propane deasphalting are the two principal processes in commercial use today for separating valuable heavy fractions from asphaltic materials in petroleum residua. Adsorption (clay percolation or clay contacting) and chemical treatment, however, are used to some extent. These four methods are used independently or at times advantageously with one another—for example, the properties of the heavy oil fractions produced by vacuum distillation are improved by clay contacting or a combination of sulfuric acid treatment and clay contacting. The particular method or combination of methods chosen by the refiner is, of course, a matter of obtaining a finished oil of satisfactory quality in the most economical manner. The type of crude oil available to the refiner dictates to some extent the choice of the method used, and with the wide variation existing in the types of crude oils being processed, all these methods for the separation of asphaltic materials from heavy petroleum fractions will continue to have a place in petroleum refining for some time to come.

The literature and patent references cited include only those believed to be pertinent in outlining progress in the development of the most important methods for the removal of asphaltic materials from petroleum.

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Solvent Extraction in the Petroleum Industry

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Development of solvent extraction processes in the petroleum industry and theoretical aspects of solvent extraction are reviewed. Six extraction processes which have received industrial acceptance are described and performance characteristics of furfural, phenol, and Duosol processes are compared. Data are presented to demonstrate the applicability of adsorption analyses for stock evaluation and prediction of commercial extraction yields. Correlations for predicting solvent requirements and layer compositions and process design and engineering considerations are included. The desirability of further fundamental work to facilitate design calculations from physical data is suggested.

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Solvent extraction is used extensively in the petroleum industry to refine lubricating oils, kerosene, and specialty oils for medicinal and agricultural purposes. It is a process that separates hydrocarbons into two phases—a raffinate which contains substances of high hydrogen to carbon ratio and an extract which contains substances of low hydrogen to carbon ratio.

This paper discusses developments in solvent extraction with emphasis on applications to petroleum fractions in the kerosene and heavier boiling range. Many of these techniques have been extended to the refining of gasoline, Diesel fuels, catalytic cracker feed and cycle stocks, and butadiene.

Early refiners utilized simple batch distillation to prepare kerosenes and lubricating oils. As the demand for these materials expanded and new crude oils were found, certain desirable and undesirable characteristics became apparent. Crude oils were selected from which products possessing desirable characteristics could be distilled—for example, oxidation stability, low smoke tendency, low carbon-forming tendency, small viscosity change with change in temperature (high viscosity index), light color, and attractive appearance were more likely to be found in petroleum of the "paraffinic" or Pennsylvania type.

As Pennsylvania type crude oils became limited in quantity and commanded premium prices, the desirability of upgrading stocks from other crudes became evident. One of the first chemicals used for this purpose was sulfuric acid, and even today sulfuric acid is used extensively to refine many petroleum products.

A whole lubricating oil fraction consists of four major classes of hydrocarbons—namely (*a*) asphalts and resins, (*b*) aromatics, (*c*) naphthenes and branched paraffins, and (*d*) paraffin wax. Sulfuric acid is remarkably effective for removing undesirable constituents *a* and *b* by a combination of reaction and extraction and has little or no effect on wax (which must be removed by other means) or the naphthenic-type materials which comprise a good lubricating oil.

In contrast to the action of sulfuric acid, the solvents utilized in commercial solvent

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extraction processes function by physical means only. Undesirable constituents are removed by selective solvent action, and the solvent is recovered by distillation for re-use. Asphaltic constituents behave like colloids instead of solutes; hence, as is described in another paper in this symposium (*13*), precipitation is used or depeptization by lower molecular weight hydrocarbons such as propane or butane for deasphalting. Aromatics are extracted by the selective solvent. The action, then, of the selective solvent is to leave the desirable naphthenic-type compounds along with the wax in the so-called raffinate layer. Dewaxing processes (*13*) are utilized to separate these two materials.

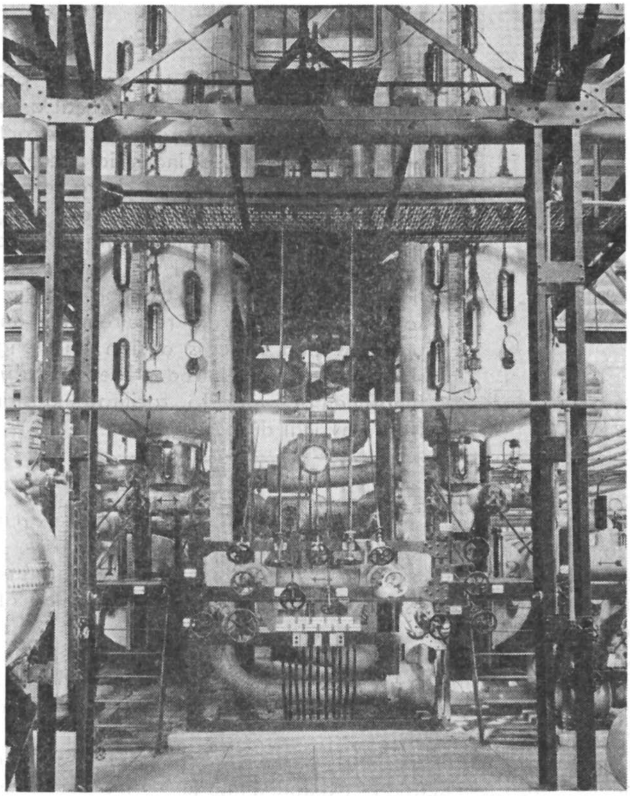

Figure 1. First Edeleanu Continuous Extraction Towers

Early in the twentieth century, Edeleanu ascertained that the poor burning qualities and high smoke tendency of kerosene distillates from Rumanian crude oils resulted from the presence of large quantities of aromatic materials. Liquid sulfur dioxide was found to possess a high solvent power for aromatics but dissolved relatively little of the saturated, naphthenic-type oils. In a paper (*9*) presented before the International Petroleum Congress in 1907, Edeleanu described the basic principles which later resulted in commercial development of the sulfur dioxide solvent extraction process which now bears his name. In 1909 at Vega, Rumania, the process was operated successfully on a small scale, and first commercial production took place at Rouen, France, in 1911. The first commercial continuous solvent extraction was accomplished at the Standard Oil Co. (California) refinery at Richmond, Calif., in 1924. This plant, prefabricated in Germany, had been constructed the previous year and was designed to operate batchwise. The ingenuity of Crawford and his coworkers resulted in a number of minor modifications which permitted operation to become continuous with an immediate threefold increase in daily production (*5*). This plant, still in operation at the Richmond Refinery, is illustrated in Figures 1 and 2.

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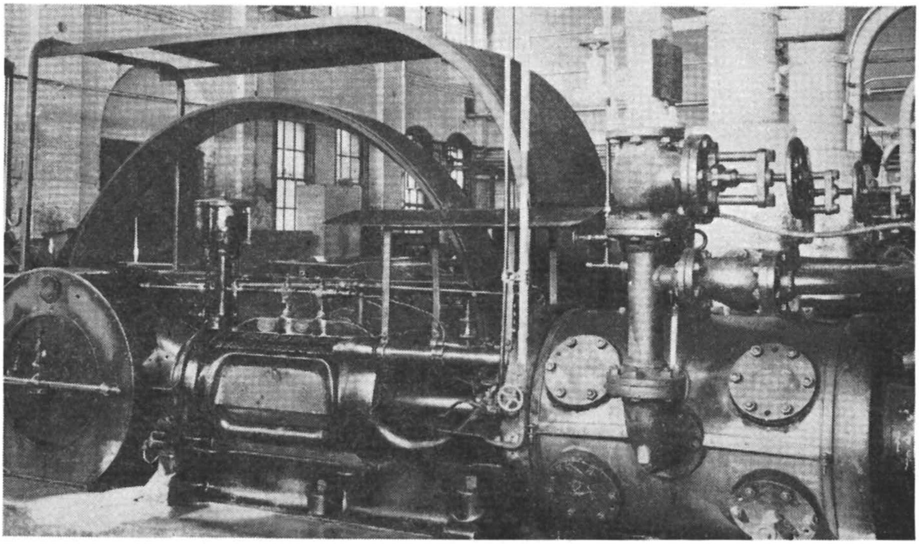

Figure 2. Sulfur Dioxide Compressors Imported from Germany in Early 1920's

Solvent extraction was limited to treatment of kerosenes with sulfur dioxide until early in the 1930's. Prior to 1930 less than 2000 barrels of solvent-refined lubricating oil were produced daily. Sulfur dioxide below its atmospheric boiling point has only a slight solvent power for aromatic and unsaturated constituents of lubricating oil fractions. Early attempts to operate at elevated temperatures and pressures gave rise to costly and annoying sulfur dioxide leakage and packing and sealing problems. In 1933 Cottrell (*4*) described the use of benzene added to sulfur dioxide to increase its solvent power.

The lack of satisfactory solvent recovery methods prior to 1930 prevented the use of selective solvents more suitable for lubricating oils. The major part of any solvent extraction plant is its complex solvent recovery system. Chemical engineering's contributions to distillation theory and process design resulted in the development of efficient solvent recovery techniques. In 1933, as illustrated by Figure 3, large commercial plants were built employing as selective solvents furfural, nitrobenzene, Selecto (cresylic acid plus

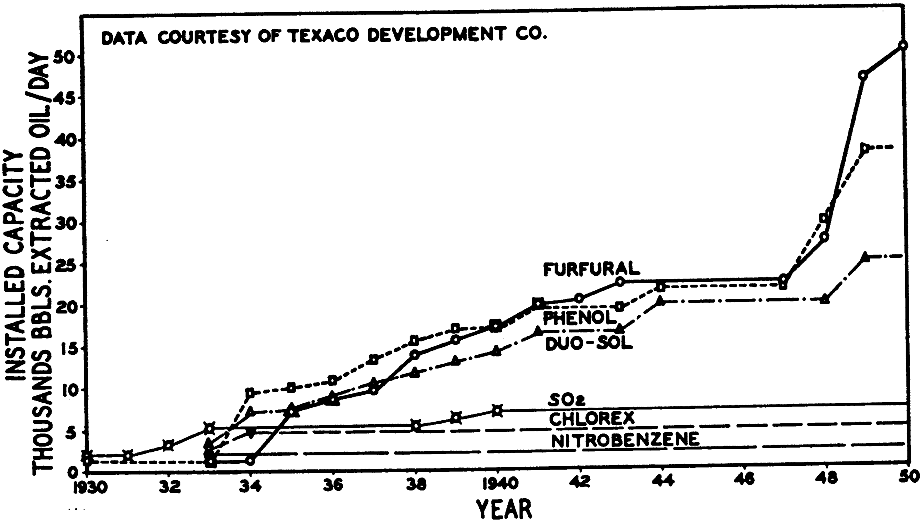

Figure 3. Growth of Lubricating Oil Solvent Extraction (World-Wide)

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phenol), propane, Chlorex, and phenol (*14*). An interesting combination of simultaneous extraction and reaction results from one refiner's use of nitrobenzene in conjunction with sulfuric acid.

Figure 3 also illustrates the rapid growth of lubricating oil solvent extraction processes. From the point of view of popularity, furfural, phenol, and the Duosol processes are outstanding. Most of the recent developments have been improvements in the solvent recovery systems to minimize solvent consumption, to reduce costs, and in the treater sections, to increase raffinate yield.

Theoretical Aspects

Although theoretical considerations are helpful to an understanding of the principles involved and may be useful for studying and predicting simple extractions of pure substances, an empirical approach ultimately must be resorted to for cases involving such complex and undefinable mixtures as kerosenes and lubricating oils. The ideal distribution law which states that the ratio of concentrations of a component distributed between two mutually insoluble phases is a constant dependent only on the temperature ($K = C_1/C_2$), is analogous to Henry's law for absorption and is rarely valid for commercial extraction problems.

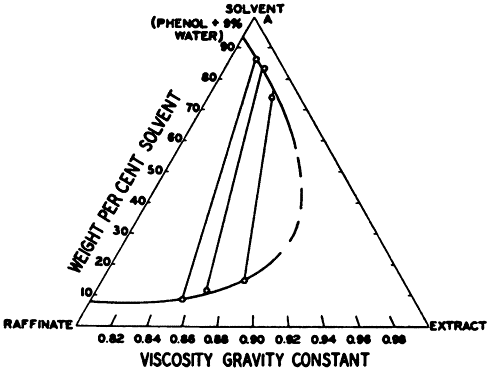

Figure 4. Equilibrium Data for Light Lubricating Oil Distillate from California Wax-Free Crude in Aqueous Phenol

Trilinear diagrams may be used for presentation of equilibrium data, for graphical calculation of solvent extraction problems, for evaluating efficiency of operations of existing equipment, and for comparison of various solvents. If three pure components are involved, concentrations in weight percentages (because of their additive nature) are used for coordinates to express behavior. It is impractical to designate raffinate and extract concentrations for complex hydrocarbon mixtures by means of percentage values, but instead it is desirable to utilize some nearly additive function such as specific gravity, refractive index, or viscosity-gravity-constant. Figure 4 presents such isothermal data for a system comprising low cold test California lubricating oil distillate and aqueous phenol. Three tie lines connecting compositions of phases in equilibrium are shown.

Figure 5, which represents commercial extraction of a California wax-free light lubricating oil distillate, is used to review graphical techniques for studying countercurrent multistage extractions.

Point *F* represents the composition of the given feed stock. If we assign as desired end conditions a raffinate and extract viscosity-gravity-constant of 0.870 and 0.955, respectively (such values would represent a yield of 58.5% by weight), we can locate points R_n and E_1. Any addition of solvent to the feed stock must effect a composition which would fall on the line *FA*. Likewise, any mixture of final extract and raffinate layers must lie on the line $r_n e_1$. An over-all materials balance requires that the solvent-feed mixture be represented by the point of intersection, *J*. The solvent for this particular case would be 53.5% of the mixture (a dosage of 115 weight % or 100 volume %).

All lines constructed to connect compositions of materials entering any stage with compositions leaving any stage intersect at a common point, *O*, called the operating point. The significance of this purely geometrical point has been discussed by Skogen and Rogers (*25*). Having located *O* and assuming that tie line data are available, one may graphically determine the number of stages required for the desired separation. A tie line through e_1 will intersect the binodal curve at r_1. Connecting r_1 with *O* locates e_2, etc. Two and a fraction theoretical stages would be required to effect the specified extraction.

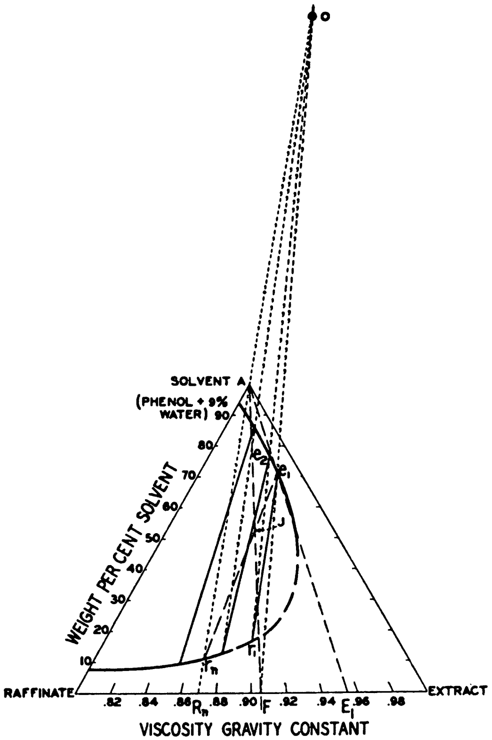

Figure 5. Commercial Extraction of Light Lubricating Oil Distillate from California Wax-Free Crude in Aqueous Phenol

Data could be obtained from such a graph to construct a McCabe-Thiele type diagram. Tie line points on the binodal curve would provide data for an equilibrium curve, and data could be obtained to construct an operating line (from lines drawn from *O* through the binodal curve).

The advantages that may justify the additional costs of reflux at the bottom of a solvent extraction tower are illustrated in Figure 6. Minimum reflux is represented by the tie line from *f* to f_e. Maximum reflux would be represented by the line *f* to *f'*, the extract layer which would exist for infinite solvent to feed ratio. Practical operation of the equipment will fall between the limits of minimum and maximum reflux, as represented by *fy*. The operating point for the enriching section of the extraction column is located by an intersection between the lines *e'E* and *fy*, and the reflux ratio is the ratio of the distances *k'e'*/*k'e* (*22*).

If, from a specified lube distillate we are required to make a given raffinate, *R*, and extract, *E*, and are given the reflux ratio for the enriching section of the column, operating points *k'* and *O* for each section may be constructed on the diagram. A line constructed

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from *f* through *k'* will intersect the line from the raffinate composition through the pure solvent at *O*. The intersection of the extract portion of the curve with this line at point *y* represents the composition of the extract solution flowing below the feed point. The number of theoretical stages then required can be stepped off utilizing operating point *k'* and tie lines for the enriching section and operating point *O* and appropriate tie lines for the upper section of the tower.

If, in the foregoing example, there had been no reflux and the same solvent dosage had been applied, the final extract composition would have been limited to that shown at point f_e. If, on the other hand, we had been required to make an extract of composition *E*, it would have been necessary to utilize a lower solvent dosage and a larger number of theoretical stages.

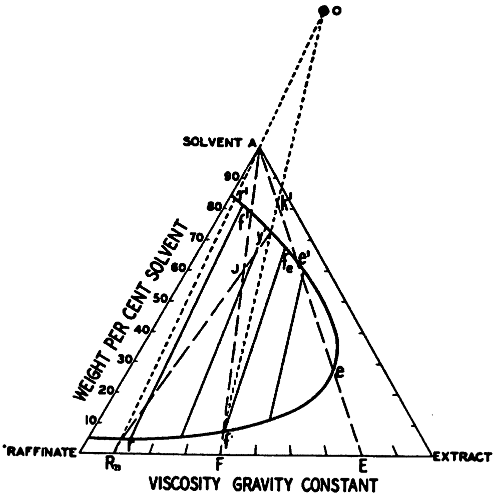

Figure 6. Construction on Trilinear Diagram to Illustrate Effect of Reflux

It is also possible to impress reflux on the top section of the tower. This type of reflux would be represented by mixing a fraction of the overhead raffinate layer with incoming solvent.

A temperature gradient may be impressed across the length of a solvent extraction tower. The result of such temperature gradient is to have at each stage in the tower a different temperature and therefore a different binodal curve. It is more difficult to handle this situation in construction on a trilinear diagram. If, for simplification, we assume that each theoretical stage has its own binodal curve, we may then proceed in a manner similar to that described for the isothermal cases. When utilizing equilibrium line considerations, it is necessary to move from one equilibrium condition to another and change equilibrium curves as the temperature changes.

In the practice of solvent extraction certain general relationships exist which are independent of the solvent and treating temperature. For a particular base stock, relationships among the following physical properties of the raffinate will be about the same regardless of solvent or temperature: specific gravity, viscosity, viscosity-gravity constant, and viscosity index. Precipitative solvents, such as propane, provide an exception to this rule. Products obtained by the Duosol process, therefore, would not conform to the curves for single solvent processes.

In general, the best solvent will be that which gives the highest yield at lowest cost. Yield relationships for any solvent in a given process may be determined graphically on the basis of laboratory data as plotted on trilinear diagrams. Costs will be a function of solvent circulation and price, number of actual stages required, solvent recovery requirements, and special equipment to control water content and corrosion.

The characteristics of an ideal solvent for extraction of lubricating oils may be summarized as follows:

1. High selectivity
2. Good solvent power for the undesirable components
3. Easy solvent recovery (wide difference in volatility between solvent and oil)
4. Low solubility for the desirable oil
5. Sufficient density difference to allow rapid separation of raffinate and extract by gravity
6. Low interfacial tension in order to permit rapid and complete separation into two liquid phases
7. Low cost
8. Ready availability
9. Reasonable temperature of application (preferably treating temperatures such that the oils have low viscosities)
10. Adaptability to a wide range of oils
11. Low toxicity
12. Chemical stability under plant conditions
13. Low freezing point (to avoid complications in cold weather)
14. Noncorrosivity to the usual metals of construction

Characteristics of Commercially Accepted Solvents

Solvents used in commercial operations at the present time are furfural, phenol, cresylic acid, Chlorex, nitrobenzene, and sulfur dioxide. The Duosol process utilizes a solvent called Selecto which is a mixture of phenol and cresylic acid. The propane used in the Duosol process precipitates the asphalt (*13*).

The disadvantages of sulfur dioxide are its high vapor pressure and its low solvent power under normal operating conditions. Fortification of sulfur dioxide with benzene to increase solvent power has been successful in some applications (*4*). On the other hand, the high volatility of sulfur dioxide results in easy solvent stripping, and its low viscosity aids rapid settling.

Nitrobenzene has the highest solvent power for extract oils and is best suited for Pennsylvania stocks. However, its high boiling point makes recovery difficult and its high solvency necessitates low temperature operation which requires costly refrigeration.

Chlorex (β,β'-dichlorodiethyl ether) also has a high solvent power which makes it particularly suitable for Pennsylvania-type oils. The hydrogen chloride in commercial Chlorex (5.5 mg. per 100 ml.) must be removed before use to prevent corrosion of common construction materials. Injection of ammonia into recovery system vapor lines is required to control corrosion.

The selectivity and solvent power of phenol can be controlled by varying the water content. Phenol extraction temperatures are sufficiently high (100° to 200° F.) to effect a reduction in viscosity, to permit imposition of a temperature gradient, and to allow treatment of waxy stocks. This results in savings in dewaxing operations. Phenol, which has excellent chemical stability, can be recovered by ordinary vacuum distillation, although steam stripping is often desirable for complete solvent removal. Drawbacks to phenol are its toxicity and relatively high freezing point. Recently, limited availability and increasing costs of phenol have caused concern.

Furfural exhibits high selectivity at elevated temperatures (175° to 250° F.); this characteristic results in the benefits of reduced viscosity and high temperature gradient and permits operation on waxy stocks. At ambient temperatures, kerosenes and gas oils may be extracted. Water in furfural has a bad effect on its extraction efficiency; therefore, solvent recovery systems must include dehydration facilities. From its chemical composition aldehyde furfural appears to be unstable. However, when handled in accordance with standard operating procedures, decomposition and polymerization are negligible.

The raw material for furfural is an agricultural waste. It is therefore readily available in unlimited quantities (largest manufacturer at the present time is the Quaker Oats Co.). The price of furfural has remained surprisingly constant during the period of

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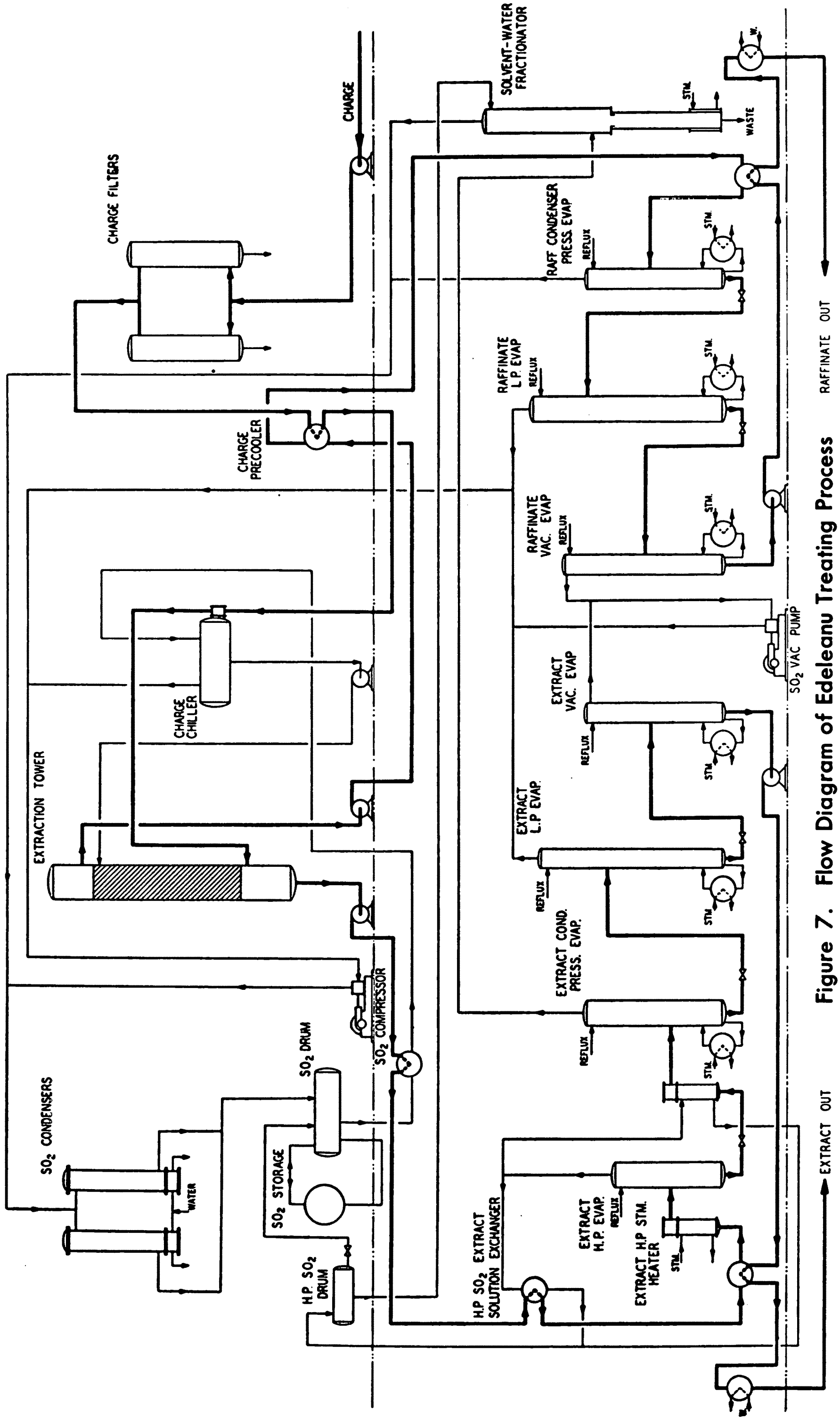

Figure 7. Flow Diagram of Edeleanu Treating Process

Information supplied by E. B. Badger & Sons Co.

inflation when other chemical costs rose materially. During early plant operations it was necessary to remove acidic materials from commercial furfural, but, as currently available, it is completely satisfactory for immediate use.

Commercial Processes

Edeleanu Process (Liquid Sulfur Dioxide). The forerunner of all commercial solvent extraction processes, the Edeleanu process, has been pre-eminently successful for treating low molecular weight stocks in the kerosene–spray oil boiling range.

The earliest commercial plants were designed to operate batchwise and consisted of hydrocarbon and solvent coolers, a mixing vessel which could also be used for settling, and evaporators to remove sulfur dioxide from the raffinate and extract phases. Figure 7 illustrates a modern, continuous sulfur dioxide solvent extraction plant used for kerosenes and light lubricating oils. Dehydrated feed stock is pumped through a heat exchanger and distillate precooler to the bottom of the extraction tower, which is packed with about 30 feet of Raschig rings (or similar packing), and may range from 3 to 8 feet in diameter. Liquid sulfur dioxide is precooled and pumped in at the top of the tower. Typical extraction temperatures range from 20° for kerosenes to 50° to 75° F. for lubricating oils. It often is desirable to hold the liquid interface at the top of the tower because the low viscosity of the extract layer permits higher feed rates than would be possible if the treater were filled predominantly with cold raffinate. Such operation is reversed for the phenol and furfural processes wherein bottom interface levels are maintained to take advantage of the extended surface area presented by the packing which is preferentially wetted by the selective solvent. The raffinate and extract layers pass through heat exchange equipment to their respective recovery systems. Modern improvements incorporating the use of multiple stage, high pressure evaporation for sulfur dioxide recovery, and the latest designs in heat exchanger equipment have greatly improved the economics of the process. Vaporized sulfur dioxide from the recovery system is passed through the coolers and condensers (to separate any light hydrocarbons) and through drying towers (countercurrent to sulfuric acid) prior to compression. It is essential that all water be removed from the system. Extreme corrosion difficulties result wherever water leaks into the system and contacts sulfur dioxide. A maximum water content of 0.05 weight % can be tolerated.

An interesting modification of the Edeleanu process was the sulfur dioxide–benzene process utilized by the Union Oil Co. at Oleum, Calif. (*6*). In order to overcome the low solvent power of sulfur dioxide, benzene was added to the solvent. The immediate result of such addition is to reduce the selectivity of the process. However, selectivity can be improved by reducing temperatures. Therefore, a combination of reduced temperature and increased quantity of solvent provides a reasonably wide range of operating conditions in which satisfactory selectivity can be obtained.

Experience at Standard of California's refineries has shown that selected lubricating oil stocks from California nonwaxy crude oils can be refined satisfactorily with sulfur dioxide without the addition of benzene. Lubricating oils above the range of SAE Grade 10 to 20 require increased temperatures and pressures.

Nitrobenzene Process. Commercial solvent extraction utilizing nitrobenzene was developed by the Atlantic Refining Co., and the following description pertains particularly to the plant operated by that company (*7*). Oil feed is mixed with a quantity of nitrobenzene layer from No. 2 extractor (to reduce viscosity), is brought to extraction temperature (30° to 100° F.), and is charged to the first of a series of five mixing and settling tanks. Nitrobenzene (100 to 300% of feed) is fed to the fifth tank. Heat exchangers on the feed stream are of the scraped type to permit operation at reduced temperatures on wax-bearing distillates and residual stocks. Raffinate and extract layers pass from No. 5 and No. 1 extractors to their respective recovery units. Recovery takes place under reduced pressure at temperatures of 215° to 350° F. Stripping steam is removed from the nitrobenzene by distillation. The water content of nitrobenzene has little effect on its usefulness for solvent extraction; therefore, it is not necessary to resort to thorough dehydration methods for the solvent.

A unique characteristic of nitrobenzene is that it operates satisfactorily on residual

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oils. Even though the solvent extraction system operates at a temperature below the solidification of the wax, the presence of solid wax crystals seems to have no deleterious effect on its action.

A modification of the nitrobenzene process, which utilizes nitrobenzene and sulfuric acid simultaneously, is in operation at the Sinclair Refining Co. refinery at Wellsville. N. Y.

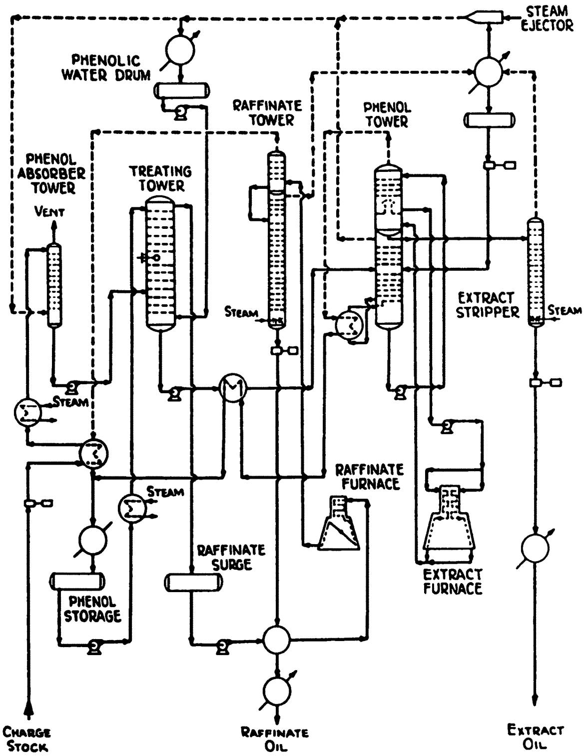

Figure 8. Flow Diagram of Anhydrous Phenol Extraction Plant

Information supplied by The M. W. Kellogg Co.

Chlorex Process (β,β'-Dichloroethyl Ether). The Chlorex process developed by Standard Oil (Indiana) (*8*) was patented in 1934. The first commercial plant to be put into operation was at Casper, Wyo., in June 1932. By August 1936 there were seven commercial plants in operation with a total throughput of 6150 barrels daily.

Because of its high solvent power, Chlorex extraction takes place at 75° to 150° F. Such ambient temperature operation effects heating and cooling economies but necessitates dewaxing prior to extraction or the use of scraped exchangers.

The Chlorex process utilizes simple countercurrent mixing and settling tanks (four to seven stages) or modern vertical packed towers. Solvent recovery involves conventional flash columns and strippers operated under vacuum (26 to 28 inches of mercury) at about 300° to 325° F. Low temperatures are desirable to minimize decomposition and formation of hydrochloric acid.

Phenol Processes—Anhydrous and Aqueous. The original patent describing utilization of phenol for solvent extraction is dated July 1908 (*2*). This was followed in 1922 by Polish patents (*20*) and in 1926 by a British (*11*) and a German (*24*) patent. These processes describe the use of phenol, either aqueous or mixed, with a variety of

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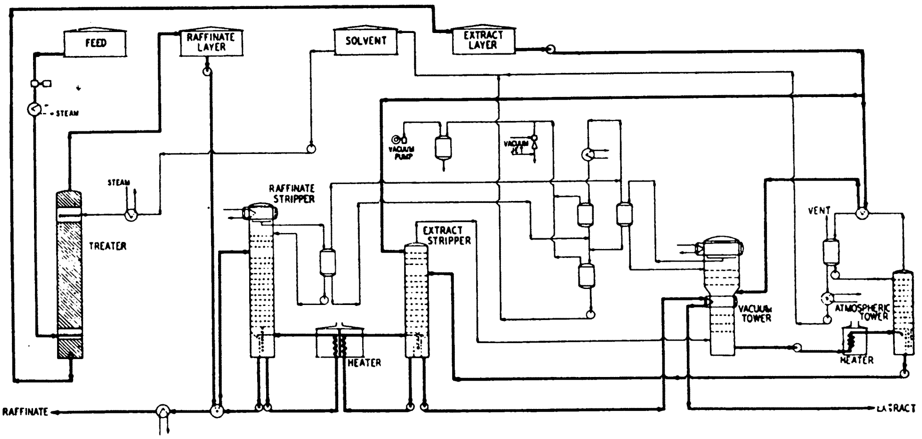

Figure 9. Flow Diagram of Aqueous Phenol Extraction Plant

materials. In 1928 Stratford and coworkers with Imperial Oil, Ltd. (a subsidiary of Standard of New Jersey), found that the phenol process, as disclosed in earlier patents, gave poor results on the stocks under consideration and in 1929 Stratford applied for a patent involving anhydrous phenol. This patent was granted December 10, 1931 (*26*). The first plant was put into operation by Imperial in Sarnia, Ont.

A flow diagram of an anhydrous phenol solvent extraction plant is shown in Figure 8. Raw distillate is passed through a tower in which it absorbs phenol from the recovery system vapor. The oil is then passed to the treating tower, generally a few sections above the bottom. Anhydrous phenol is introduced at the top of this tower. Phenolic water condensate from the solvent recovery system (about 9.5% phenol) is introduced at the bottom of the tower to effect reflux. A temperature gradient of 10° to 75° F. may be

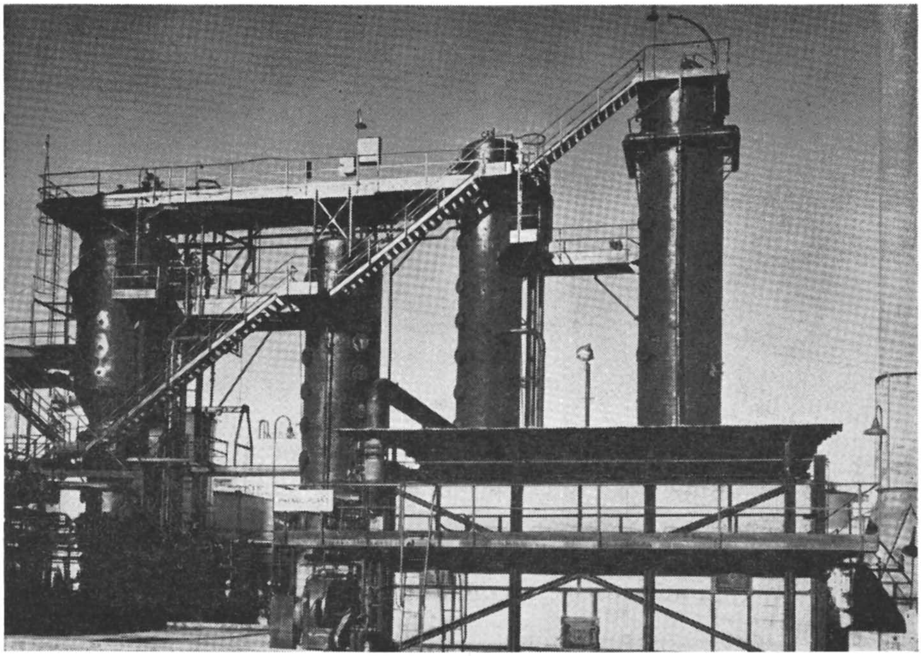

Figure 10. Aqueous Phenol Solvent Extraction Plant

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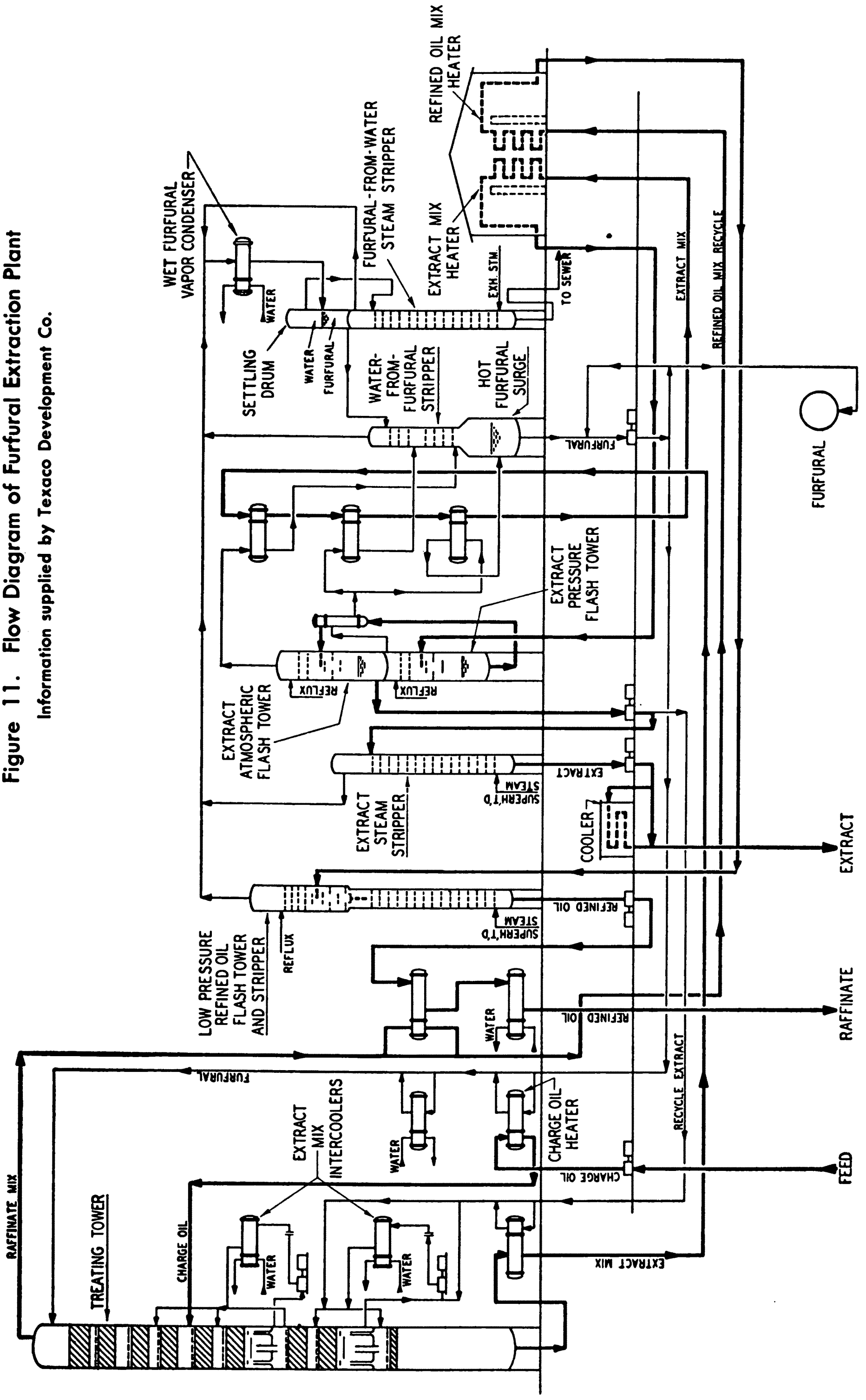

Figure 11. Flow Diagram of Furfural Extraction Plant

Information supplied by Texaco Development Co.

impressed on the tower; this also effects internal reflux. The raffinate layer leaving the top of the solvent extraction tower contains from 10 to 20% phenol. Raffinate and extract layers are freed of solvent in their respective solvent recovery systems which involve exchangers, fired heaters, flash columns, and vacuum steam strippers as indicated. Extraction tower design involves a combination of vertical and cross flow which ensures intimate contact between the two phases without channeling.

Whereas Stratford and his coworkers utilized anhydrous phenol to effect satisfactory solvent treatment of the oils under examination, aqueous phenol (up to 12% water) is necessary for phase separation at 100° to 175° F. when treating California-type low cold test lubricating oil distillates. Such a plant designed and installed by the Standard Oil Co. of California at its Richmond Refinery in 1934 is represented by Figures 9 and 10.

Distillate feed stock is pumped through a heat exchanger to the bottom of the packed solvent extraction treater; phenol containing a controlled amount of water is introduced into the top of the treater. The raffinate layer passes from the top of the tower through appropriate heat exchange into a raffinate recovery tower where, under high vacuum and with the bottoms circulating through a fired heater, the raffinate layer is stripped of phenol. The extract layer solvent recovery system consists of a vacuum flash tower, atmospheric pressure flash tower, and dry vacuum stripper. Use of these two high vacuum dry stripping columns provides constant water content in the solvent during operations on one stock.

Furfural Process. A patent involving furfural for solvent extraction of lubricating oils was issued to Eichwald of the Royal Dutch Shell Co. in 1925 (*10*). The first commercial application of the furfural process was at the Lawrenceville, Ill., refinery of the Indian Refining Co. in December 1933.

Modern furfural solvent extraction plants utilize vertical counterflow towers packed with about 20 feet of Raschig rings with redistribution equipment at about 4-foot intervals. Charge rates average about 35 gallons of oil per hour per square foot of over-all tower cross-sectional area. However, rates as high as 70 gallons per square foot per hour have been observed. A flow diagram of a typical furfural solvent extraction plant for lubricating oil is illustrated in Figure 11. Raw feed at a temperature of 110° to 220° F., depending on the nature of the oil, is introduced at the center of the extraction tower. Furfural is fed into the top of the tower at about 200° to 290° F. Recycled extract is introduced into the lower section of the tower for reflux. Likewise, internal reflux is effected by the temperature gradient which is brought about by introducing the solvent at an elevated temperature and by intermediate cooling systems. Furfural is removed from raffinate and extract layers in conventional distillation and stripping equipment.

The water content of furfural is critical and must be kept to a minimum. In order to dehydrate the solvent a pair of distillation columns is utilized. Condensed wet solvent separates into two layers in a settling drum. The top layer, which is lean in furfural, is separated into saturated solvent vapor and solvent-free water in the furfural-from-water stripper. The solvent-rich layer is separated in the water-from-furfural stripper into wet solvent vapor and dry furfural.

Azeotropic distillation is used to recover furfural from light gas oils, kerosenes, and Diesel fuels.

Duosol Process. The Duosol process developed by the Max B. Miller Co. (*28*) is an outstanding example of commercial adoption of a double solvent extraction process. Patents (*27*) for this process date from May 1933 and cover numerous aspects of the problem including a variety of paraffinic solvents (ethane, propane, butane, petroleum ether) and "naphthenic" solvents (wood tar acids, cresols, creosote, and phenol). Present commercial application utilizes propane and Selecto (a mixture of phenol and cresylic acid, normally ranging in composition from 20 to 80% phenol).

Propane acts as a raffinate solvent and as a deasphalting agent. For normal operating temperatures of from 60° to 150° F., wax is held in solution in the propane so that the advantage of solvent refining prior to dewaxing can be utilized. Distillation into cuts can be delayed until after refining and dewaxing.

In single solvent extraction processes, it is generally preferable to solvent treat dis-

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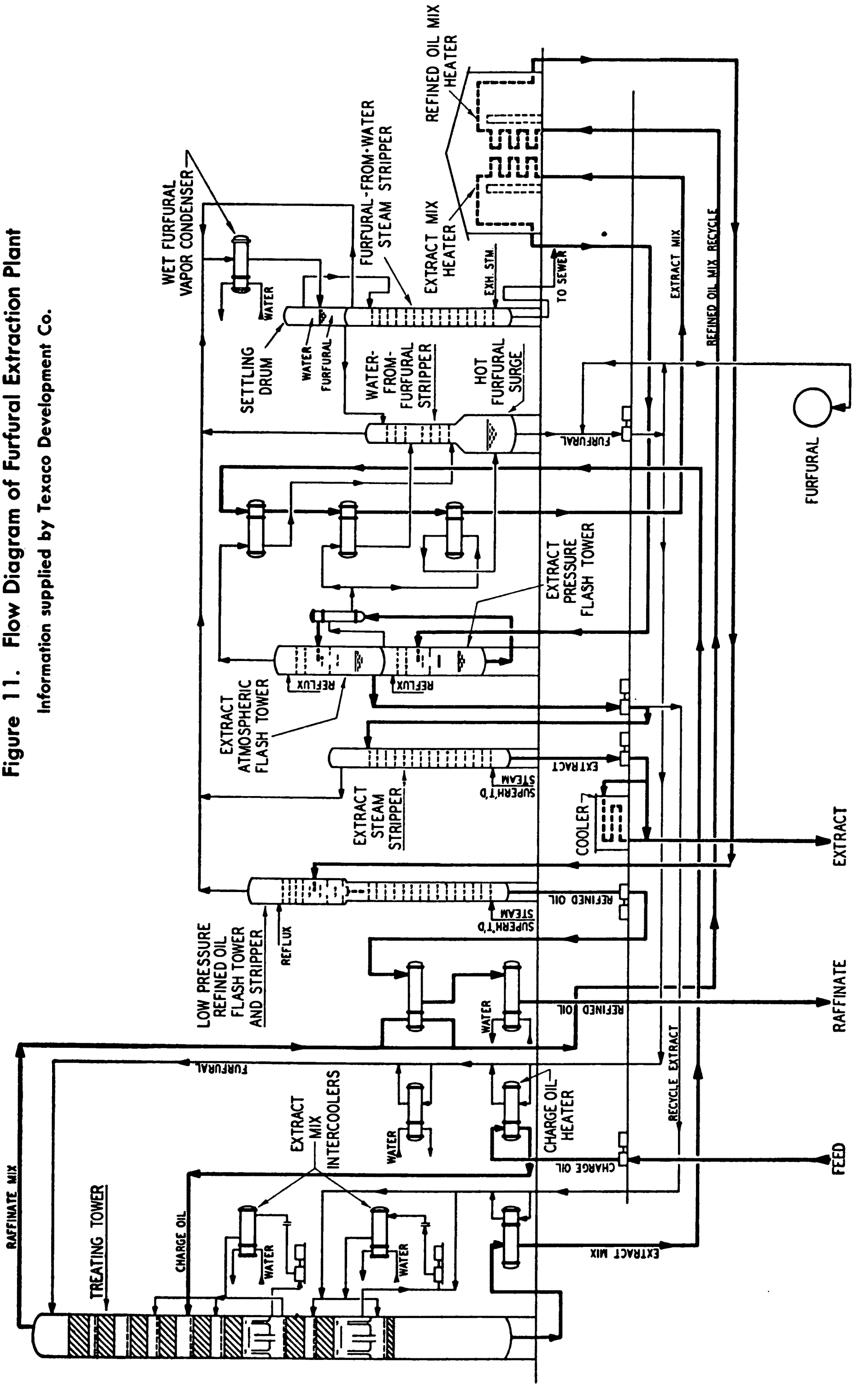

Figure 11. Flow Diagram of Furfural Extraction Plant

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tillate cuts and a deasphalted residuum to recover all lubricating oil fractions from a given crude oil. Duosol operation permits treatment of the whole range of lubricating oil components in a long residual stock of, say, 450° F. flash point. Distillate fractions may be treated separately if desired.

The practical range of operating temperatures is limited on the high side (about 150° F.) by the high vapor pressure of propane and on the low side by the tendency for emulsion formation as wax precipitates or possibly as phenol freezes as in high phenol content Selecto. Operation between these limits provides no difficulty because the solvent power of Selecto can be altered by changing the ratio of phenol to cresylic acid.

Solvent dosages in the Duosol process are usually high, up to 400%. Experience has indicated that by carefully coordinating the effects of treating temperature and Selecto composition, a point of optimum operation can be attained that will permit minimum solvent dosages and maximum throughput.

The effects of operating variables on the Duosol extraction system are complex and are best determined empirically. As would be expected, an increase in Selecto results in increased refinement and reduced yield. An increase in propane results in improved raffinate color and decreased viscosity index, but its effect on carbon residue is unpredictable.

Figure 12 presents the flow diagram of a modern Duosol solvent refining plant. Figure 13 shows the extraction system. Charge oil enters the process through a mixer into the third of seven countercurrent extraction stages. Selecto is introduced into the No. 7 extractor and pure propane into the No. 1 extractor. The raffinate layer passes through the upper sections of the system, rising to the top in each vessel and carrying with it the refined oil. The extract layer which settles to the bottom is pumped countercurrently to the raffinate layer. Extractors 1 and 2 effect a form of reflux on the system. Additional reflux within the system is imposed by a temperature gradient. Raffinate and extract layers pass, respectively, from separator No. 7 and separator No. 1 to their solvent recovery systems. The two recovery systems are similar: propane is recovered at elevated pressure (about 250 pounds per square inch absolute) in the first column, and the bottoms pass to the second column (85 pounds per square inch absolute), from which Selecto is passed overhead to a drying tower. Two stages of stripping are employed (85 pounds per square inch absolute and vacuum) to remove final traces of solvent from the raffinate and extract streams. Vapor from the top of the dryer (a constant boiling mixture) is separated into two layers, and the water layer is used to generate stripping steam in a closed system.

Process Selection

Process selection for new solvent extraction facilities involves numerous considerations; some may be evaluated numerically and others can only be evaluated on the basis of judgment, experience, and personal taste. Approximate numerical evaluation may be computed for installation, operating and royalty costs, yields, and product quality. However, the important considerations of design and operating experience, availability of construction materials, solvent availability, toxicity, stability, and price trends, and process flexibility are not so tangible. Even more intangible, but likely to influence the refiner, are such considerations as the popular acceptance of various processes and the relation between the prospective builder and the licensor of a process. As illustrated by Figure 3, the three processes which are used to refine the bulk of the nation's solvent-treated lubricating oil are furfural, phenol, and Duosol.

Consideration of installation costs cannot be restricted to the solvent refining step. A residuum of 460° F. flash point usually will contain all usable lubricating oil. In addition to the cost of solvent extraction facilities, the expense of equipment to fractionate the oil into usable cuts, to deasphalt, to dewax, and to clay filter, all must be

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Figure 12. Flow Diagram of Duo-sol Solvent Extraction Process

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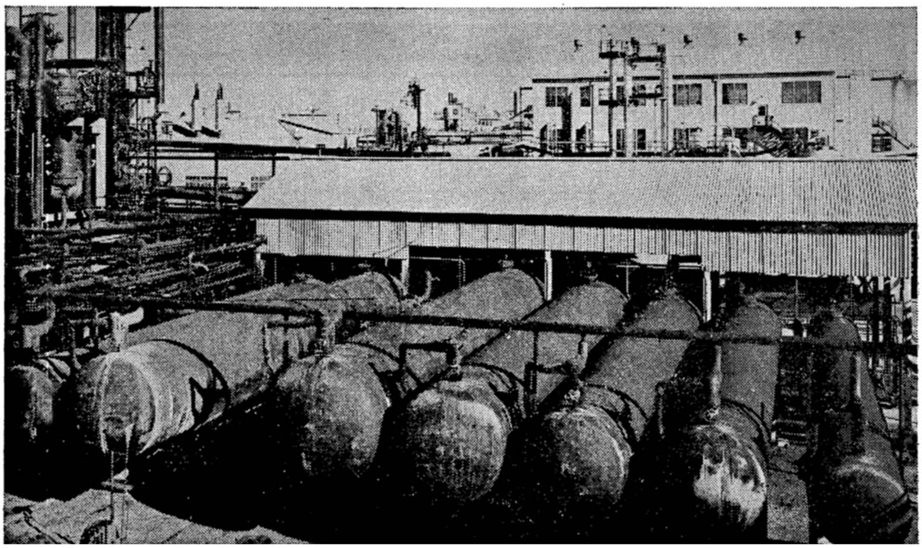

Figure 13. Duosol Plant Extractors

taken into consideration. Fractionating and deasphalting equipment will be about the same for the single solvent processes, phenol or furfural. If the Duosol process is used, no deasphalting plant is necessary and the fractionating equipment can be located downstream of the solvent refining step either on the raffinate or dewaxed oil stream. On the other hand, equipment cost for a Duosol plant is higher than that for a single solvent plant. Piping is slightly more costly for phenol than for furfural plants; however, the treating tower is more costly in furfural than in phenol plants. Dewaxing plants in all cases would be the same if the Duosol raffinate were fractionated prior to dewaxing. Clay-treating facilities for operation on a number of narrow fractions require more filter equipment than for combined clay-treating and fractionation of a long cut. The result of these counterbalancing items is a highly competitive situation which can be decided only on the merits of each individual case.

Fuel and utilities costs for the Duosol process frequently are slightly higher than for deasphalting and single solvent refining because of higher solvent dosages. Fuel costs run 20 to 30% higher in phenol than in furfural plants because of water in the solvent. When Duosol is used, less fuel is required for the fractionating equipment which can be located downstream of the solvent refining step. Labor costs are about the same for all processes; usually four men per shift, exclusive of supervision, are required for Duosol or deasphalting plus single solvent refining. Chemical costs for Duosol operation may tend to run slightly higher than those for single solvent operation because of higher solvent make-up which is roughly proportional to circulation.

Royalty cost also is a factor in process selection. It varies with the individual plant under consideration; hence, its economic significance cannot be evaluated in general terms.

Considerable data have been published and additional unpublished confirmatory data have been collected which indicate that for a given degree of refinement, measured by increased viscosity index or decreased viscosity gravity constant, the quality of refined oils produced by all popular solvent refining processes is so nearly equivalent that there is no clear-cut generalization possible which would favor one process over another. From the point of view of economy, two other considerations are important—namely, selectivity and refining power. Kalichevsky (*19*) has defined selectivity as the ratio $\frac{P_0 - P}{L}$. He also defines refining power as $\frac{P_0 - P}{S}$. Selectivity provides an indication of yield versus degree of refinement. Refining power is a measure of the quantity of solvent needed to secure a desired improvement in oil properties. For each solvent, a temperature and solvent dosage can be chosen which will result in the same selectivity. On the other hand, for a given dosage and selectivity, the refining powers of phenol and furfural are nearly equivalent and slightly higher than the solvent power of Chlorex (the only other solvent evaluated).

Numerous process selection studies have led the author to the conclusion that for phenol, furfural, and Duosol processes, correlations of yield versus viscosity index (or any other measure of degree of refinement) will be identical.

Evaluation of Stocks for Solvent Refining

Analytical techniques to evaluate potential lubricating oil stocks are essential to a refiner's planning program. When sulfuric acid was the sole chemical used to refine burning oils and lubricants, it was a simple matter to carry out acid-treating experiments on a small scale in the laboratory, and results so obtained were quite reliable. With the advent of solvent treating, analytical techniques were developed which consisted of single or multiple-batch laboratory extractions in conjunction with correlations based on plant experience (*17*).

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Data may be obtained from a large number of batch solvent extractions and binodal curves may be plotted on triangular diagrams as described earlier in this paper. Such information will permit calculations of the number of stages and solvent requirements. Considerable specialized equipment and care are necessary to obtain reliable data of this nature.

Many licensors and contractors who must obtain data from which to design and build solvent extraction plants utilize large, elaborate pilot plants which simulate commercial plant conditions. Many refiners have constructed such plants to obtain data from which to guide commercial equipment and prepare samples for engine test evaluations. Plants of this sort cost $200 to $300 daily to operate. An evaluation of a single stock may require weeks and cost thousands of dollars.

During recent years pilot scale equipment, smaller than the prototype pilot plants described and capable of operating with exceedingly high efficiency, has been designed. Such equipment as the York-Scheibel solvent extraction tower and the Podbielniak countercurrent centrifugal mixer and extractor are typical. Data from this equipment may be correlated with commercial performance.

Furby (*12*) has developed a method for evaluating stocks in the lubricating oil range that results in a breakdown of components into asphaltenes, resins, wax, and dewaxed oil and provides a yield–viscosity index relationship for the dewaxed oil. The author has found such analyses very useful and inexpensive for evaluating a large number of potential lubricating oil stocks. Furby's method utilizes petroleum ether to precipitate asphaltenes, a fuller's earth–petroleum ether fractionation to isolate resins, methyl ethyl ketone–benzene dewaxing on the deasphalted-deresinified material to separate wax, and an adsorption fractionation to provide cuts from which the yield–viscosity index relationship for dewaxed, solvent-refined oil is obtained.

From adsorption analysis data, it is possible to calculate theoretical yields of deoiled wax, asphalt, resins, and solvent extraction yields of waxy raffinate. Nearly 100 different stocks have been so evaluated by California Research Corp. during the past few years and many of these data have been correlated with operations in refinery equipment and with pilot plant operations.

Figure 14 illustrates a comparison between solvent extraction yields predicted from adsorption analyses and actual raffinate yields in commercial solvent extraction plants. Few commercial yields have ever equaled those obtained by adsorption analyses and none has exceeded those values; hence, curve *A* (45° angle) represents the ultimate in solvent extraction. Curve *B* represents solvent extraction in commercial equipment on stocks ranging in viscosity index from +25 to +110, and for viscosity index improvements ranging from 30 to 130. Extremely viscous stocks or those which require a very large viscosity index improvement have been observed to follow more closely lines *C* and *D*.

For convenience "dewaxed oil" is defined as 0° F. pour point oil, and "wax" as material containing 0% oil. A useful rule of thumb is that a 5° F. increment in pour point is

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about equal to one point of viscosity index of the dewaxed oil. This fact when combined with the slope of the yield–viscosity index relationship curve obtained from the adsorption analysis will give a clue to the effect of pour point on the yield in the solvent refining plant. Observations of many yield–viscosity index correlations indicate that the percentage solvent extraction loss per unit gain in viscosity index of dewaxed oil $\left(\frac{L}{VI}\right)$ will range from 0.5 for wax-free California stocks through a value of approximately 1.0 for California waxy and mid-continent stocks to as high as 1.5 or 1.6 for Arabian stocks.

Prediction of commercial plant operating conditions is essential to provide design data for new plants or guide the refiner with existing plants.

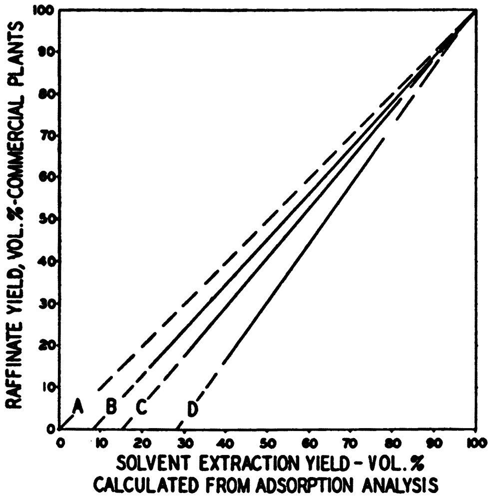

Figure 14. Comparison of Commercial Extraction Plant Yields vs. Yields Estimated from Adsorption Analyses

A = Commercial yield equals absorption yield
B = Normal relationship
C and *D* = Relationships for difficult extractions

Pilot plants can be used to predict solvent dosages and other operating conditions, but such operations are expensive and should be minimized. It is, therefore, desirable to establish correlations of operating variables. Kalichevsky (*16*) describes correlations of solvent extraction equilibrium data which indicate that the percentage dissolved in the extract layer, L, is related to the solvent dosage, S, by the expression

$$\log L = a \log S + b \tag{1}$$

Figure 15 illustrates such a dosage-yield relationship for a light lubricating oil distillate from California wax-free crude treated in commercial equipment with aqueous phenol (8% water). Figure 16 presents a similar correlation of data for Duosol treatment of California waxy and Arabia residua.

Compositions of the raffinate and extract layers must be predicted to establish material balances from which equipment can be sized. Triangular diagram data can be used to present equilibrium data, but this requires tedious laboratory studies and a large number of measurements. A mathematical approach suggested by Kalichevsky (*18*) makes use of existing data to predict the effects of variations in operating conditions on extract and raffinate layer compositions. Expressed graphically, a straight-line relationship exists between the logarithm of the solvent dosage and logarithm of the solvent content of the raffinate layer. Figure 17 summarizes data that corroborate this straight-line relationship. Curve *D*, which represents nitrobenzene treatment of a mid-continent distillate, is obtained from Hunter and Nash's data (*15*), which was used by Kalichevsky in the derivation of this correlation method. Curves *A*, *B*, *C*, *E*, and *F* represent a variety of California stocks treated at 120° and 140° F. with aqueous and anhydrous phenol ranging in water contents from 0 to 10%. An interesting observation is that the slopes of all of these lines are nearly equal and are very close to a value of $-1/3$. From these data it is suggested that for single solvent extraction the concentration of solvent in the raffinate layer is proportional to the cube root of the reciprocal of the solvent dosage, expressed in volume per cent. Such a relationship is found useful in predicting the effect of changes in solvent dosage on material balances in single solvent extraction systems. The effect of temperature is difficult to predict because changes in temperature alter the quality of the raffinate oil and therefore its affinity for solvent. Likewise, Duosol treatment is not straightforward because of complications which arise from the introduction of propane, the precipitating solvent.

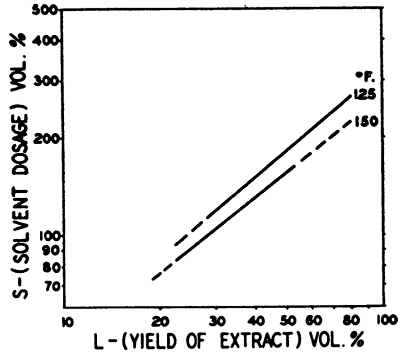

Figure 15. Dosage-Yield Relationship, California Wax-Free Light Lube Distillate Treated with Aqueous Phenol (about 8% H_2O)

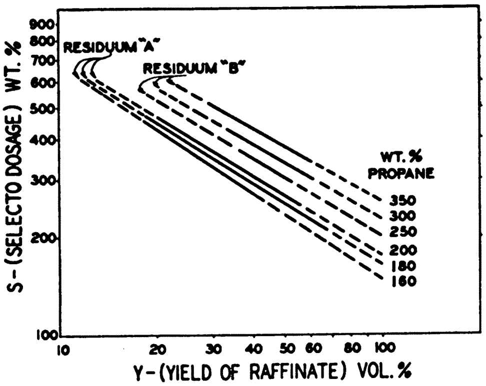

Figure 16. Duosol Treatment

A = California waxy residuum
B = Arabia residuum (constant temp. about 140° F.)

In summary, it is possible to predict for a given stock the yield which can be expected for any given viscosity index of the finished oil. Given this yield and a minimum of experimental data, it is possible to predict the necessary solvent requirements; given the solvent requirements, material balance relationships may be obtained from correlation which give the concentration of the solvent in the raffinate layer. Experience has indicated that the weakest link in the chain is the prediction of solvent requirement for treatment to a given yield or viscosity index.

Process Design Considerations

The height of a solvent extraction column is determined by the number of theoretical stages and by the height equivalent to a theoretical stage. The number of theoretical stages can be determined from consideration of trilinear diagrams, provided sufficient equilibrium data are available to construct the binodal curves and determine the tie lines. The effect of reflux must not be overlooked, for by this means it is possible to produce separations which would not be possible even with an infinite number of stages, and likewise proper use of reflux can be used to offset poor selectivity of a solvent. By such means the height of a column is shortened; on the other hand, reflux requires additional solvent dosages and a higher energy input per unit of feed.

Prediction of the height equivalent to a theoretical stage presents a difficult problem. A lack of fundamental data necessitates an empirical approach, and at the present time pilot plant or commercial experience is the only satisfactory method for prediction of height requirements for packed countercurrent solvent extraction equipment.

Colburn and Welsh (*3*) have discussed the application of individual transfer resistances in countercurrent liquid-liquid extraction and have considered in a preliminary way the effects of viscosity, density, and diffusion coefficients on individual H.T.U. They obtained correlations which indicated that, other variables being equal, the phase with the largest H.T.U. should be made discontinuous. Additional work is required to provide fundamental data for individual film resistances and individual H.T.U. which could be used to interpret existing empirical data and permit predictions from physical properties.

The diameter of solvent extraction equipment, particularly packed solvent extraction towers, is a function of the flooding rate. Maximum efficiencies appear to exist when operating just below the incipient flooding point for the equipment. Colburn (*23*) has suggested a correlation of flooding data for packed extraction columns which involves relative flow rates and the difference in specific gravities of the two phases. Undoubtedly other physical properties such as viscosity and interfacial tension are important. Although it is suggested that a conservative safety factor of 1.75 times the flooding area be used when considering the data, it should be emphasized that too great a safety factor will result in a tower of excessive diameter and operation at efficiencies below normal.

An important feature in the construction of continuous countercurrent extraction towers is the design of the nozzles through which the solvent and oil feed enter. Nozzles should be designed to distribute the stream evenly over the cross-sectional area of the tower in order to minimize channeling and to make maximum use of the packing near the inlet. Consideration should also be given to the use of intercoolers to enforce a temperature gradient.

Heat exchangers are a large fraction of the investment cost of modern solvent extraction plants. Careful heat exchanger selection is necessary to minimize the cost of large solvent recovery systems. Recovery system towers can be considered as flash towers except for the final strippers in which last traces of solvent are removed. Furnaces should be designed to maintain low heat absorption densities and therefore to keep the individual skin temperatures as low as possible in order to prevent coking and decomposition of the solvent. A circulating hot oil heating system has been employed in one modern furfural plant (*21*). Although some solvents are very stable, furfural, which is one of the most commonly used solvents, appears to have a definite upper temperature limit beyond which decomposition is accelerated.

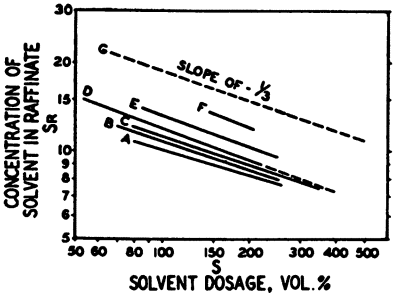

Figure 17. Effect of Solvent Dosage on Concentration of Solvent in Raffinate Layer

Curve	Distillate	Solvent	Temperature, ° F.
A	Calif. naphthenic, 72 S.S.U. at 210° F.	Aqueous phenol, 10% H_2O	140
B	Calif. naphthenic, 72 S.S.U. at 210° F.	Aqueous phenol, 7% H_2O	140
C	Santa Fe Springs, dewaxed	Aqueous phenol, 2% H_2O	140
D	Mid-continent	Nitrobenzene	50
E	Calif. naphthenic, 42 S.S.U. at 210° F.	Aqueous phenol, 7% H_2O	140
F	Santa Fe Springs, dewaxed	Anhydrous phenol	120

Instrumentation on the solvent extraction equipment will usually consist of recording flow and recording temperature controllers on the feed stream, a pressure controller on the raffinate exit line, temperature recorders on the column intercoolers, and a liquid level recording controller at the liquid-liquid interface to set the extract layer withdrawal rate.

Solvent losses constitute an expensive item which must be predicted when designing and evaluating commercial solvent extraction processes. A solvent make-up cost of $250,000 annually would not be unusual for a large lubricating oil solvent extraction plant; of this loss, it is likely that only 40 to 60% would be found in the residual streams from raffinate and extract strippers. The balance would disappear as leakage, decomposition, and unexpected upset losses.

Solvent make-up requirement generally is expressed as per cent of solvent circulation. For furfural and phenol this value will run about 0.03%, both for single solvent extraction and Duosol plants. Propane losses in Duosol plants and in propane deasphalting plants will be from 0.1 to 0.5% of circulation; an average of 0.2% would be a reasonable estimate.

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Future Developments

It certainly is apparent that today's countercurrent packed extraction tower is not the ultimate in contacting and separating equipment. These huge towers, 40 to 80 feet in height, are often equivalent to only 1.5 to 4 theoretical stages. The desirability of a more compact, economical, efficient device is self-evident.

One attempt to improve the situation has been successful for small to moderate scale operations where high purity is required—namely, the Podbielniak centrifugal countercurrent contactor and separator, which dominates the solvent extraction phase of penicillin manufacture.

Most commercial extraction solvents currently are utilized to produce an improved raffinate. Recently, American Cyanamid announced availability of various dipropionitriles which are capable of recovering pure aromatics with exceptional selectivity. Extractive distillation to recover benzene or toluene from petroleum fractions has become an accepted commercial process. The possibilities of utilizing selective adsorption for concentration of aromatics has been receiving serious consideration.

Product quality and manufacturing cost evaluations have made it apparent that many spray, white, and lubricating oils can be benefited by a combination of solvent extraction followed by acid treatment; such benefits are further enhanced by utilization of continuous acid treating in place of the classical batch method.

It is hoped that the next twenty-five years will see the development of chemical engineering techniques for predicting solvent dosages and operating characteristics for extraction processes which will utilize basic physical chemical properties and the fundamental concepts of mass transfer involving individual film resistances and driving forces.

Acknowledgment

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Nomenclature

K = ideal distribution law constant
C_1 = concentration of solute in first of two immiscible phases
C_2 = concentration of solute in second of two immiscible phases
F = composition of feed to solvent extraction operation
VGC = viscosity gravity constant
R_n = composition of solvent-free raffinate from nth theoretical stage
E_1 = composition of solvent-free extract from first theoretical stage (no reflux)

r_n = composition of raffinate layer from *n*th theoretical stage
e_1 = composition of extract layer from first theoretical stage (no reflux)
O = operating point on trilinear diagram
J = composition of mixture of feed and solvent or of raffinate and extract layers
f = composition of feed saturated with solvent
f_e = composition of extract layer in equilibrium with saturated feed
f' = composition of extract layer for case of infinite reflux
E = composition of extract (solvent-free) from treater with reflux
e' = composition of extract layer from treater with reflux
y, e = construction points on trilinear diagram
k' = operating point for enriching section of extraction column
Po = an additive property of feed
P = an additive property of the product (raffinate)
L = extraction loss or yield of extract, % of feed
S = solvent dosage, % of feed
VI = viscosity index
a, b = constants
y = raffinate yield in solvent extraction
H.T.U. = height of a transfer unit

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Petroleum Distillation

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Today's petroleum distillation plants are compared with the units in existence in 1925, and a review is presented of the advances during the past 25 years in construction practices and materials, instrumentation, and engineering design, which have made possible the current technology. The theory and application of special processes, such as azeotropic and extractive distillation and Hypersorption, are discussed. The development of molecular distillation and rotary columns is described to indicate possible trends to be expected in the future.

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Twenty-five years of progress in the distillation of petroleum. That means going back to 1925, and some 32,245,073,000 barrels of petroleum have been produced in the United States since then; substantially all of this production has been distilled—part of it several times. This paper reviews the development of distillation processes, equipment, theory, and engineering during this period and suggests probable future innovations.

Commercial Distillation Units

In 1925 petroleum refiners were on the verge of an extended use of fractionation in all phases of refining, but because of the normal time lag between the most advanced technology and general practice, the predominant type of equipment being used for primary crude distillation consisted of a battery of horizontal cylindrical shell stills with separate fire boxes arranged so that residual oil would flow by gravity from one shell to the next in the series. Direct firing was applied to each still to produce vapors which were condensed and collected separately. Generally, the condensers were of the total condensation type, although partial condensation to separate the vapors further was used in some units. A typical arrangement of this kind is shown in Figure 1. A few enterprising refiners were making use of the partial pressure effect of live steam injection to increase the amount of overhead obtainable without cracking.

The most advanced primary crude distillation units of this period, however, were constructed with continuous pipe stills for initial heating and partial vaporization, the effluent from the pipe still heater being discharged into a large evaporator, where the vapors were separated from the residual liquid.

The flue gases from the heater were introduced into a firebrick enclosure around the evaporator to compensate for heat loss and to supply additional heat required for enthalpy of vaporization. Vapors produced from the evaporator were then fractionally condensed in a battery of dephlegmator condensers. Although normally termed "condensers," these vessels were actually small rectifying columns with a cooling coil at the top and a steam heating coil at the bottom; baffle plates of various types were installed in the body of the column to effect some vapor-liquid contact. The cooling coil at the top of the vessel induced some reflux and the steam heat at the bottom prevented some light ends from escaping with the bottoms product. Thus, as illustrated in Figure 2, several fractions were produced.

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Gasoline and kerosene rerunning was accomplished primarily in horizontal batch shell stills heated by direct firing or internal steam coils and surmounted by a vertical rectification column with partial condensers to supply reflux. The rectifying column in some installations was packed with iron rings, pipe fittings, earthware crocks, tin cans, or any suitable material readily available. In other units a fairly common type of column was the Heckmann bubble cap tower.

A schematic diagram of the type of redistillation unit described is shown in Figure 3. The most advanced redistillation units were being supplied with continuous pipe stills for initial heating and partial vaporization, followed by bubble cap fractionating columns to produce the final light and heavy fractions.

In cracking plants of this period, distillation technique was probably more advanced than in any of the refining processes previously mentioned. The bubble cap fractionating column was commonly used in these units to split the synthetic crude produced from the cracking stills into naphtha and residuum fractions. It was general practice in the newest installations to provide both a rectifying and a stripping section complete with reflux, bottoms reboiling, and simple automatic controls.

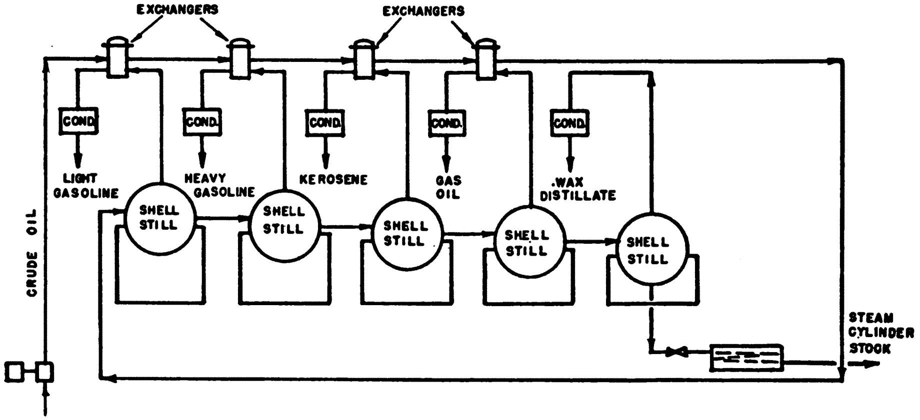

Figure 1. Continuous Battery of Shell Stills

Vacuum distillation was relatively new in 1925. In fact, commercial distillation at 300 mm. of mercury absolute pressure was rather exuberantly termed "high vacuum." Some batch horizontal shell stills were being utilized in vacuum distillation to produce lube oils, but extensive development in this field occurred later.

It is apparent that around 1925 distillation equipment in the petroleum industry varied in design and complexity from the simple horizontal shell stills with fractional vapor condensation to the continuous pipe stills with the progenitor of the present bubble cap fractionating columns. The basic processing principles were being rapidly extended, and the foundation was well established for the further development of distillation technology.

From our vantage point today, we can observe the results of this expanding knowledge. Modern refining units are replete with bubble cap fractionating columns of manifold sizes and shapes. The principles of rectifying and stripping, side cutting and side cut stripping, circulating reflux, and bottoms reboiling are universally applied. Examples of the extent to which distillation is applied today are: vacuum distillation columns up to 36 feet in diameter operating at 40 mm. of mercury absolute pressure; two-stage primary crude distillation units producing as many as seven fractions; gasoline stabilization with subsequent separation of ethane, propane, butanes, and pentanes; 70-plate columns employed in butane-isobutane splitting; superfractionation in the equivalent of 100-plate columns to produce high octane blending stocks; and low temperature distillation to separate normally gaseous hydrocarbons such as methane, ethylene, and ethane.

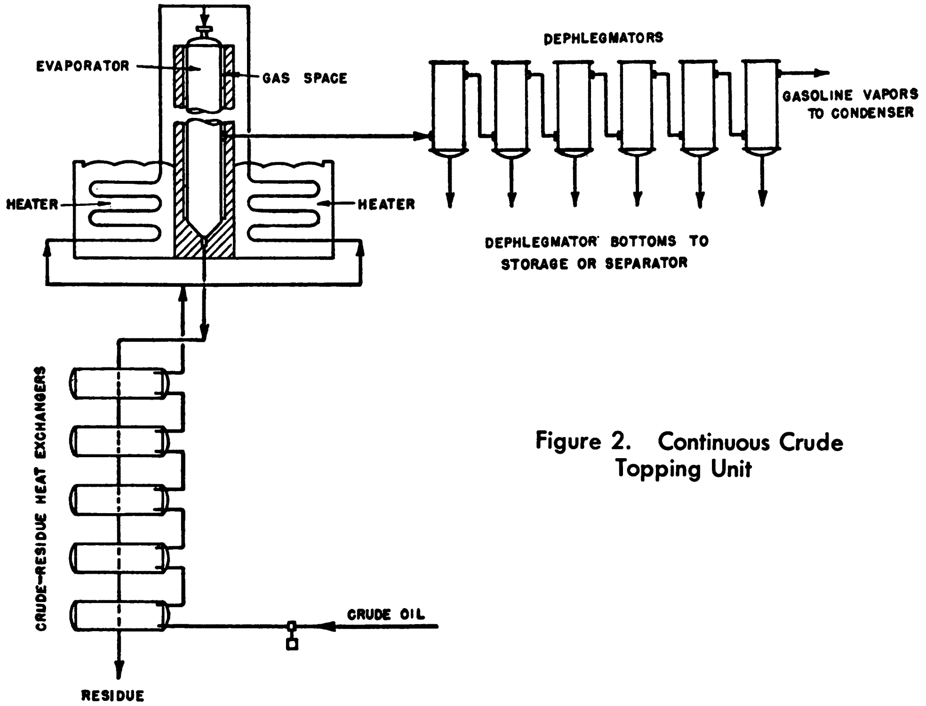

Figure 2. Continuous Crude Topping Unit

In fact, taking a short look into the future, it is difficult to envisage further startling developments in conventional petroleum fractionation units. Improvements in bubble cap and bubble plate design will undoubtedly be introduced, but the most strenuous efforts will probably be directed to methods of replacing the bubble cap with more efficient types of contactors. Steps in this direction have been made in the recent application of Stedman packing (*5*), the development of the corrugated metal lath tray (*51*), and the Koch Kascade tray (*30, 38*), which, when installed, reflect considerable reduction in tower size and initial cost for a given throughput and degree of separation. Process changes to produce further operating economies will continue to appear, but present trends indicate that considerable research is being applied to develop other methods of separation which will supplement the art as exemplified by simple or ordinary distillation.

Construction Practices and Materials

Much of the commercial distillation art practiced today would have been impossible without a preceding development of equipment to handle the processing conditions involved. In 1925 the vessels used rather extensively for primary crude distillation were constructed of light-wall steel plate, overlapped and riveted at the ends. Such vessels were adequate for low pressure, low temperature operation, but with the advent of cracking processes requiring pressures up to 1000 pounds per square inch gage and temperatures up to 800° F., the riveted joint was inadequate. Such precautions as calking the seams and welding around the top of the rivet heads proved ineffectual against vapor and liquid leaks. Consequently, new methods of fabricating pressure vessels were investigated, starting with forge-and-hammer lap welding and proceeding through machine forge welding to oxyacetylene and electric-arc welding. After a time, the fusion electric arc welding and annealing process was developed and is almost exclusively used in current fabrication practice.

Concurrently with the advance in fabrication methods came the independent improvement of pumping practice. The positive displacement pump, predominantly the reciprocating steam-driven type, was commonly used in 1925 to transfer liquids; most refiners were still suspicious of the newer centrifugal and rotary pumps. Higher capacity requirements for the tube-type oil heaters and continuous fractionating columns, however, soon forced the acceptance of the centrifugal pump. The development of continuous distillation units prevalent today was greatly expedited by the prior production of pumps capable of operation at temperatures up to 800° F. and pressures up to 1000 pounds per square inch gage.

All the obstacles in the path of distillation progress, however, were not equipment fabrication and design problems. It was discovered very early in the running of sour crudes that the shell still corroded severely at the vapor-liquid interface line and in that portion of the shell in contact with vapors. At the same time severe corrosion in pipe stills and tube stills, along with overheating and coking, resulted in expensive equipment failures. These problems started metallurgists on a chain of developments which produced the corrosion- and heat-resistant alloys used in modern oil heaters and the alloy liners used in distillation columns.

The progress of distillation in the petroleum industry was not independent of advancements in other fields, but rather was dependent upon, and to some extent followed metallurgical developments and the refinement of oil heaters, pumps, and heat exchangers. It is probable that further innovations in distillation methods will be equally dependent upon engineering developments in other fields.

Instrumentation

The march of refining techniques and equipment design during the past 25 years has been matched, step by step, by advances in instrumentation. Twenty-five years ago the few instruments available were used primarily as a guide to operation, and it was perfectly possible to control a batch still with only two or three thermometers and a hydrometer, to yield products adequate for the needs of that period. Today we depend on instruments to control distillation units and anticipate trends with greater speed and accuracy than is possible by an operator.

It has been said that we have had four eras in instrumentation:

1. The pressure gage era
2. The recorder era
3. The controller era
4. The analyzer era

This trend can perhaps be best exemplified by the experiences of one refinery. In 1922, the Los Angeles Refinery of the Union Oil Co. had only fifteen instruments, principally thermometers and pressure gages. By 1927 this number had grown to 1900, and today more than 11,000 instruments provide smoothness of operation through control of heat, pressures, velocities, and product characteristics. These instruments include valve positioners, liquid displacement meters, indicating, recording, and controlling devices for temperature, pressure, flow, and liquid level, and indicating and controlling analyzers for carbon dioxide, oxygen, hydrogen, pH, concentration, density, end point, and initial boiling point.

The movement to analytical instruments for control purposes is very significant and important. The increasing demand for specialized products requires, for the control of operations, instantaneous analytical information of great variety, obtainable only by instrumental methods. The analyzer era had its inception perhaps a decade ago, and one very impressive trend has been the tremendous advance made in the instrumentation of analytical techniques and methods for automatic operation, recording of data, and the controlling of processes by the nature of the product. Among the physical properties peculiar to petroleum refining which can now be measured, and thus controlled, are density, refractive index, thermal or electrical conductance, radiant energy absorption, pH, heat of combustion, and viscosity. In fact, it is no longer a question of what can be done, but whether the process will justify the use of more expensive instrumentation.

Every new instrument developed to solve or aid a given situation, by its unforeseen versatility and applicability, develops a host of demands for its services in solving other

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problems and questions, formulated in many cases through having a method of answering them. In this, then, lies the probable future development in this field.

Engineering

Construction of the distillation units of 1925 was based to a large extent upon the practical experience and know-how of refinery men rather than upon theoretical design methods. In fact, the theory and practice of distillation which had been developed primarily by the wine industry were not adopted by the petroleum industry until the widespread use of the automobile forced the refiners to better distillation methods to increase their yield of gasoline and to improve its quality.

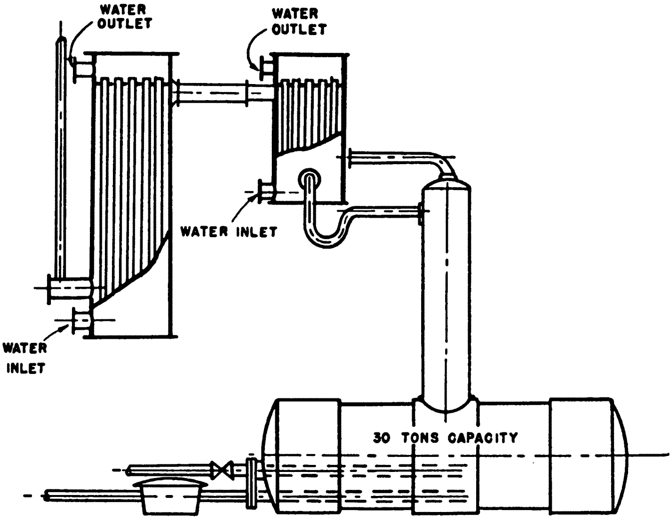

Figure 3. Gasoline Redistillation Still

A mathematical procedure for the design of fractionating towers developed by Sorel (*54*) in 1893 had little acceptance by the petroleum industry because it was based on treatment of binary mixtures, such as alcohol and water; the required vapor-liquid data on petroleum products were in general not available; the calculations were laborious; the original publication was in French and not widely available to American industry; and the builders of refinery equipment were seldom staffed to use the procedure.

However, the picture was changing. Petroleum was becoming the greatest user of distillation equipment. In 1922 the Division of Industrial and Engineering Chemistry of the American Chemical Society thought the subject important enough to hold a Symposium on Distillation. Among the papers presented was one by Lewis (*33*) with modifications of Sorel's method which simplified computations and made possible presentation of results in graphical form. Another by Peters (*44*) introduced the concept of the height equivalent to a theoretical plate. However, probably the greatest practical advance of this period occurred in 1925, when McCabe and Thiele (*39*) advanced their graphical method for the solution of distillation design problems. Although it has been improved somewhat, the basic procedure is still in use today.

These basic methods were the inspiration for scores of papers, ranging from simplifications based on various assumptions to shortened rigorous mathematical derivations applicable to more or less specific distillation problems. Among these may be mentioned those of Fenske (*19*). Dodge and Huffman (*13*), Smoker (*53*), Jenny (*27*), and Underwood (*56*).

While substantially all early procedures were developed for binary mixtures, preliminary steps were being made to apply them to multicomponent mixtures. The concept that aided materially in this application was the utilization of key components as exemplified in the work of Lewis and Wilde (*36*) and Lewis and Smoley (*35*) about 1930.

In 1932 several methods for applying design calculations to multicomponent mixtures were presented at a symposium of the AMERICAN CHEMICAL SOCIETY's Division of Petroleum Chemistry. Noteworthy among these were the algebraic procedure of Lewis and Matheson (*34*), the graphical procedure of Cope and Lewis (*9*), and the absorption factor method of Brown and collaborators (*6*). As in the case with those for the binary systems, these early multicomponent methods have been generally modified by later investigators. Most recently the work of Scheibel (*49*) and Underwood (*55*) in simplifying the calculations necessary to determine the exact number of trays required in a multicomponent distillation by the introduction of a function G, which permits graphical representation, has been of interest.

Of importance in evaluating the many suggested procedures and making them more useful to the design engineers have been the two comprehensive series of papers on design methods and applications of thermodynamics by Edmister (*17*). Furthermore, recently published texts and handbooks summarize the more important developments made during and since World War II and thus assure that graduates of our engineering schools will be cognizant of this work.

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Need for Fundamental Data. The major obstacles to the use of the methods previously discussed in the design of equipment for the processing of petroleum have been, and are, the paucity of fundamental physical and equilibrium data as well as the lack of exact knowledge of the composition of feed and product streams. This was recognized early, and by the late twenties papers were appearing containing data on individual hydrocarbons and on mixtures of hydrocarbons. A major step was the application of the Cox (*10*) vapor pressure chart to key components. In 1933 a Symposium on Physical Properties of Hydrocarbon Mixtures (*45*) resulted in the presentation of several papers of interest. Since then the determination of fundamental data and the development of correlations by which properties that are not known may be estimated have progressed rapidly. Many persons are making valuable contributions, but such men as Rossini and Boord of API Projects 6, 44, and 45, and Sage and Lacey of the California Institute of Technology are noteworthy.

The determination of the exact composition of feed and product streams is also receiving attention. By precision fractionation in the laboratory, often at 100 plus plates and reflux ratios of equal magnitude, narrow boiling fractions are obtained that are further resolved by separation procedures such as azeotropic distillation, extractive distillation, chromatography, solvent extraction, and crystallization. In addition, the instrumental methods of analysis are increasing our information on the composition of complex hydrocarbon fractions.

Concurrently with all these developments, work was in progress on actual distillation units, both laboratory and commercial, checking the new methods and determining actual stream and plate compositions. Studies were being made on plate efficiencies, pressure drop, entrainment, tray hydraulics, vapor and liquid velocities, feed plate location, and numerous other pertinent variables in the design and construction of distillation equipment. These studies have resulted in satisfactory methods for the design and location of bubble cap trays to give optimum contact between vapor and liquid, to decrease channeling and entrainment, and, in general, to obtain true equilibrium between vapor and liquid.

Now a look into the future for this phase of distillation; the search will continue for the utopia in design methods—namely, a short, simple, but rigorous method for determining column requirements for separation of specific components or fractions from complex multicomponent hydrocarbon mixtures. However, at present the methods, though tedious, are frequently more accurate than the available data or correlations, particularly in the higher boiling ranges. Hence, it is believed that the next few years will be mainly devoted to improving and extending the knowledge of the fundamental behavior of hydrocarbons and hydrocarbon mixtures. Furthermore, as the processing of high-sulfur crudes increases, similar data on sulfur compounds such as are being developed by H. M. Smith and his collaborators on API Project 48 will be required.

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Another evident trend is the application of mechanical computers for the rapid calculation of distillation problems. At least two papers have already appeared, one by Weil (*57*) on the use of an electronic computer, and the other by Rose and Williams (*47*) on the application of the IBM card punch technique. If a short rigorous method is not forthcoming, machine calculations may be the answer to accurate design of fractionating equipment.

The use of specialized procedures, such as azeotropic and extractive distillation as well as absorptive and adsorptive separations, is another important trend in hydrocarbon fractionation. These processes are discussed in the following section.

Special Processes

Azeotropic Distillation. The concept of azeotropic distillation is not new. The use of benzene to dehydrate ethyl alcohol and butyl acetate to dehydrate acetic acid has been in commercial operation for many years. However, it was only during World War II that entrainers other than steam were used by the petroleum industry. Two azeotropic processes for the segregation of toluene from refinery streams were developed and placed in operation. One used methyl ethyl ketone and water as the azeotroping agent (*31*); the other employed methanol (*1*).

Azeotrope formers, generally polar compounds, have the ability to form, with hydrocarbons, nonideal mixtures having vapor pressures higher than either component in the mixture and therefore lower boiling points. Fortunately, different types of hydrocarbons show different degrees of nonideality with a given azeotrope former. For example, benzene and cyclohexane boil at about 176° F., while the methanol-cyclohexane azeotrope boils at 130° F., and the methanol-benzene azeotrope boils at 137° F., a difference of 7° F. Hence, fractionation of a mixture of benzene and cyclohexane in the presence of methanol effectively separates the two hydrocarbons.

An even more advantageous condition exists in the case of the toluene range hydrocarbons when methyl ethyl ketone and water are added. A ternary azeotrope of methyl ethyl ketone–water–nonaromatic hydrocarbons distills below 176° F. Neither methyl ethyl ketone nor methyl ethyl ketone–water forms an azeotrope with toluene; hence, toluene will not distill until a temperature of 231° F. is reached, unless excess water is present. Thus, it is relatively easy to produce pure toluene from petroleum fractions.

Many other azeotropic separations are known. Butadiene, styrene, benzene, and xylenes are examples of compounds that may be segregated from refinery streams by this means. In fact, any separation of nonaromatic from aromatic hydrocarbons lends itself to this method, but requires the selection of the proper azeotrope former and processing conditions. In bench scale operations, azeotropy has been applied up to and including the lubricating oil range.

Another field in which azeotropic distillation is finding application is in the separation of the complex mixtures of organic acids, aldehydes, ketones, and alcohols produced by the Hydrocol process. As petroleum stocks are utilized more and more for the production of chemicals, processing of azeotropic mixtures and the use of azeotropic separations should assume increasingly greater importance.

Many azeotropic combinations exist among hydrocarbons themselves. Aromatic hydrocarbons, for example, are almost always found in petroleum fractions distilling below the true boiling point of the aromatics. Marschner and Cropper (*41*) accurately delineated the limits of azeotropy for benzene and toluene with saturated hydrocarbons, and Denyer *et al.* (*11*) did the same for the thiols. Consideration of such data is desirable in the design and operation of equipment for the distillation of gasoline fractions to produce specialized products.

Lecat (*32*) is responsible for most of the azeotropic data on binary and ternary systems. Recently, however, Horsley (*25*) has compiled extensive tables of azeotropic data, thus making the information more available. These experimental data may be supplemented by estimations of the azeotropic composition and behavior of unknown systems by several reasonably reliable methods. Graphical methods, based on curves developed from experimental data, have been proposed by Lecat (*32*), Mair *et al.* (*40*), Horsley (*26*), Skol-

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nik (*52*), and Meissner and Greenfield (*42*). Qualitative predictions are suggested by Lecat (*32*), based on heats of solutions, and by Ewell *et al.* (*18*), based on the hydrogen bonding concept.

The theoretical and mathematical treatment of azeotropic data has been covered by several authors, including Benedict and coworkers (*1*), and Scheibel and Friedland (*50*). Licht and Denzler (*37*) have discussed the thermodynamic conditions necessary and sufficient for azeotropism. Colburn (*8*) has reviewed the calculations associated with azeotropic and extractive distillation, and Hodgson (*24*) stresses the relationship between azeotropic distillation, extractive distillation, and liquid-liquid extraction.

The future of azeotropic distillation may well be in the development of new and more efficient azeotrope formers for the specific separations desired. Design methods and equipment for azeotropic processes are essentially the same as for ordinary fractionation; hence, substantially all developments in that field will be applicable to azeotropic distillation.

Extractive Distillation. In extractive distillation a fraction comprising compounds of similar volatility is vaporized and passed countercurrent to a liquid solvent stream in a packed or bubble cap tower. The operating conditions of temperature and pressure are regulated so that one or more of the components of the mixture are dissolved in the entrainer and removed in a liquid phase extract, while the remaining vapor is taken overhead and condensed or discharged as gaseous effluent.

Two important extractive distillation processes were placed in commercial operation during World War II: the recovery of butadiene from a C_4 fraction using furfural as the entrainer (*7, 22*); and the segregation of toluene from petroleum fractions by means of phenol (*14–16*).

Frequently, though not always, an efficient entrainer for extractive distillation will, within certain temperature limitations, also be a good azeotrope former and a selective solvent for liquid-liquid extraction. The specific process to be used is a function of the characteristics of the fraction to be processed and of the temperature and pressure to be used—for example, phenol, which boils at 360° F., is an excellent entrainer for the separation of aromatic and nonaromatic hydrocarbons. With petroleum fractions distilling from 140° to 190° F., and 190° to 240° F., it is used in extractive distillation to segregate benzene and toluene, respectively; with fractions distilling in the range 280° to 500° F., it may be used as an azeotroping agent to prepare special Diesel fuels; and with still higher boiling fractions it is employed as a selective solvent to separate the more aromatic components from the relatively paraffinic materials. The interrelationship among azeotropic distillation, extractive distillation, and liquid-liquid extraction has been noted by Benedict and Rubin (*2*), Hodgson (*24*), Hibshman (*23*), and others.

The literature on extractive distillation is rather sparse. In addition to that on the design and operation of the commercial units, the bench scale work of Griswold and coworkers (*21*) at the University of Texas and that of Dicks and Carlson (*12*) at the University of Pennsylvania are noteworthy. Pertinent thermodynamic data on extractive distillation systems have been presented by Wohl (*59*), and Colburn and coworkers (*20, 43*) have published vapor-liquid equilibria for several systems. Scheibel (*48*) has presented an approximate method for design of extractive distillation units.

Future advances in extractive distillation may well follow the same trend as those in azeotropic distillation—that is, where the products can justify the higher processing cost, efficient entrainers will be developed and utilized in commercial operations.

Vapor Phase Absorption. Absorption is closely related to extractive distillation, in that a solvent is used for the separation of one or more constituents from a gaseous mixture. In absorption, however, the mixture to be treated is comprised of compounds having relatively large differences in volatility and condensation cannot be conveniently used. The various absorption processes differ primarily in the means used to separate product and absorber oil. A typical example of the application of vapor phase absorption in the petroleum industry is the recovery of gasoline from natural gas.

Vapor Phase Adsorption. Although vapor phase adsorption is not strictly a distillation process, it accomplishes a similar type of separation, and therefore has been included in this paper.

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The development of adsorption as a method of fractionation has been analogous to the development of distillation. In both cases the operation was originally carried out in a simple batch unit. After many years, rectification was added and close fractionation became possible. In the case of distillation this was done by adding a packed or bubble plate column to the still kettle. In the case of adsorption it involved the use of an adsorbent-packed column to obtain chromatographic separation, which gave a rectification effect.

The third and final step in both cases consisted of operating the column or tower continuously with a constant feed and constant draw-off of products. In distillation this step is represented by the large continuous fractionating columns now used in many petroleum and chemical plants. In adsorption it is represented by the Hypersorption process (*3*, *4*, *28*, *29*).

In Hypersorption a feed gas stream—e.g., a hydrocarbon mixture—is introduced into the middle of a vertical tower and passes countercurrent to a moving bed of adsorbent carbon. The adsorption capacity of the carbon, generally speaking, is preferentially satisfied by the constituents of higher molecular weight; thus, when the inlet gas reaches the carbon, the materials of high molecular weight displace those of lower molecular weight that have already been adsorbed in the upper portion of the tower. Proper location of side stream take-offs permits recovery of several fractions from a single tower.

A steam stripping section located at the bottom of the tower frees the carbon of adsorbed material, which is drawn off directly above or passes on up the tower as reflux. However, traces of heavy material remain on the surface of the carbon and these are removed by continuously withdrawing a fraction of the circulating carbon and passing it to a high-temperature steam stripping section.

This process provides the petroleum and chemical industries with a new tool for resolving various complex mixtures. Some of these segregations are:

Recovery of ethylene and acetylene from cracked hydrocarbon gases
Separation of pure methane and ethane from natural gas
Purification of hydrogen

It is expected that among the advances in the next few years will be the expansion of the use of activated carbon to other separations and the development of new adsorbents and improved commercial equipment.

The separation art is now a continuous band extending from simple distillation through azeotropic distillation, extractive distillation, vapor phase adsorption, and solvent extraction to liquid phase adsorption.

New Developments

In 1925, absolute pressures equivalent to 300 mm. of mercury were considered "high vacuum" in refinery operations; in 1950, 40 mm. is commonplace, and 1 to 10 mm. is being used in pilot plants. Still lower pressures are being investigated in petroleum laboratories. Commercial operations using molecular distillation are not now employed by the petroleum industry, but this method has had extensive application in the distillation of fish and vegetable oils for the production of vitamin concentrates. Its great advantage lies in the extremely short residence time at the distillation temperature, an important consideration in processing high boiling or heat-sensitive materials. In commercial units the feed stream continuously enters at the apex of a heated wide-angle cone-shaped plate rotating at high speed. On this rotating cone the feed spreads to a thin film and passes rapidly to the outer rim, where it is continuously removed. The portion evaporated while crossing the rotor is condensed and recovered separately. It is essentially a one-theoretical-plate operation.

Another development that may well influence the distillation science of tomorrow is the rotary column under study by API Project 6 and the Bureau of Standards (*58*).

This unit has a rotor enclosed in a cylinder, with a 1-mm. annular space between the cylinder and rotor surfaces. The rotor revolves at speeds up to 8000 r.p.m. and is cooled internally, so that the cold rotor surface acts as a condenser. The shell is heated to cause partial vaporization of the condensate which is thrown from the rotor. Thus, alternate condensation and evaporation take place as the vapor moves up the column. It is claimed that 500 theoretical plates can be developed at a throughput rate of 1 gallon of liquid per hour in a unit having a rotor 5 feet long and 5 inches in diameter.

The centrifugal supercontactor developed by Podbielniak (*46*) is another fractionation apparatus in which centrifugal force is applied to the distillation process. The principal feature of the unit is a rotating spiral passageway which permits the employment of vapor velocities from 50 to 70 times greater than are possible without excessive entrainment in a bubble tray tower.

The units discussed in this section all involve the use of centrifugal force to overcome the limitations interposed by gravity on the mass rate of contacting vapor and liquid, thus permitting higher liquid and vapor velocities in a correspondingly smaller unit. The major advance of the future in petroleum distillation may well be the application of centrifugal principles to refining operations.

Conclusion

The advance of distillation in the petroleum industry may be epitomized by saying that we started with simple evaporation and condensation, progressed through rectification, and now are in the age of fractionation—that it was formerly an art and is now a science.

These advances are the culmination of the work of many men working in many disparate fields of science and technology. The pure scientists and mathematicians who expanded the theory of fractionation and fluid mechanics and applied the principles of thermodynamics to design methods; the metallurgists who produced the metals and alloys necessary for fabrication of the vessels; the instrument technologists who developed the equipment necessary for automatic operation and control; the engineers who designed the units, supervised their construction, and planned their operations; the analysts who provided data for product control and for evaluation of performance; the stillmen who kept the units running; and the consumers who bought the products and thus furnished the monies necessary to keep our economic system of free enterprise functioning—all these, working together, have brought distillation of age.

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Internal Combustion Engine Fuels

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The problems involved in the production and utilization of internal combustion engine fuels since the early days of the industry, those now facing the industry, and the broader aspects of the future are discussed. Although economic factors have been and still are of major importance, consideration of national security has become of equal importance during the past decade and in large part will guide the developments to be made in the future. Technologically the industry has advanced greatly since 1925 and the role of the research investigator has undergone a pronounced transition, based largely on the accomplishments that have been made and in anticipation of the progress yet to be made.

In discussing fuels for internal combustion engines—past, present, and future—it becomes readily apparent that certain simplifying steps must be taken to complete the assignment in any presentation of reasonable length. The first step in this direction is to concentrate only on problems and trends of major significance pertaining to the production and utilization of internal combustion engine fuels. A second and equally important step is to concentrate on the major product or products falling within this range of fuels. This selection is facilitated by reference to Figure 1 which shows the consumption of internal combustion engine fuels from 1926 to 1950.

The dominant position of motor gasoline is evident from this chart. In 1950 86% of all internal combustion engine fuel consumed in the United States was motor gasoline. Diesel fuel was next at 9%; then aviation fuel at 4%; and finally tractor fuel at about 1%. Basically there are only two types or grades of motor gasoline—regular and premium—whereas there are numerous grades and types of Diesel and aviation fuel, particularly the latter which includes both aviation gasoline and aircraft gas turbine fuel. The growth of the petroleum industry and of the automotive industry has proceeded hand in hand and the petroleum industry's primary market since the turn of the century has been the passenger car (*7*).

Consequently, this discussion is based primarily on the demands and requirements of gasoline-powered motor vehicles as they have affected and may be expected to affect the research, development, and manufacturing activities of the petroleum industry.

The Past

As a starting point it is in order to consider the basic purpose served by gasoline and to ask why gasoline has been and is the major source of energy for transportation purposes. The fundamental requirements for any energy source for mobile use are somewhat as follows (*2*):

1. It must have a high energy content on both a weight and volume basis.
2. It must be available in abundance and at low cost.

3. It must be convenient to transport and handle.
4. It must be capable of convenient and efficient conversion into useful work.

Petroleum fuels, and gasoline in particular, meet these requirements readily and consequently account in very large part for the widespread use of the automobile as a means of transportation.

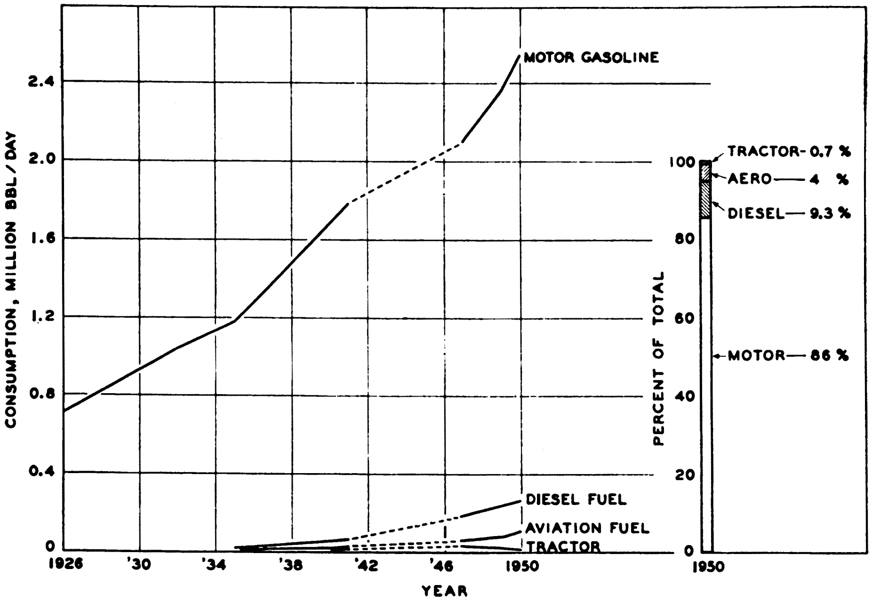

Figure 1. United States Consumption of Internal Combustion Engine Fuels

Motor gasoline includes nonhighway, industrial, and miscellaneous
Tractor refers to kerosene-type fuels

A further examination of these four requirements shows that items 1 and 3 are relatively fixed in nature, once the approximate characteristics for a petroleum fuel have been established. In contrast, items 2 and 4 are subject to modification, wherein research and engineering can be applied to reduce the cost and increase the convenience of transportation. Obviously the convenience and efficiency of converting the fuel energy into useful work are dependent in major part on the characteristics of the machine which effects the conversion. It is also true, but somewhat less obvious, that the availability and cost of the fuel are equally dependent upon the nature of the engine and vehicle in which the fuel is used.

Low Volatility. In the early days of the industry, prior to 1925, the major problem was to produce enough fuel to meet the volume demands of the ever-increasing automotive population. In order to meet these demands the refiner had to cut deeper and deeper into the crude oil, resulting in a gasoline of high final boiling point. By 1925, however, a balance was achieved as a direct result of the broad application of thermal cracking which was first applied commercially about 1913. This first major development in fuel refining operations made it possible to increase gasoline volatility, as shown in Figure 2, and at the same time meet the volume demand for this product (*9*).

Nevertheless, the most pressing problems of motor.fuel utilization were a direct result of the heavier fuels being marketed. (At this time the problem of fuel "knocking," although recognized, had not reached the prominent position which it has maintained during the past 20 years.) Two problems associated with fuels of low volatility were hard starting and poor warm-up. However, the foremost problem with heavy fuels and engines then in use was crankcase dilution—dilution of the lubricating oil with unburned gasoline,

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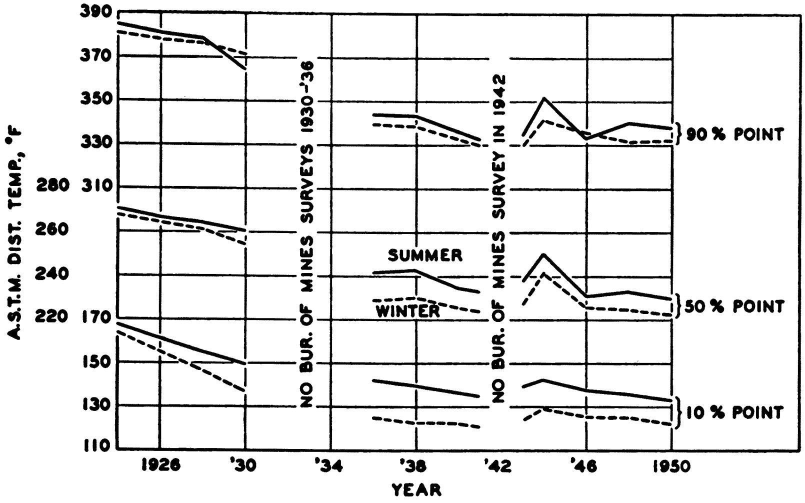

Figure 2. Volatility Characteristics of United States Motor Gasolines

Weighted average of regular and premium grades

The problem in 1922 was sufficiently serious to warrant the formation of a joint council consisting of representatives of the American Petroleum Institute and the National Automotive Chamber of Commerce (*17*). (This group was the nucleus of the Cooperative Fuel Research Committee, CFR, which later was formed into the Coordinating Research Council.) Acting on a recommendation from this group, the National Bureau of Standards undertook fuel research on the problems created by low-volatility gasolines. Improved engine starting and conservation of crude oil were named as secondary aims of this program, in their relation to fuel volatility. The basic recommendation of the National Bureau of Standards was that gasolines should not exceed a final boiling point of 437° F., a compromise value between crankcase dilution and maximum gasoline yield per barrel of crude oil which still stands today.

Sparked in large part by this first research on fuel utilization, the petroleum and automotive industries set to work on the problem—the petroleum industry to provide separate summer and winter grade fuels having higher over-all volatility, the automotive industry to provide less critical engines by means of crankcase ventilating systems and better thermostatic control of engine temperatures.

Antiknock Quality. While work in this field was progressing, a new problem was coming to the forefront—antiknock quality. Although the basic problem of detonation was recognized prior to 1920, and tetraethyllead was used as early as 1923, antiknock quality problems did not become serious until about 1928–30. It was well recognized by then that thermal cracking—in addition to providing greater gasoline volume per barrel of crude and thereby enabling the production of more volatile gasolines—also gave gasolines less prone to knock than their straight-run counterparts the improvement in quality resulting from the formation of olefinic hydrocarbons. This, in turn, led to the expanded installation of thermal cracking facilities (Figure 3) and to the development of the thermal reforming process in 1928 to 1935. Thermal reforming consists essentially of cracking straight-run gasoline of low octane number to produce a gasoline of higher octane number—the higher quality resulting from the conversion of paraffins to olefins. At the same time a more volatile gasoline is produced; however, the loss in gasoline yield (primarily as a result of gas formation) and the manufacturing cost of the operation have to be charged against the primary objective of higher octane number.

High Volatility. The problem preceding that of antiknock quality was concerned with fuels of low volatility. Volatility again became a problem in the early thirties as a result, in part, of extended thermal operations to make higher octane numbers. This time, however, the problem was one of high volatility leading to vapor-locking in automotive fuel systems. Although known to aircraft engineers, whose fuels had always been lighter and their operating environments more severe, vapor lock was new to the automobile. Automotive engineers went to work on the problem from the standpoint of fuel system design, while the petroleum technologist contributed materially by closer seasonal control on vapor pressures.

Unfortunately, despite the efforts of the fuel system designer, significant quantities of light petroleum hydrocarbons had to be excluded from finished motor gasolines to minimize vapor-locking troubles. This excess of light stocks—stocks of high octane number—led to the development of processes for converting volatile hydrocarbons into liquid fuel. This development was made possible by the early research work on catalytic processes and the first such process to be applied extensively, about 1935, was the catalytic polymerization of light olefins to make liquid olefins, also of high octane number. Hydrogenation of the product from polymerization of C_4 olefins (selective polymerization) resulted in a commercial iso-octane which was used in making the first aviation gasoline of 100 octane number. Development of this process was accompanied by commercialization of the alkylation process which produced, primarily, a mixture of iso-octanes using isobutane and C_4 olefins as the charge stocks. Application of this process for making aviation blending stock of high octane number was more attractive, inasmuch as no hydrogenation step was required.

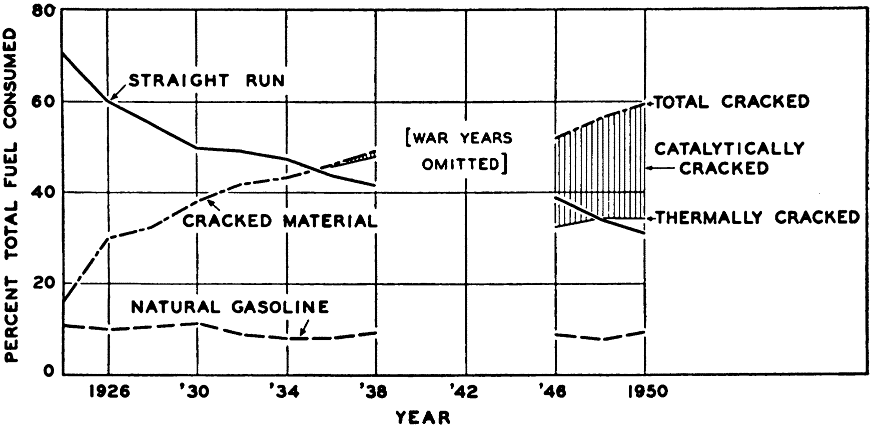

Figure 3. Components of United States Motor Gasolines

Catalytic Cracking. While these developments were proceeding, with the continuing objective of providing adequate quantities of high octane number gasoline with controlled volatility, a new development destined to have a major effect was in the mill. Early research work on catalytic processes had shown the possibility of cracking gas oils in the presence of a catalyst to yield a gasoline of higher octane number than could be produced by thermal cracking and at the same time provide a better over-all distribution of the products from the cracking process. The higher octane number characteristic of gasoline produced by catalytic cracking is related to the formation of aromatic and isoparaffinic hydrocarbons in addition to the formation of olefins, which is characteristic of thermal cracking and thermal reforming. While the yield of gasoline from crude was about the same as that from thermal cracking, more distillate fuel oil and less residual fuel were produced. In addition, the gas fraction resulting from catalytic cracking was more olefinic in nature and consequently of greater value in alkylation and catalytic polymerization operations.

Although catalytic cracking was introduced commercially in 1936 and its advantages were obvious to many observers, the principal impetus to the wide use of this process was the demand for aviation gasoline occasioned by World War II. Catalytic cracking capac-

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ity rose to a level of about 1,000,000 barrels per day by the end of the war. So successful was the application of this process during the war years that, since the conclusion of the war, additional installations and modifications to existing units have been made bringing the total domestic capacity up to nearly 2,000,000 barrels per day.

This development, again the result of intensive research and engineering by petroleum technologists, brought with it numerous problems to be solved by further research. Many of these problems pertain directly to the process itself and to the problems associated with the catalyst in its relation to gasoline yield and quality—its susceptibility to poisoning by trace constituents in the charge stock, its ability to be regenerated by burning off the coke formed on and in the catalyst, and numerous other factors. By comparison the fuel utilization problems introduced by catalytic cracking have been minor and, for the most part, similar to those encountered with thermally processed fuels. One minor exception has to do with the question of fuel volatility in its relation to crankcase dilution and, to some extent, deposits in the power section and crankcase of the engine. In contrast to straight-run and thermally processed gasolines, the higher boiling fractions in catalytically cracked gasolines are of high octane number, due to the presence of substituted aromatics, and consequently are best utilized directly in motor gasoline. However, the problems resulting from the inclusion of high boiling catalytic fractions in finished motor gasolines have not been of major significance, in large part, because of developments in engine design and in lubricating oils.

Color, Odor, and Stability. Despite the emphasis on volatility and antiknock quality, these were not the only problems facing the petroleum refiner. In fact in 1920–25 the major commercial criteria to be met were absence of color—i.e., a water-white product—sweet odor, and stability of color and odor under marketing conditions (*12*). The odor problem was not new; "doctor" treating, or something approaching it, for converting the offensive mercaptans (thiols) to disulfides had been in use for a number of years and was almost universally applied at refineries. (In doctor treating, aliphatic mercaptans are converted to lead mercaptides by the action of a sodium plumbite solution, and these mercaptides are then converted by reaction with elemental sulfur to aliphatic disulfides and lead sulfide. The lead sulfide separates from the gasoline and is reconverted with sodium hydroxide solution to sodium plumbite.) In contrast, poor color had arrived with thermal cracking which gave a yellow cast to blends and, without regard to engine performance, the yellow color was looked upon with disfavor (*4*).

Gum formation was also beginning to assert itself as a corollary of color instability. In 1926 the Standard Oil Co. of New York carried out fairly extensive tests of the gum-forming tendencies of cracked gasolines in storage and made the then surprising discovery that the size of the container was a major variable. Supplementing the early research on stability per se, investigators found that the operation of engines on unstable cracked gasolines resulted in brown varnishlike deposits in the induction system, and became familiar with the problems of stuck intake valves, clogged air and fuel passages, and gummed-up throttle linkages.

While doctor treating of gasolines resolved the odor problem, the only technique generally effective in improving color and gum stability was treatment with sulfuric acid. In some instances caustic washing of the gasoline was found effective and a third process—vapor phase contacting of the gasoline with activated clay—also gave some improvement in gasoline gum stability.

Again while these processes were being employed and further developed, the nature of the problem underwent a change with regard to color stability. Following the commercialization of tetraethyllead in 1925, and because of its toxic nature, good practice decreed that leaded gasolines be dyed for identification and most motor gasolines were soon artificially colored. This effectively dispelled interest in treating gasolines for so-called good color and left, essentially, only the problem of gum stability.

Although acid treating was very effective in controlling stability, the process left much to be desired from an economic point of view and with regard to the problems incurred in handling sulfuric acid and in disposing of the resultant acid sludge. Having then a definite incentive, the chemist investigated the fundamental factors affecting the

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oxidation of cracked fuels and the means by which the oxidation reactions could be prevented or retarded. The result was the development of chemical antioxidants which, when added to the gasoline in very minute quantities, would impart the desired storage stability characteristics (*13*, *16*). As improved antioxidants were developed through the 1930's and up to the present time, their use became widespread and, currently, antioxidants are generally added to commercial motor gasolines in the proportion of about 5 to 10 pounds per 1000 barrels (0.002 to 0.004 weight %). Among the effective compounds employed in this fashion are *N*-*n*-butyl-*p*-aminophenol, *N*-isobutyl-*p*-aminophenol, *N*,*N'*-di-*sec*-butyl-*p*-phenylenediamine, 2,6-di-*tert*-butyl-4-methylphenol, and 2,4-dimethyl-6-*tert*-butylphenol. In combination with relatively modest treating operations, such as caustic washing, this preparation of the fuel for normal handling and use provides satisfactory protection from gum in most instances.

One other phase of refining developments is worthy of mention. The doctor process for converting malodorous mercaptans into disulfides which have relatively little odor has been and still is used very widely. However, after the introduction of tetraethyllead, and when it became increasingly difficult to meet higher octane number levels, the desirability of removing mercaptans entirely from the gasoline became apparent because of the adverse effect of sulfur compounds on the efficiency of lead in raising octane number. Here again extensive research on the part of the laboratory chemist led to the discovery of materials such as methanol and cresylic acid which, when added to caustic solutions, alter the mercaptan solubility characteristics so that these sulfur compounds can be extracted from the gasoline. In this fashion the odor of the gasoline and its response to tetraethyllead addition are improved.

It should be recognized that one of the major utilization problems since 1925 has been concerned with the effects of leaded gasoline on engine durability and engine deposits. However, this topic is the basis for another of the symposium papers and consequently was not considered in this presentation. Nevertheless, it may be noted that the solution of this problem is a tribute to the efforts of the chemists and engineers concerned with the development of lead scavenging agents and with engine design and construction.

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The Present

Twenty-five years ago the primary objective of the petroleum industry was to produce enough gasoline to meet the requirements of a rapidly growing automotive industry and at a sufficiently low cost to encourage the further growth of motor vehicle usage. A basic consideration even at that early stage in the development of the industry was the conservation of the nation's liquid energy resources. Since then increased attention has been given to efficient production and refining operations to protect the not inexhaustible supply of raw material. However, with the advent of other spheres of power aimed at dominating social and economic life on a global basis, a new objective has been joined to the basically economic considerations. National security and its dependence on petroleum in its many forms rank equally with the earlier objective based on the demands of the country under a peacetime economy.

Many of the current problems of the petroleum industry are not new, particularly those which relate directly to economic considerations. However, taking into account national security, some new problems do appear. Fortunately, there has been a marked transition in the industry from the purely empirical to the scientific approach in solving problems as they appear and in anticipating the problems of the future. In 1924 one observer noted that no industry of anything like the magnitude of the petroleum industry had such a dearth of fundamental chemical knowledge on which to base its operations (*3*). To state that the industry now has a complete understanding of all the chemistry involved in the refining of petroleum would be foolish. It is sufficient to state that the industry is now cognizant of the value of such information and of the contributions that have been made and can yet be made by the research chemist.

On the foregoing basis, it can be assumed that the incentive exists and the manner of approach has been established for the solution of problems pertaining to the more effective production and utilization of internal combustion engine fuels. Consequently, the primary task is to define the problems which exist today, thereby posting the guide for research technologists who frequently—and understandably—work so close to the technical aspects that it becomes difficult to maintain a good perspective of the over-all objectives. For simplicity, these problems are considered as they pertain to the individual power fuels—namely, motor gasoline, aviation fuel, and Diesel fuel.

Motor Gasoline

Of necessity, motor gasoline octane number is the primary fuel characteristic requiring extensive consideration. Motor fuel octane number still provides the basis for the single largest concentration of industrial research effort in the nation's history. At the present stage of automotive engine development the use of higher octane number fuels can be justified only by improvements in the efficiency of converting fuel energy into useful work. The improved efficiency of engine operation must be weighed against the loss in efficiency in producing the fuels required for this operation. Obviously, the octane number quality necessary for given levels of engine efficiency, and the manufacturing requirements and consequent economics for producing fuels of given quality levels, must be known. Both the automotive and petroleum industries have been negligent in this regard, as evidenced by the confusion concerning the fuel quality requirements and economy characteristics of experimental vehicles on the one hand and by the paucity of information concerning the economics and efficiency of motor gasoline production on the other.

Undue significance has been attached to compression ratio, per se, as the means of achieving automotive efficiency. Looking at the question objectively, compression ratio is obviously a means to an end—not the end itself. The terminal objective is the cost of transportation in terms of miles per barrel of crude oil, reflecting the efficiency of converting the fuel energy into useful work, and in terms of miles per dollar, reflecting the efficiency of the conversion in terms of the steel and manpower required. The research chemist must have the economic and energy factors in mind in considering any new processes for making motor gasolines of higher octane number.

This field for research effort—the development of new processes for efficiently producing gasoline of high octane number—is broad and cannot be defined in detail without lengthy discussion. This type of activity is best illustrated at present by the progress in catalytic reforming processes. A somewhat similar situation, although more specific, exists with regard to improving the efficiency of tetraethyllead utilization. The adverse effect of sulfur compounds on tetraethyllead susceptibility has been discussed but, although long recognized, the essential problem remains unsolved. While economical processes have been developed for removing aliphatic and aromatic mercaptans from gasoline, the processes developed for removing other types of sulfur compounds are not attractive when considered in the light of required capital investment and operating costs. Lower sulfur fuels for motor vehicles may also result in some decrease in automotive maintenance; but the primary factor is and will remain the desire to improve tetraethyllead susceptibility (*11*).

Definite progress is being made in this direction despite the complexity of the problem. It appears that the major accomplishments of the future will be based on the current research aimed at segregating and identifying the individual sulfur compounds in crude petroleum and in petroleum products.

Effect of Engine Deposits. Another approach to the antiknock quality problem is concerned with the effect of engine deposits on the octane number requirement of the engine. Allied to this is the relation of these same deposits to engine durability and maintenance requirements. Until recently combustion chamber, piston, crankcase, and bearing deposits were thought to be due solely to the breakdown of the lubricating oils. Tests carried out during the war, however, led to postwar investigations which have definitely established the partial responsibility of fuels for every type of deposit occurring within the engine (*1*, *5*, *15*). Although there is evidence that the lubricating oil can also be a primary factor, engine design, mechanical condition, and type of operation can, in

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many instances, overshadow both fuel and oil in the degree to which they influence deposition.

Despite these obvious complications, the problem of controlling power-section deposits is particularly absorbing to the petroleum technologist. Not only does his past success with chemical additives in other applications foretell a satisfactory outcome, but the rewards of success are also substantial, particularly if the engine design and operational factors are brought under control at the same time. A clean engine means, primarily, a longer-lasting engine, as to both total life span and period between overhauls. It means fewer breakdowns, less expense for maintenance, and lower oil consumption—all worthy goals. Clean combustion chambers have two important virtues: less increase in antiknock requirement, and less total power loss. Recent data have shown that loss of full-throttle power may range from 2 to 15% after 10,000 to 20,000 miles of operation, due to deposits alone, and antiknock requirement may rise 10 octane numbers in the same period and for the same reason (*5*, *14*).

The application of fuel additives to these problems has been undertaken only recently, and so far as is known none have yet reached the commercial stage. At least one investigation has discovered effective materials for reducing significantly the formation of sludge and varnish deposits, but unfortunately these materials cause undesirable intake valve deposits (*1*). This is not wholly surprising, when it is considered that fuel antioxidants can contribute to varnish and sludge formation. Less is known about how to control combustion chamber deposits chemically, although there are much interest and considerable activity in this field. A recent paper has described the effectiveness of boron and silicon compounds in the fuel in reducing the antiknock requirement effects of combustion chamber deposits without actually inhibiting deposit formation (*10*). The authors postulate that this is due to poisoning of a catalytic surface in the combustion zone. Although promising, this novel approach is still in the experimental stage.

Volatility. In contrast to the antiknock quality situation, most of the problems of engine performance attributable to fuel volatility characteristics were relatively dormant by 1950. Except during the war, the boiling range of average motor gasolines had changed only slightly since 1936 (Figure 2), indicating the achievement of a fairly stable compromise between the economics of refinery operation and the volatility requirements of the automobile.

This long period of relative stability enabled engine designers to bring their equipment into line with available fuels. The old problems of abnormal volatility—those arising from incomplete vaporization and poor distribution, on the one hand and too-ready evaporation on the other—had become the special province of the experimenter and the field engineer. The former concerned himself with surpassing the already notable performance of average automotive vehicles, and the latter with succoring the not inconsiderable number of cars operating on abnormal fuels. For despite the satisfying appearance of graphs and average values, there are fairly wide deviations in volatility throughout the industry. These are due to differences in processing equipment, crude sources, and market conditions for various individual refiners. If for no other reason, both the automotive and petroleum industries will remain conscious of volatility problems and continue to seek the most effective compromise between volatility and performance in terms of product availability and equipment design.

Storage Stability. The final current problem of importance associated with motor gasoline is long-time storage stability, which is essentially a problem concerned with military activities. A fairly recent contribution to improvements along this line are the so-called copper deactivators or metal deactivators—chemical additives such as N,N'-disalicylidene-1,2-diaminopropane whose effect is to reduce or eliminate the pro-oxidant catalytic activity of copper which is frequently present in trace quantities as a result of processing or handling operations. As very small quantities of copper—less than 1 p.p.m.—have a pronounced catalytic effect, preventing contamination is not feasible and consequently the use of suitable deactivators represents a very practical solution.

However, despite the accomplishments through use of antioxidants and deactivators, the fundamental problem in military operations is the lack of reliable, accelerated laboratory tests which will predict accurately the stability characteristics of gasolines over extended storage periods. Not having such a test at the present time makes it difficult to study the effects of fuel composition, treating processes, chemical additives, storage conditions, and type of container on long-time storage stability.

Aviation Fuels

The years immediately preceding World War II were years of accelerated research and development on high output, low weight aircraft engines and their fuels. While emphasis was placed initially on high lean mixture octane number fuels, isoparaffinic in nature, the need for aromatic components—toluene, xylenes, etc.—to provide good rich mixture antiknock performance was also recognized and the fuels developed under the stresses of the war emergency combined both properties. In addition, the severe storage conditions for military aviation gasoline and the sensitivity of the aircraft engine to induction system deposits led to the combined usage of processes (*6*) and antioxidants which gave excellent stability characteristics.

Immediately after the war, it appeared as if the reciprocating aircraft engine was doomed to rapid obsolescence by the gas turbine engine. The trend is still correct, but the process will take longer than originally anticipated. However, because this trend exists and because of the extended research and development on reciprocating engines and their fuels conducted prior to 1950, no further major advances in aviation gasoline technology are anticipated.

The present status of jet fuel technology can be aptly described as being at the same point as motor fuel technology 25 years ago. Volatility and stability requirements have been recognized and current research activities are directed toward the solution of these problems.

In contrast, very little is known of the mechanism of the combustion process in the gas turbine engine or of the fuel characteristics which would improve combustion performance. Despite the classified nature of much of the work in this field, it is apparent that very extensive research investigations—both fundamental and applied—are in progress. A substantial portion of this effort is in connection with the mechanics of combustion itself and, because of the necessarily fundamental approaches in this field, it is reasonable to expect that the results to be obtained will apply to all fuels, whether or not derived from petroleum, and may even be extended into the field of lubrication.

Diesel Fuels

Throughout most of the past 25 years the demand for Diesel fuel has been such that a fuel having a high cetane number (45 to 50) and excellent stability characteristics could be readily provided by the refiner. However, the marked increase in demand for Diesel fuels in the post–World War II era, resulting largely from the dieselization of the railroads together with the ever-growing demand for home heating oils, has led to increasing usage of catalytically cracked Diesel fuels. Diesel fuels from catalytic cracking tend to be of lower cetane number, higher sulfur content, and poorer stability than straight-run fuels, all of which can have deleterious effects on the life and reliability of Diesel engines. Solvent extraction procedures have been used to a limited extent for improving the quality of Diesel fuels, but appear too expensive for widespread usage. Additives have been developed for raising the cetane number of Diesel fuels, but to date have not been sufficiently attractive for commercial acceptance. In contrast, effective additives for preventing the formation of gum and sediment in Diesel fuels appear to be on the edge of commercialization.

The Diesel fuels referred to above are products with a maximum end point of 750° F. A number of manufacturers of larger bore, low speed engines for industrial and marine use have been studying the performance of the cheaper, residual-type fuels to make these engines more attractive commercially. The continuance of this development will be largely the function of the engine builder, unless the petroleum technologist can devise very economical processing techniques and/or additives to improve the heavier fuels.

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Any technique for effecting improvement which would cause a substantial increase in the fuel cost is bound to failure, inasmuch as the basic objective is to take advantage of the low cost of the heavier fuels.

While the foregoing comments reflect essentially the normal situation, recognition of a potential military emergency casts another light on the Diesel fuel picture. Recent studies have shown that in the event of an emergency, the availability of high quality distillate fuels would be limited, particularly in certain areas. Recognition of the paramount requirement of the railroads for Diesel fuel in peace and war leads to the question of what compromises can be made in fuel quality so that an adequate volume of fuel will be available at all times. This problem is being studied intensively by the industries concerned and may be resolved in large part by developments in lubricating oil formulation to take up some or all of the load imposed by lower quality fuels.

The Future

The nation's petroleum resources are not inexhaustible, although its potential energy resources are adequate for centuries to come (*8*). These include, in addition to liquid petroleum, natural gas, oil shale, tar sands, and coal. Above and beyond these resources is the basic energy to be derived from the sun, winds, tidal action, and nuclear forces. For the present purpose, no consideration of these ultimate energy sources is required.

Inasmuch as there is no foreseeable shortage of energy, the essential question concerns the form and source of future fuels for internal combustion engines. As stated previously, the nature of the machine for converting potential energy into useful work affects in large part the desirable form of the fuel. However, whether this machine be a super-high-compression ratio spark ignition engine, a Diesel engine in present or modified form. or a gas turbine engine, elementary consideration dictates that the fuel be available as a liquid.

This consideration as well as those concerning cost, convenience of use, and availability leads to the conclusion that petroleum fuels will be used for transportation purposes in preference to other fuels as long as crude petroleum is available. Although liquid fuels can be produced from gas, coal, or shale oil, the high energy losses involved in the conversion make such operations unattractive from an energy conservation point of view. Obviously, the direct utilization of gas and coal as produced and of the type of crude oil which can be produced from oil shale by simple retorting is the most desirable procedure and should be followed until petroleum is so scarce or expensive to find that the free play of economic forces dictates the synthesis of liquid fuels.

This does not mean that research should not be conducted in the synthesis of liquid fuels. This type of research should be conducted on a rational basis rather than, as in the early 1920's and late 1940's, on a basis of fear that petroleum supplies are running out. The efficiency of current synthesis operations is low—in the range of 40 to 60%. These efficiencies can be improved and, while this is being accomplished, it is reasonable to predict that petroleum prospecting and production will become more costly. Consequently there is a logical meeting point in the future, indistinct at the moment, where synthesis operations may logically be utilized. When this situation develops, natural gas supplies will probably also be limited and coal, oil shale, and tar sands will constitute the basic raw materials.

Another factor to be considered from a long-range point of view is the change in utilization efficiency that may be expected in the power plants used for transportation. The potential improvements in efficiency are very large, and may be considered a major factor in extending the availability of petroleum fuels. However, in accomplishing this increase in efficiency, the broad picture of economic well-being and national security must be kept in mind. Whatever the mechanical change to achieve higher efficiency, it must be measured against the requirements it imposes upon basic raw materials—crude oil, steel, chemicals, and manpower.

Looking into the future necessitates dealing in rather broad concepts rather than with specific chemical problems. Nevertheless, as the machines used in transportation are modified and redesigned toward the end objective of lower cost and greater reliability,

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specific problems will continually be forthcoming. And frequently the solution to these problems will, in turn, create new problems, as in the case of tetraethyllead and most of the processing developments that have been made. Concurrently it is probable that a greater interest will develop in the by-products from petroleum refining operations. No great vision is required to see that the role of the chemist—and the physicist also—is destined to become increasingly important. And the greater the store of basic information developed about the nature of petroleum, the contaminants found therein, the reactions that ensue in the combustion of fuels, and how these may be modified, the greater will be the ultimate reward socially and economically.

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Tetraethyllead

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This paper discusses the properties which make tetraethyllead practical as an antiknock agent, and treats briefly the problems involved in its use and the progress that has been made in methods for its manufacture. The importance and interrelationship of high antiknock gasoline and efficient automotive engines are outlined, and probable future progress in several phases of the broad problems of fuels and engines is forecast. The part that tetraethyllead has played in the improvement of gasoline quality is discussed, and some suggestions are made as to possible future improvements in its utilization.

Twenty-five years ago, tetraethyllead was just being reintroduced to the petroleum industry after having been withdrawn from the market for a year while the United States Public Health Service was carrying out the extensive investigation which led to the conclusion that the material, in concentrations not exceeding 3 ml. per gallon of gasoline, was safe when used in motor fuel. The 25 years following have seen a steady growth in the use of tetraethyllead, until today practically all United States motor and aviation gasolines contain it, and many foreign gasolines as well. This progress has not been without opposition and difficulties. At one time, few motor manufacturers approved its use, despite its potential advantages, because of its real or fancied effects upon engine parts, and it is a tribute to the real value of the product that intensive work to correct such problems as actually existed has been done and is being done by the automotive and aircraft industries, the petroleum industry, and the producers of tetraethyllead.

Likewise, exactly 25 years ago, at the fall meeting of the AMERICAN CHEMICAL SOCIETY, there was announced the synthesis and high antiknock value of a paraffin hydrocarbon, 2,2,4-trimethylpentane, which was later to become commonly known as iso-octane.

The importance of the discovery of iso-octane lay in its pointing the way for the petroleum industry to improve the antiknock quality of gasoline without the use of antiknock agents, but by altering hydrocarbon structure. Experience has shown that the two methods are supplements rather than substitutions. Tetraethyllead and iso-octane appeared together in 100 octane aviation gasoline of World War II, and were credited with playing a substantial part in winning the Battle of Britain.

Today, through a research program, sponsored by the American Petroleum Institute, nearly 300 different pure hydrocarbons of all types in the gasoline range have been synthesized and their antiknock effectiveness has been measured with and without tetraethyllead under many different engine conditions. And today, the petroleum refiner carries out operations which are deliberately designed to produce hydrocarbons of the specific types that have high antiknock quality and add tetraethyllead to the resulting gasoline. Our present high quality gasolines, the best in the world, are made by using both of the above lines of approach.

Selection of Tetraethyllead as Antiknock Agent

When the decision was made more than 25 years ago that tetraethyllead was the most promising antiknock to commercialize, the data were very scanty in comparison with our knowledge today, yet even if we were beginning all over again we would still select tetraethyllead. The choice would be made from three broad classes of compounds: the hydrocarbons, the amines, and the organometallics. An indication of the relative effectiveness of compounds in these classes is given in Figure 1. The hydrocarbons should be regarded as fuels rather than as antiknocks, and although the petroleum industry has made tremendous strides in manufacturing either individual hydrocarbons (such as iso-octane or cumene) or petroleum fractions high in blending value, their antiknock effectiveness is not comparable with that of the amines and metals. The amines as a class have been thoroughly explored, and although some have been discovered (unpublished work) which are substantially higher in antiknock value than the simple amines such as aniline, there appears no prospect that they can compete economically with tetraethyllead. Their usefulness would appear to be confined to special cases, such as the use of xylidine or monomethylaniline to supplement tetraethyllead in aviation fuels.

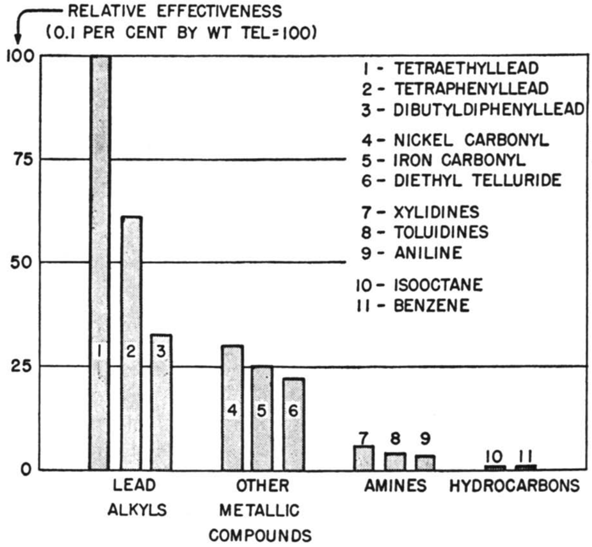

Figure 1. Relative Effectiveness of Antiknock Compounds

Representative single-cylinder engine test data *(1, 2)*

Of the organometallic compounds, there are many which exhibit antiknock value; however, lack of one or more of the essential qualities of solubility, volatility, stability, and low cost has so far ruled out all but two—the lead alkyls and iron carbonyl. The latter is probably the cheapest known source of antiknock increase. It was marketed for a time in Germany and to a limited extent in this country, until it became generally recognized that the great increase in engine wear which its abrasive combustion products produce makes its use impractical. Only limited success has attended the tremendous amount of effort to reduce this wear, and there appear to be no prospects of the commercial use of iron carbonyl as an antiknock agent.

This leaves only the lead alkyls, of which there are many, varying in intrinsic antiknock effectiveness, volatility, stability, and cost. The original selection of tetraethyllead from this group may be regarded as a stroke of genius, good fortune, or both, for it has about the maximum antiknock effectiveness of the group; it possesses good stability;

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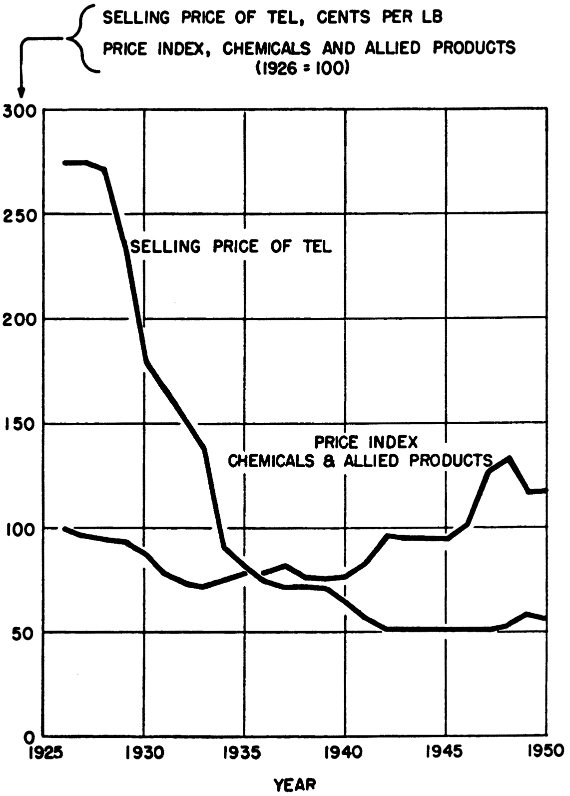

Figure 2. Comparison of Tetraethyllead Price with Commodity Price Index for Chemicals and Allied Products

Yearly average

its volatility is a happy compromise between the high value desirable for use in the fuel and the low value desirable for safety in manufacturing and handling; its cost is also about the minimum. Although research in the field will continue, as fuels and engines change, there appears in the light of our present knowledge no prospect of an antiknock that will be better than tetraethyllead on the basis of three criteria: low cost of manufacture, effectiveness under different conditions of use, and relative freedom from disadvantages in use.

These three criteria deserve more detailed consideration.

Manufacture and Cost of Tetraethyllead Fluids

Tetraethyllead was originally manufactured by the reaction of disodium-lead alloy with ethyl bromide, but for about the past 25 years it has been manufactured by the reaction of monosodium-lead alloy and ethyl chloride. During this time, continued research and development have improved manufacturing methods to an extent which has permitted the sales price to be reduced remarkably. Figure 2 illustrates this well. This reduction has been made possible by: (1) the shift from the ethyl bromide reaction to the ethyl chloride reaction; (2) substantial improvements in yield in the alkylation reaction, now around 90% of the theoretical; (3) increases in size of the charge to the reaction vessel and reduction of the time required for the operations of alkylation and distillation (in the past 13 years alone, the time cycle has been more than halved, thus more than doubling the plant throughput); (4) the general economics usually inherent in large scale

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manufacture; and (5) most important of all, reduction in the cost of intermediates, sodium-lead alloy and ethyl chloride (which today constitute about 80% of the total cost), and of the cost of the added constituents of the fluid, ethylene dichloride and ethylene dibromide. The manufacture of ethyl chloride from petroleum ethylene rather than from alcohol and the manufacture of ethylene dibromide from bromine separated from sea water were important milestones in cost reduction. Plans for a continuous process for tetraethyllead manufacture have been announced in the press, but in the absence of technical details no evaluation of this process is possible.

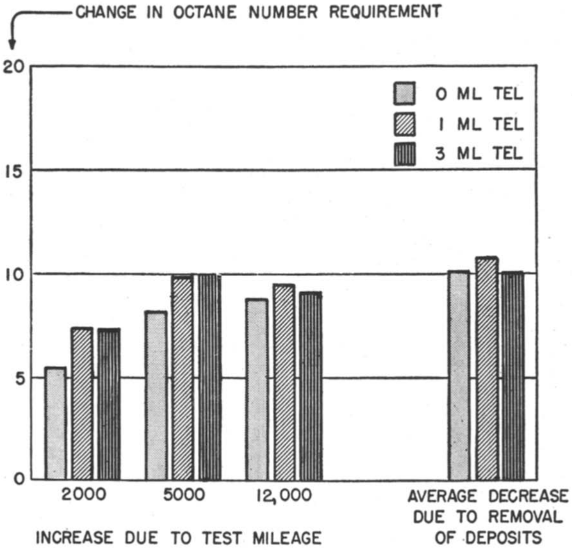

Figure 3. Effect of Tetraethyllead Content of Fuel and Test Mileage on Octane Number Requirement

Fleet of 66 1946 Ford, Chevrolet, and Plymouth cars operated in normal city and country service. Fuel catalytically cracked naphtha. Oil 100% Pennsylvania regular, changed at 5000-mile intervals

Meanwhile, extensive investigation of other of the many reactions by which tetraethyllead can be synthesized, such as the substitution of magnesium and other alkylating metals for sodium and of other ethyl esters for ethyl chloride, has led to the conclusion that none of these is likely to replace the lead–sodium–ethyl chloride method in the foreseeable future. Further reduction in cost would appear most likely to come from refinements in the existing process, and further reduction in operating hazards. One important factor in the cost is not susceptible to improvement by research—the cost of pig lead, which today represents about 18% of the selling price of tetraethyllead as motor fluid. The present price of pig lead is about three times that during most of the past 25 years.

Properties Concerned with Use

Although no more practical antiknock is now known than tetraethyllead, it cannot be said that all of its properties are ideal for its purposes. Its less desirable properties can well be discussed.

Toxicity. Tetraethyllead itself is a highly toxic material, and safe methods for its manufacture and handling have required extensive study. The problem is now under excellent control, but eternal vigilance is necessary to keep it so. At one time, many doubts existed over the safety even of gasoline containing it, but 25 years of intensive study and experience have proved that gasoline containing not over 3 ml. of

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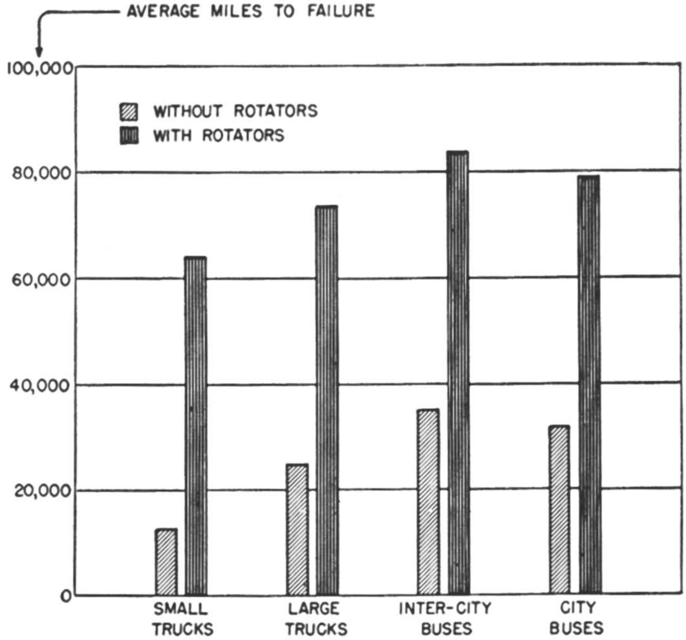

Figure 4. Improvement in Exhaust-Valve Life by Use of Valve Rotators

tetraethyllead per gallon is safe as normally used. Research now in progress may some time determine just what the safety factor is—in other words, how much more than 3 ml. could be safely used. Experience with aviation gasoline containing up to 6 ml. per gallon does not answer the question, because of differences in the manner of use and the volatility of the gasoline.

Storage Stability. Tetraethyllead is entirely stable at ordinary temperatures in the absence of light or oxygen. At one time there were some problems involving instability in gasoline, but at present small amounts of the usual antioxidants, plus the present practice of well-nigh complete removal of bismuth in the manufacture of the tetraethyllead itself, have practically eliminated the formation of solid deposits in gasoline in storage.

Volatility. The low volatility of tetraethyllead (2 mm. of mercury at 50° C.), while a great advantage in reducing manufacturing and handling hazards, may result in some maldistribution relative to fuel in individual cylinders of multicylinder engines. Research in progress shows that this is a most complicated problem, but in general the practical effects are not serious. The use of mixed lead alkyls of higher volatility than tetraethyllead would fail to provide a practical solution, as their intrinsic antiknock value is lower than that of tetraethyllead and their manufacturing cost would be higher.

Sensitivity to Sulfur. The effectiveness of tetraethyllead as an antiknock is markedly reduced by one of the normal constituents of gasoline—sulfur. The different types of sulfur compounds show varying degrees of tetraethyllead destruction, but all have a deleterious effect, and as much as two thirds of the effectiveness of tetraethyllead may be lost in a gasoline high in sulfur.

Engine Deposits. Tetraethyllead when burned alone with gasoline in the engine leaves an "ash" composed largely of lead oxide, which has certain deleterious effects on the engine. This fact was early recognized, and numerous agents were designed to eliminate the ash or otherwise minimize its effects. Organic bromides and chlorides were found to be the most effective scavenging agents, and today we know of nothing better. However, later research has shown that the proper kinds and proportions of these halides vary with the nature of the engines and the conditions of operation. The actual mixtures

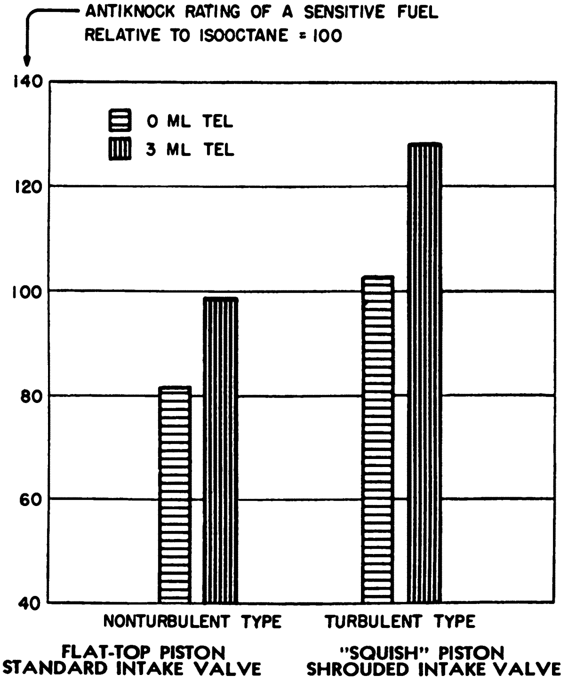

Figure 5. Effect of Combustion Chamber Design on Relative Antiknock Rating of Sensitive Fuel

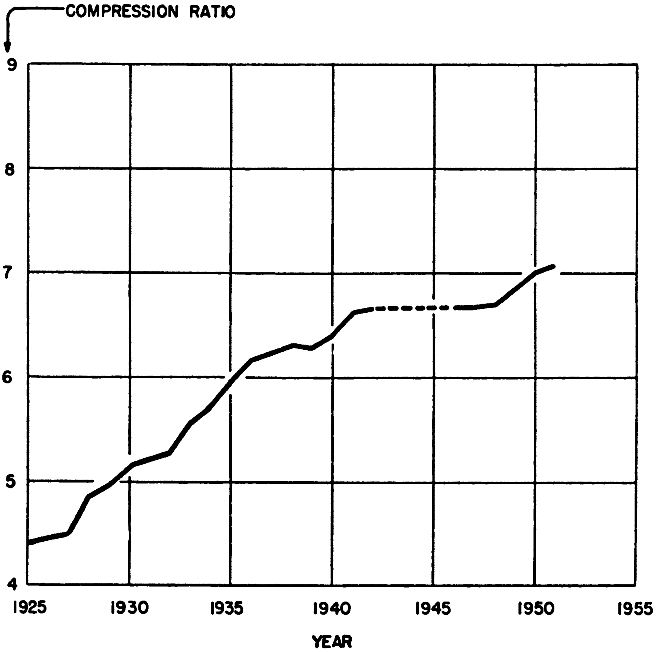

Figure 6. Average Compression Ratio of Passenger Car Engines

1942–45 no production

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now used are designed to give over-all optimum results for the use to which they are to be put; thus, aircraft and automotive engines require different mixtures. During 25 years, several changes in composition of the antiknock mixtures have been made, reflecting changes in average conditions of use with different engines, fuels, and lubricants. Recent research work indicates that in heavy-duty service the use of bromine and chlorine components of volatility close to that of tetraethyllead may offer promise of some further improvement.

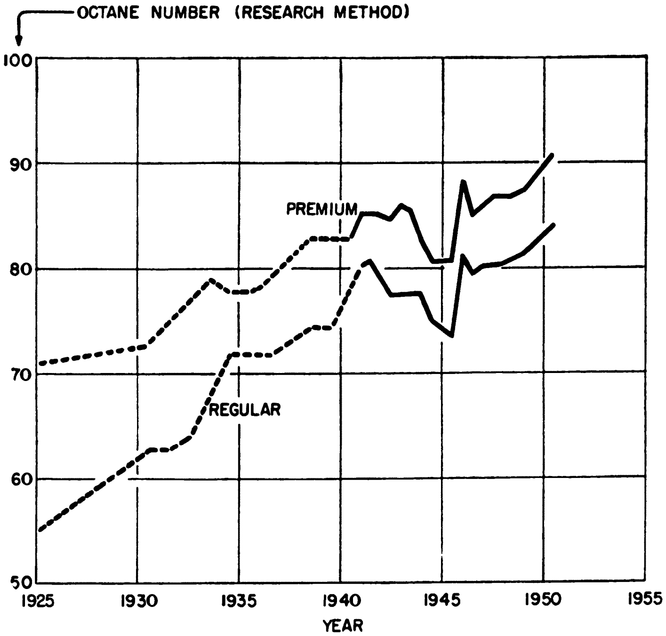

Figure 7. Average Antiknock Quality of Regular and Premium Grade Motor Gasolines

Winter and summer averages. Data prior to 1941 estimated from Motor method ratings

Oxidation or combustion of any fuel and oil in an engine tends to form troublesome deposits on all exposed parts: intake and exhaust valves and manifolds, combustion chamber, spark plug, piston, cylinder wall, and crankcase. The presence of tetraethyllead fluids may aggravate these troubles, may have no effect, or may even lessen them. During the past 25 years, tetraethyllead has frequently appeared to be the "whipping boy" for almost all deposit troubles, and it has required extensive and continuing research to develop the true facts, the problem being complicated by the interrelationship of tetraethyllead, fuel, oil, engine design, and operating conditions. Today, the broad problem of all engine deposits is well recognized by both the petroleum and automotive industries, as well as by the suppliers of antiknocks. Cooperative work is in progress to find practicable means of solving the various problems, one by one.

Studies of the formation, chemical composition, and properties of deposits have shown that they consist of partially oxidized organic material, including more or less nitrogen, sulfur, and phosphorus. Compounds of iron, silicon, calcium, and other metals are present in small quantity, together with substantial amounts of lead oxides, sulfates, and halides from combustion of the antiknock fluid. The effects of these deposits are both physical and chemical in nature; they may physically interfere with lubrication, heat transfer, gas flow, operation of valves and spark plugs; chemically, they may bring about corrosion and oxidation.

Probably the most serious effect brought about by deposits is the increase in octane

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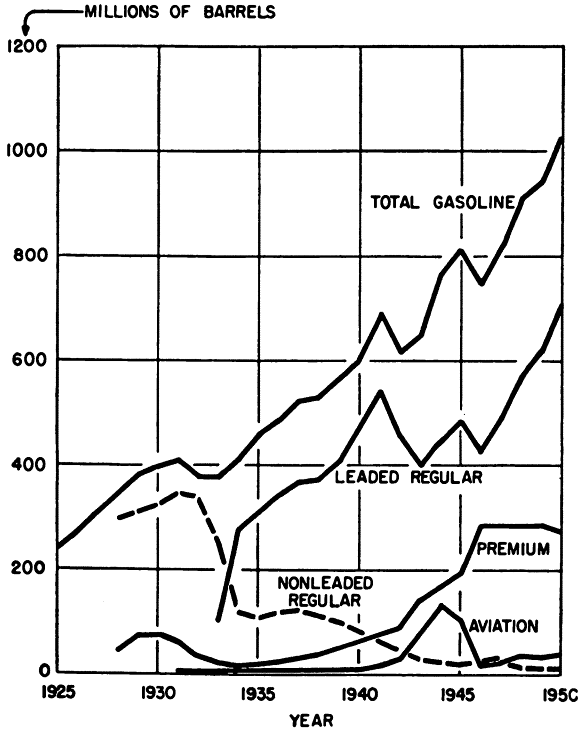

Figure 8. Total Yearly Volume of U. S. Gasoline

Data for motor and aviation (1949–50) from *(4)*. Data for aviation (1928–40) estimated by Standard Oil Co. (N. J.). Data for premium and regular grades from Ethyl Corp.

number requirement of the engine. This increase averages about 10, but may be as great as 25 or 30 octane numbers in extreme cases. The effect is practically independent of the presence or amount of tetraethyllead in the fuel, as shown in Figure 3. Other problems which appear to involve lead are exhaust valve burning, exhaust valve guide corrosion in heavy-duty engines, and spark plug fouling.

Major steps toward solving the general problems of deposits have been made: (1) by engine manufacturers through selection of engine designs, materials of construction, and maintenance procedures which make engines less sensitive to fuels, lubricants, and additives; and (2) by petroleum refiners through selection of fuels, lubricants, and additives which are compatible. For example, in heavy-duty automotive engines the use of sodium-cooled valves and/or valve rotators has increased valve life 300 to 400% (Figure 4), making it approximately equal to piston ring life; in aircraft engines improved design and operating technique have doubled spark plug life.

In general, it would appear that some degree of trouble must always be expected from deposits—trouble which in some part, though by no means wholly, is due to the antiknock compound. However, progress has been made to the point where the present problems cannot be regarded as critical. Moreover, present research indicates that there is hope for substantial further improvement. In any case, the extent to which tetraethyllead contributes to these problems is a small price to pay for its value as a fuel constituent.

High-Antiknock Gasoline

The selection of the power plant and fuel combination for a specific job with any given performance is, in the long run, based on initial cost and operating convenience.

For vehicular use, many and various combinations have been tried, which include steam, electricity, gas, gasoline, and fuel oil engines of widely different types. There have been much more research and invention along this line than is generally appreciated, and out of it all has come the modern reciprocating internal combustion engine burning gasoline. It appears improbable that fundamentally new discoveries will be made in this field; future improvements are likely to be refinements of what we have today. It also appears probable that for a very long time to come all passenger cars and the majority of trucks, busses, tractors, and light aircraft will be powered by the conventional gasoline engine.

The high output and excellent economy of the high-compression engine have been long known, and the average compression ratio of automotive engines has increased steadily during the past 25 years. However, as a result of developments in the production of high antiknock fuels within the last few years, new engines have been designed which are really high-compression engines, built to permit operation at compression ratios well above those permitted by present gasolines. Perhaps the most important single factor in the design of these engines has been the increased stiffness of the crankshaft and other parts, which has been shown to remove the "roughness" that was characteristic of earlier high-compression engines. Already four new postwar engines embodying this principle have appeared, and others are expected in the not too distant future. The trend appears definitely to be in the direction of Vee engines of short stroke, with well cooled overhead valves, and with combustion chambers designed as far as possible to minimize the antiknock requirement of the engine at a given compression ratio.

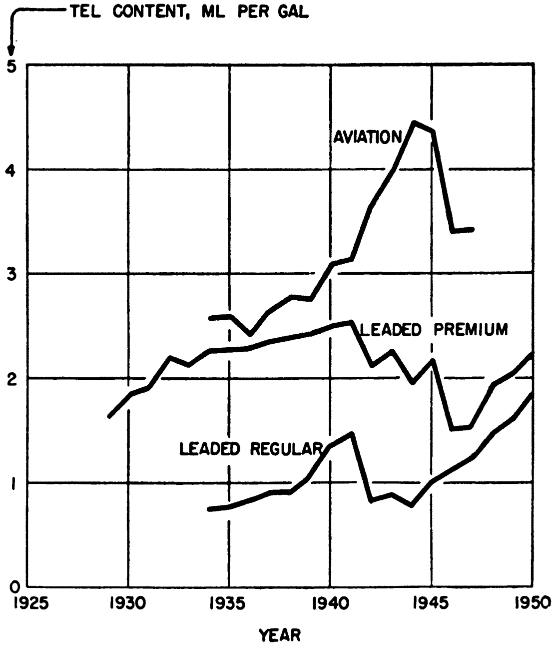

Figure 9. Average Tetraethyllead Content of Leaded Gasolines

The principal limitation on increases in compression ratio is the requirement for high antiknock fuel. Engine designers are well aware of this, and large amounts of research are in progress on so-called "mechanical octane numbers"—i.e., any means of lowering the fuel antiknock requirement for a given engine performance or, preferably, of increasing the performance for a given antiknock level. Methods which have been studied include: (1) better cooling and elimination of hot spots, down-draft carburetion, and straight-through type mufflers; (2) more accurate ignition timing; and (3) pistons and combustion

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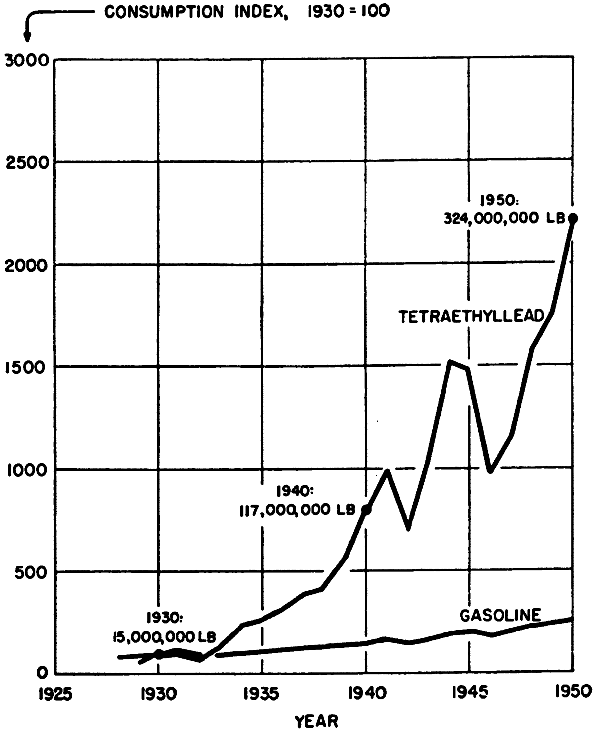

Figure 10. Consumption Index for Tetraethyllead and Gasoline

chambers designed to obtain turbulence in the charge. An illustration of the advantages of turbulence, particularly in fuels of high "sensitivity," and these particularly when treated with tetraethyllead, is shown in Figure 5.

Other methods of minimizing the need for fuels of high antiknock value are based on the fact that in a given engine the maximum antiknock requirement is needed only part of the time, usually although not always at full throttle and low speed. In present engines, automatic change in ignition timing and mixture enrichment at full throttle take advantage of this. Suggested dual-fuel systems or supplemental fuel injection are also effective but inconvenient and frequently costly. The low price of gasoline even of high antiknock level tends to discourage these means of obtaining the desired performance.

It may be concluded that much progress will be made in reducing the fuel antiknock quality required at a given engine compression ratio. However, it seems likely that such progress will be utilized by engine manufacturers to increase compression ratios, because of the fuel economy and engine performance to be gained thereby. The end result will be a demand for fuel of still higher antiknock quality rather than a reduction from present levels.

Figures 6 and 7 illustrate the trends to high-compression engines and high gasoline antiknock quality for the past 25 years. These trends may be expected to continue, except as modified temporarily by restrictions imposed by national defense needs, shortages of materials, etc.

Tetraethyllead as a Component of Gasoline

During the past 25 years, while the total gasoline volume has increased greatly, the use of tetraethyllead has increased even more rapidly. In Figures 8, 9, and 10 are shown, plotted against the years: the barrels of leaded and nonleaded regular grade, premium grade, aviation, and total U. S. gasoline; the average tetraethyllead content of these gasolines; and a comparison of the rates of increase in gasoline consumption and tetraethyllead use.

Now an interesting question may be asked—namely, what value does this added tetraethyllead have, and what would have been the cost of obtaining the same end result without its use?

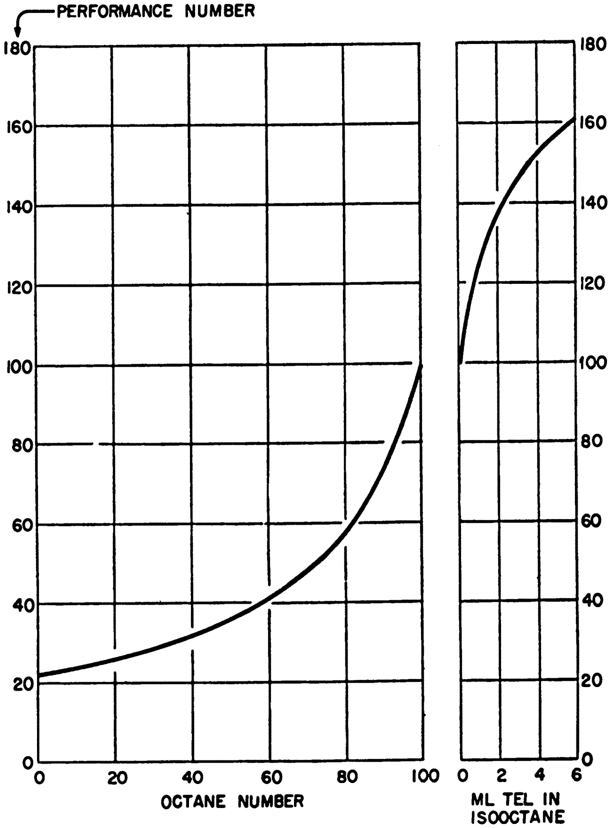

Figure 11. Performance Number Equivalents for Octane Numbers and Tetraethyllead in Iso-octane

To discuss this question intelligently, it is necessary to comment briefly on the octane number scale, and to examine some substitution for it. The octane number scale is an invaluable device for measuring in the laboratory the antiknock quality of fuels, but the numbers so determined are by no means a linear yardstick of the value of a fuel in terms of its performance in an actual engine. Here the maximum allowable compression ratio and degree of supercharge in a supercharged engine are the important characteristics of the fuel, and these are best expressed in terms of performance numbers. The performance number is essentially a linear measure of the maximum—i.e., knock limited—power developed in an "average" variable compression or supercharged engine on a given fuel compared with the power developed on pure iso-octane, the latter being taken at 100. Hence performance numbers may be taken as a linear measure of a fuel's potential value. (Inasmuch as performance numbers have a defined relation to octane numbers below 100 and to iso-octane plus tetraethyllead above 100, the conventional laboratory octane number data can be directly translated into performance numbers, as shown in Figure 11.)

Using this performance number scale as the measure of quality, an appraisal of the average regular and premium grades of motor gasoline of 1950 is shown in Figure 12. It

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is apparent that, in both grades, a substantial portion of the total performance number is contributed by the addition of tetraethyllead. The effectiveness per milliliter of tetraethyllead is the same in the two grades, despite the fact that the premium grade has a higher level base stock and a higher tetraethyllead concentration than the regular grade.

The cost of obtaining incremental performance numbers by refining processes is difficult to determine because of variations in refinery practices and equipment, in product demand from refinery to refinery, and in crude sources. The cost of obtaining a similar incremental increase in performance number by use of tetraethyllead can be accurately obtained.

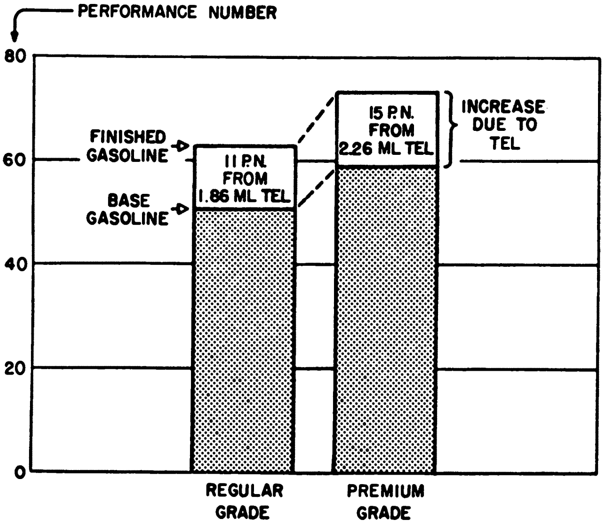

Figure 12. Increase in Antiknock Quality Due to Tetraethyllead

Typical 1950 motor gasolines

If we consider the typical 1950 gasolines mentioned above, with and without tetraethyllead, any reasonable method of estimation shows that the cost of the increased antiknock quality obtained by tetraethyllead is substantially less than the cost would have been for the same increase by refining operations. The almost universal use of tetraethyllead in gasoline is in itself a demonstration of its economy. Furthermore, its use permits flexibility in day-to-day refinery operations required to make gasoline of a given specification.

In aviation gasoline, the value of tetraethyllead is still greater, as it would be practically impossible to manufacture aviation gasoline of the desired quality in quantity great enough to meet the demand, were it not for the use of an antiknock agent.

In general, the trend toward increasing costs of producing crude oil and of processing it to high antiknock gasoline, which has been emphasized by Holaday (*3*), increases the economic value of tetraethyllead, while at the same time the higher retail prices of gasoline (including taxes) emphasize the importance of the fuel economy which higher quality gasoline makes possible.

Future Possibilities

Accomplishments to date in the utilization of antiknock agents have been largely made by cut and try methods, rather than by the application of theory. It is logical to expect that continuing basic research will provide a better understanding of knock and antiknock action, and of the tetraethyllead-fuel relationship, and this should lead to de-

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velopments of practical value. Despite the increases which have occurred in base fuel quality, we are nowhere near the point of diminishing returns in the antiknock effectiveness of tetraethyllead. If we analyze the data of API Project 45 and other research work in terms of performance numbers, we find that the percentage increase in performance number due to tetraethyllead is generally the same in high antiknock hydrocarbons as in low antiknock hydrocarbons of the same chemical type; hence the actual increase in value of tetraethyllead is greater at high antiknock levels, as a greater actual rise in performance number is obtained. This may be seen in Figure 13, where the performance numbers of an assortment of paraffin and naphthene hydrocarbons are plotted with and without 3 ml. per gallon of tetraethyllead. A similar, but less consistent effect is observed for aromatics and olefins.

Among the possibilities for further improvement in the utility of tetraethyllead in motor gasolines at high antiknock levels are at least three: (1) development of still "milder" engines for best use of sensitive fuels with tetraethyllead; (2) discovery of economic means of reducing the sulfur in gasoline to very low levels or of otherwise minimizing its deleterious effect on tetraethyllead; (3) production of base gasolines which, blended with tetraethyllead, will give higher road antiknock values than indicated by conventional laboratory test methods. A striking example of this last possibility is given in Figure 14, which shows the road ratings of a conventional gasoline base and a special blend, each having the same ratings by the laboratory methods. With or without tetraethyllead added, the special blend is far superior to the present-day gasoline.

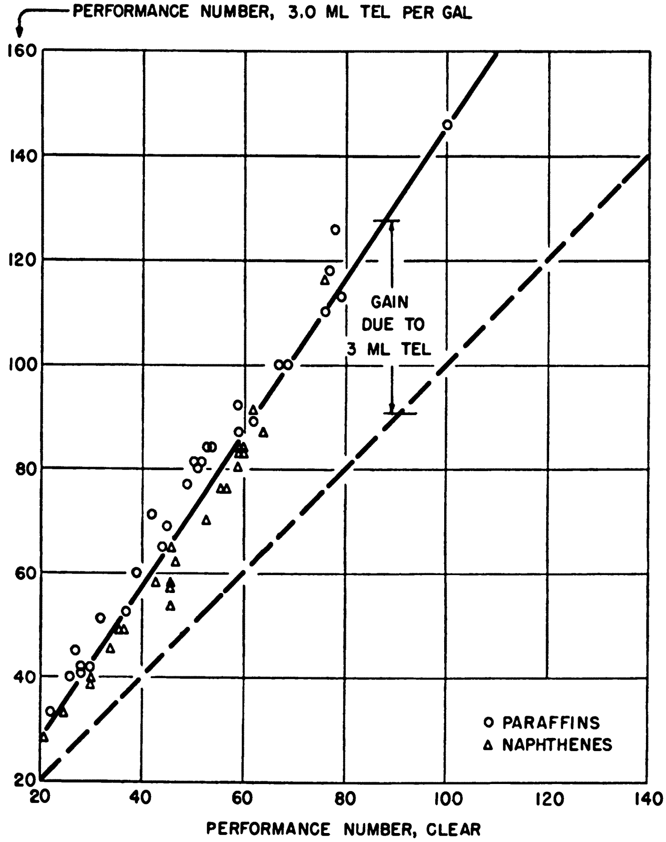

Figure 13. Effect of Tetraethyllead in Paraffin and Naphthene Hydrocarbons

Research method ratings

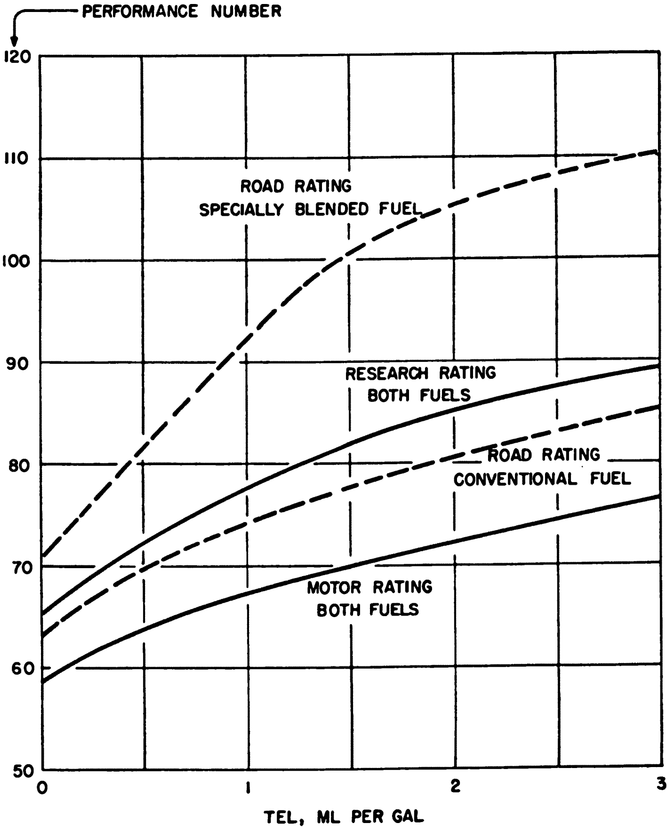

Figure 14. Road Antiknock Ratings of Conventional Fuel and Specially Blended Fuel

Identical laboratory antiknock ratings

Conclusions

The trends of the past 25 years toward increasingly better quality gasolines and concurrent improvement in engine performance are expected to continue. Improvements take time and no radical overnight developments are anticipated. Much further research, design, and investment will be needed, but the end of the road is not in sight and the petroleum and automotive industries are not apt to stand still so long as progress is possible.

In the progress which has occurred, tetraethyllead has played an important part, and its utility as a component of gasoline may reasonably be expected to increase still further in the future.

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Petroleum Lubricants

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During the past quarter century improvements in color, pour point, and resistance to sludging of lubricants derived from petroleum have been achieved, in part, by extension of processes involving solvent extraction and chemical treatment. But in the past decade or more, no marked improvements in the functional properties of lubricants have resulted from development of new refining methods. Improvements in the mechanical application of lubricants have noticeably bettered the conditions under which lubricants operate. In the past few years, the performance of most lubricants has been improved to meet more severe conditions of temperature, bearing loads, and length of use by compounding oils and greases with additives such as antioxidants, detergents, extreme pressure agents, antifoam agents, and other synthesized chemicals. The major applications of these modifying additives are discussed. Some improvements in engineering design, including bearings having improved resistance to fatigue, and bearings and gears which carry higher loads, have generally improved performance of lubricants, but have sometimes led to use of additives to offset deficiencies in operation of conventional oils in conjunction with the new designs. Because the equipment itself, by its design, establishes the lubrication problem, the mechanical factors must be assured so that the chemical situation can be determined. Both mechanical factors and chemical improvements are discussed.

During the past quarter century improvements in the performance and quality of petroleum lubricants have been far more outstanding than for gasoline and other fuels. The general upgrading of lubricants has been possible because of (*a*) the application of newer refining methods (*15*, *18*) to remove unstable sludge-forming hydrocarbons; (*b*) the invention of thousands of additives for improving the performance of oils; and (*c*) the development of new laboratory methods for evaluation of oils as to their probable performance in service. A few outstanding synthetic lubricants are also of interest. These are not strictly petroleum products but are derived entirely or in part from starting materials of petroleum origin. New types of greases are manufactured from metallic reactants and fatty acids which are now available in commercial quantities. The resistance of greases to oxidation has been improved by the use of more highly refined oils and by the invention of antioxidants. Some new synthetic oils are used in manufacture of greases which are especially suitable for lubrication over an unusual range of high and low temperatures.

In PROGRESS IN PETROLEUM TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1951.

Improved methods of chemical treatment and solvent extraction of petroleum oils remove aromatic hydrocarbon molecules which oxidize readily to form sludge and which have high temperature coefficients of viscosity (low viscosity index). Such treatments have a secondary beneficial effect because oils so treated are more susceptible to further improvement by antioxidants and detergents.

Solvent extraction has become the most widely used method of refining lubricating oils. Selective solvents which extract the less desirable constituents include phenol, furfural, dichloroethyl ether, mixtures of cresylic acid and propane, and liquid sulfur dioxide. Liquid propane precipitates asphaltic constituents and wax and retains the more desirable oil components in solution. Dewaxing may also be accomplished by other solvents such as mixtures of benzene and methyl ethyl ketone.

Treatment with aluminum chloride is one of the few chemical methods applied commercially to lubricants in the past 25 years. Aluminum chloride reacts with the undesirable sludge-forming hydrocarbons; the complex reaction product is removed by settling.

These newer refining methods have come into common use in the last 25 years, largely replacing treatment with sulfuric acid and separation of wax by cold settling or by centrifuging (*6*). The net result of recent improvements in refining methods is to provide petroleum lubricating oils of lower pour points, higher viscosity index, greater resistance to formation of gum and sludge by oxidation, and better susceptibility to further improvement by addition of antioxidants and detergents (*17*).

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Industrial Lubricating Oils for Moderate Duty

The general industrial oils for bearing service are usually employed in relatively easy service. Line shafting, bearings in machine tools, stamping presses, electric motors and generators, turbines, pumps, and similar machines are usually designed for rather moderate unit loads (90 to 200 pounds per square inch of projected area), and since there is little restriction on weight and size, the bearings are not in any way pinched for area. With the exception of the power equipment (motors, generators, and turbines), the rubbing speeds are usually moderate, about 30 feet per second maximum, and the ambient is room temperature. Most of these bearings are ring-oiled, sight or wick feed. Therefore, there is no mechanical circulation of the oil for cooling, which will in general be accomplished by conduction through the bearing support. Under these circumstances oil temperature is rarely as high as 250° F., and oxidation rates would be relatively low. The oils for the above uses are either ordinary straight mineral with no additives, or with antioxidants and rust inhibitors.

The power group, especially the steam turbines, present a somewhat different situation. Here the rubbing speeds are high, not less than 50 feet per second and up to 350 feet per second, and clearances in bearings are of the order of 0.001 inch per inch diameter of shaft. The shear rate is rather high and low viscosity oils must be used to keep the rate of heat generation down to reasonable values. In all the large units oil is supplied by forced circulation, and performs practically the entire cooling task. The turbine system usually consists of a main supply tank, gear pumps for circulation, a cooler, and either centrifuges or filters, or both, for batch or continuous cleaning. In general, the temperatures are moderate. The highest temperatures will be found in the front end turbine bearing, next to the high pressure steam chest. In some cases heat is conducted along the turbine shaft and through the housing. Top temperatures may reach 280° to 300° F., although the bulk of the turbine or generator bearings will not exceed 250° F. The cooler brings the temperature down to around 140° to 150° F. Contact with air is also usually moderate; the systems are substantially closed, and designers are learning to avoid splash (dropping oil on a free surface) at the tanks and bearing intermediate catch points.

The major contaminant is water, usually from leaks in the cooler. Demulsibility is, therefore, a factor. The centrifuges and filters generally employed take care of solids as well as water, but the major factor is the extremely long service life expected of turbine oil—50,000 to over 100,000 hours. Consequently, stability is of greatest importance.

About 1928–29, antioxidants were developed to inhibit or retard oxidation of oils for lubrication of steam turbines. 2,6-Di-*tert*-butyl-4-methylphenol made by alkylation of *p*-cresol with diisobutylene (*30*) is an antioxidant commonly added to turbine oils. Such antioxidants are especially effective in highly refined oils and much less effective in poorly refined oils. Uninhibited oils may have a useful life of perhaps 3 months to a year until oxidation has proceeded to such an extent that formation of acidity and sludge becomes excessive. Addition of a fractional percentage of an inhibitor may increase the useful life of the oil by 15 years or more.

Oxidation of uninhibited turbine oils proceeds with sufficient rapidity to form adequate amounts of polar organic acids which are effective in preventing rusting within the turbine. These acids are preferentially adsorbed on steel surfaces, preventing access of water to the steel. Because the addition of antioxidants to turbine oils may eliminate this early formation of organic acids, the steel surfaces may be left unprotected against water. Some cases of rusting attributable to oxidation-inhibited oils have occurred. The difficulty is overcome by addition of polar organic compounds such as dicarboxylic acids (*23*) of high molecular weight to the oil-containing antioxidants. Some such antirust additives promote foaming of oil in turbines. Foaming may be reduced or prevented by addition of traces of polymethylsiloxanes (*33*). Thus several compounds, each having a specific function, may be added to an oil to improve its performance.

Industrial Oils for Severe Duty

This group may be typified by the oils for roll-stand and calender bearings. The steel mill roll-stand bearings carry about the highest unit loads of any industrial bearings (up to 3000 pounds per square inch per square inch of projected area), are subjected to considerable heat by conduction from the hot rolls, and large quantities of quench water may produce contamination, together with mill scale and other solids. Maximum temperatures may run up to 300° F., and in a few cases higher. Disregarding the old solid brasses, which have mostly disappeared, roller bearings are now available for a few installations, and a large number of the sealed-end type of journal bearing, typified by Morgoil. This bearing is a big step forward from the old crude brasses. The working surface of the journal is a hard steel bushing, accurately machined to a fine finish. The bearing surface is properly fitted, and the ends of the bearing are generally sealed by collars to prevent the free egress of the oil. The effect is the same as lengthening the bearing, for it raises the effective pressure over the effective load-carrying area. The viscosity must be stepped up for these bearings, as the loads are extremely heavy, and the rubbing speed low (2 to 15 feet per second). Medium to high viscosity oils are indicated for this service, as the loads are very high, although intermittent.

Contact with air is no worse than for the general industrial bearings, because most of the systems are now designed substantially closed. However, water contamination is prominent, because of the large quantities of quench water. Demulsibility is highly important; oxidation stability probably is next in importance. Antioxidants, antirust agents, and antifoam agents are used in some oils for such service.

Internal Combustion Engines

Operating Conditions. The oils used for internal combustion engine lubrication are probably subjected to more diversely severe conditions than in any other service. In the internal combustion engine the bearings generally run at fairly high temperature (up to 300° F.), the piston surfaces and rings may reach 500° F., and the combustion chamber sustains temperatures in excess of 4000° F. The internal combustion engine is the only prime mover in which combustion takes place in the same mechanism that converts pressure and volume change into power. Here there are machined and lubricated surfaces that are expected to function as successful parts of a pressure-volume power producer, and at the same time are exposed to temperatures far above the minimum cracking temperature for petroleum oils.

A further difficulty is that in high-speed engines the oil is thrown off in thin sheets or drops and is rather extensively atomized. This yields an enormous surface contact with

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not only oxygen, which is quite hot, but products of combustion, some more readily dissolved than air, and inviting cavitation in the oil pump.

A further trouble—in neither the gasoline engine or the Diesel—is the fuel, which is never perfectly burned. Consequently, since the ring-packed piston is the only two-way pump known to man, there are unburned fuel, air, combustion gases, half-burned byproducts that can form lacquer, varnish, sludge, and some carbon, moving down from the combustion chamber to the crankcase. Water vapor, one of the products of combustion, is also present. Oxidized products coming from the crankcase oil include sludge and acids.

These two groups of materials meet in the ring belt and combine their various ill effects. Since the temperatures are high, especially at the top ring, and a stream of gas containing some oxygen is always present as blow-by, the result is a high rate of oxidation. This condition produces varnish and lacquer on the pistons, the oil rings become clogged with sludge, and the rings stick, especially the top two.

The slow-speed, stationary Diesel engine used for industrial power does not present the same problems because its bearings are not severely loaded, for in this type of design there is ample room for bearings. In some designs the pistons are liquid-cooled (oil or water) and the resulting lower ring-belt temperatures are much better for the oil. Valve temperatures are also lower than for gasoline engines, on account of the much greater expansion ratio in the Diesel. In addition, many designs use adequate oil coolers, so that crankcase and bearing temperatures are notably lower than for gasoline engines. These low-speed, stationary engines do not pose any very serious lubricating oil problems.

Up to the present, therefore, slow-speed Diesel engines have operated very satisfactorily on straight mineral oils, although compounded oils are now used as well. There is a noticeable trend toward increasing horespower, even in old engines, by supercharging. The increased temperatures and higher loads will undoubtedly put these engines into the same severe conditions experienced with high-speed Diesels and gasoline engines.

Probably the earliest general need for compounding automotive oils was caused by the move from babbitt-bearing metal to the higher lead alloys. The reason for the general adoption of these alloys is simply that in high-speed engines, there is not room enough, in most cases, to provide bearings for the loads suitable to babbitts (except passenger car engines with low load factor). Part of the troubles with copper-lead bearings was unquestionably from improper maintenance practice in the early period. When the maintenance crews learned how to set up copper-lead bearings (quite different from babbitt), failures decreased.

At nearly the same time, a Diesel manufacturer working with an oil company found that detergents could be useful in washing the oxidized products from the ring belt, or from valve parts, before they were oxidized further to form lacquer or carbon. In this way a great advance in engine cleanliness has been accomplished. The detergents, by keeping the varnish-forming materials in suspension, prevent them from settling down in the ring belt for more cooking. Of course the detergent cannot do a perfect job and it cannot do it forever, but it is an immense improvement.

The difference in severity of service shows up plainly in the service hours expected before change of oil—for the steam turbine 50,000 to 100,000 hours, for the high-speed internal combustion engine much shorter periods of perhaps not more than 100 to 1000 hours.

The heavy-duty gasoline engine is now approaching the Diesel in ring-belt severity, and the bearings operate at higher temperatures. Heavy-duty oils improve bearing, ring, and valve life, and keep the engine cleaner. Within the next few years heavy-duty oils will probably be used fairly extensively in the new high-compression passenger car engines. One of the problems here is sticking of no-lash valve lifters.

Aircraft Engines

Aviation engines present the severest operating conditions of the engine group for two reasons. First, the maximum brake mean effective pressure is much higher—consequently higher average temperatures; secondly, the bulk of these engines are air-cooled.

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Brake mean effective pressure for passenger cars averages about 118 pounds per square inch, maximum; for two high-compression new engines, 142 pounds per square inch. Truck and bus engines are the same in brake mean effective pressure, but the load factor is higher. Aviation engines run up to 220 pounds per square inch brake mean effective pressure. Peak explosion pressure runs up to 1400 pounds per square inch, exceeding the Diesel.

Air cooling does not raise piston temperature much but does increase barrel and head temperature considerably; a 400° F. barrel temperature is not uncommon. Uncooled valves would be hot enough to be inoperable for large high-output engines, and so they are sodium cooled. Investigation shows that compounded oils in commercial aircraft can be of material benefit. The British used inhibited oils in military aircraft during World War II for in-line liquid-cooled engines, but here there apparently still is a problem of combustion chamber deposits. These not only encourage detonation, but foul spark plugs. Therefore, suitable additives must be found or deposits must be reduced in some other way.

In many lubrication systems, especially automotive or aviation, the admixture and absorption of air, or combustion gases, are a problem almost wholly controllable by proper design. During World War II, especially in tanks and planes, this problem became very serious, and the cause and cure were largely defined (*27, 28, 34*). Foaming of lubricating oil can usually be controlled to an unobjectionable level, or eliminated, by means of designing oiling systems to prevent excessive aeration of the oil or by addition of antifoam agents such as silicones (*33*) to the oil.

However, during the war and now, there is the problem of a fix on existing apparatus; in all mobile vehicles the space and surface for entrained air release in oil tanks are generally too small.

Improved Oils for Internal Combustion Engines

Before 1925, there were a few compounded oils made for special purposes, such as lubrication of marine engines and steam cylinders, but additives were not used in automotive crankcase oils. In the 1930's, chemical compounds made by condensation of chlorinated paraffin wax with naphthalene were found to lower the pour points of oils. Pour depressants (*9*) apparently are adsorbed on small wax crystals which separate from oils when they are chilled. The protective adsorbed layer of additive prevents the normal interlacing of larger wax crystals which forms a gel. In 1934 polymerized unsaturated hydrocarbons first came into large scale commercial use to lower the temperature coefficient of viscosity of oils. Other compounds for increasing the viscosity index of oils have since become common.

During 1930–35, pour depressants and viscosity index improvers came into use for lowering the pour points and temperature coefficients of viscosity of automotive crankcase oils. Further improvements were found necessary to prevent corrosion of the relatively new alloy bearings (cadmium-silver) which came into use at that time. Water-soluble and fairly volatile organic acids of low molecular weight are formed by oxidation of some refined crankcase oils. These acids can corrode cadmium-silver, cadmium-nickel, and copper-lead bearings (*12*) and babbitt bearings of low antimony content. Such corrosion may be eliminated by suitable types of antioxidants, notably certain organic compounds containing sulfur, phosphorus, or both (*12*). Sulfurized sperm oil and zinc methyl cyclohexyl dithiophosphate are typical examples of such antioxidants. Hundreds of patents issued since 1935 describe oxidation inhibitors and corrosion-preventive additives.

Antioxidants have been effective in preventing excessive formation of varnish and sludge in the crankcase, and in protecting bearings against corrosion. The antioxidants are not effective in preventing cracking and oxidation of oils on the pistons and cylinder walls nor oxidation of gasoline which sometimes drains down past the pistons and dilutes the oil in the crankcase. Sludge and varnishlike or lacquerlike materials and carbon may be deposited on the internal surfaces of engines lubricated either with uncompounded mineral oils or oils containing only antioxidants (*12*). These deposits clog oil rings and ring grooves in the pistons, and coat pistons, rocker arms, valve stems, and oil filter screens, interfering with normal operation of the engine. Although technologists have been familiar for many years with the cleaning power of soaps and other detergents, it was not until after 1930 that oil-soluble soaps were successfully used in crankcase oils for keeping engines clean (*8*). This development was spurred by a search for oils which would reduce deposits on pistons and cylinder walls, in ring grooves, and in the holes of oil-control rings (*29*). The effectiveness of detergents and the prevention of ring sticking was first demonstrated in Diesel engines in the mid 1930's. Oil-containing detergents are now commonly used for lubrication not only of internal combustion engines in heavy-duty service, but also some passenger car engines in moderate service (*4*).

The detergents first employed were pro-oxidants. They increased the rate of deterioration of the lubricating oils to insoluble sludges and the formation of those acids which are corrosive to alloy bearings. Further development led to the combined uses of antioxidants with detergents to overcome the pro-oxidant effect of the latter. Early detergents included compounds such as calcium salts of oxidized paraffin wax, aluminum, calcium, or nickel naphthenate, made from naphthenic acids derived from petroleum, and calcium dichlorostearate. Types of oil-soluble detergents in current usage, in percentages of about 1 to 10% in crankcase oils, include:

Calcium petroleum sulfonates
Barium petroleum sulfonates
Calcium or barium alkyl phenol sulfides
Calcium or barium wax-substituted phenates

Hundreds of detergents intended for improvement of crankcase oils have been described in the patent and technical literature. While these detergents disperse or emulsify sludge, soot, dirt, or other contaminants in crankcase oils, they usually promote foaming by stabilizing bubbles of air released at the surface of the oil. Additions of traces of silicones are generally effective in eliminating foaming (*1*).

Some additives of the detergent type reduce wear and rusting of engine parts. The rate of wear of ferrous rings in Diesel engines is roughly proportional to the percentage of sulfur in the Diesel fuel (*26*). When added to crankcase oils in relatively high concentrations, some of the detergent additives markedly reduce the rate of wear attributable to acids formed by combustion of the sulfur compounds.

Wear in gasoline engines is believed to be greatest during the warm-up period (*35*) when the engine is cool. Wear on ferrous rings and cylinder walls is accelerated by moisture from combustion of the gasoline, aided by carbon dioxide and acids from oxidation of any sulfur compounds in the gasoline. The rate of wear is very much less when the engine is hot and dry. In the presence of moisture the wear may be considered to be a combination of rusting of the steel surfaces and erosion of the thin layer of products of corrosion. This type of wear is markedly reduced by inclusion in the oil of some additives of the detergent type, especially those which are alkaline.

Hydraulic and Transmission Oils

Brake, hydraulic, and recoil-cylinder fluids fall in much the same field of operating conditions. These are employed in systems in which operating units are exposed to low temperatures, and in practically all cases the connecting tubing lines are so exposed. Temperatures are not likely to go very high, but for aviation, temperatures as low as −70° F. may be frequent. Practically all brake systems and many hydraulic systems employ reciprocating units packed with synthetic rubbers. Hydraulic systems employ rotary pumps and often rotary motors; these cannot be soft packed but are only capillary-sealed—i.e., close clearances. These pumps and motors drop in volumetric efficiency as viscosity falls.

From the foregoing it is easy to define the problem:

1. The fluid must not exceed a definite maximum viscosity at the lowest ambient temperature so that the pump can induct the fluid under an ambient of, say, 4 inches of mercury (46,000-foot altitude), and the resistance to flow in the pipes be kept sufficiently low.

2. The fluid must not fall below a definite viscosity at, say, 160° F. so that the rotary pump and motor volumetric efficiency keeps above a minimum value to operate the system satisfactorily.
3. The fluid must not deteriorate soft packings used.
4. A moderate lubricating value must be obtained, sufficient for the rotary members.

It is quite clear, then, that a very high viscosity index liquid is desirable from the hydraulic designer's point of view, the higher the better.

The earlier brake fluids of such materials as castor oil, glycerols, and alcohols could not meet the requirements of wide temperature range; if the liquid was low enough in viscosity at the low temperature, it was too thin at the high for the pumps to operate motors at speed. If high enough in viscosity at the upper temperature, it was cheese at the low. Operators found that out in Arctic maneuvers, by way of broken shock absorber arms, burst brake and hydraulic system tubing, and sheared pump shafts.

The improvements have come by way of petroleum oils with viscosity index improvers, or synthetics with naturally high viscosity index. The problem of packing deterioration, or rusting, is chiefly a chemical matter. Hydraulic fluids for the various applications include those made from petroleum, synthetic oils, and aqueous solutions containing antifreeze and rust inhibitors. Antifoam agents are necessary in some hydraulic fluids.

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Automotive Gears and Gear Oils

The situation on gears has changed very materially in the last 25 years. In general gears in use ran at pitch speeds not often above 100 feet per second, and tooth loads were low enough so that uncompounded mineral oils at the higher viscosities performed satisfactorily. But the introduction of the hypoid gear brought tooth loads so high that scoring was very serious, except for gears surfaced and contoured more exactly than is feasible for commercial production. The introduction of extreme pressure additives interposed a film that prevented the local welding.

The introduction of high-speed gears such as are found in supercharger trains of aviation engines and turbo-prop drives, brought pitch line speeds up to 400 feet per second. These speeds preclude the use of the higher viscosity oils on account of the high heat generation. Consequently, low viscosity oils reinforced with additives to provide the same kind of protection as found in hypoid gear lubricants may have to be provided.

Since 1935 the increased loads carried by automotive transmission gears, and especially differential gears, have necessitated inclusion of high percentages of so-called extreme pressure additives in automotive gear oils. Conventional transmissions sometimes can be lubricated satisfactorily with uncompounded mineral oils. But the modern differential gear is the hypoid gear, in which the high loads per unit of area, heavy shock loading, and high rates of rubbing of tooth surfaces require compounded lubricants to prevent welding, galling, or seizure (*14*). When lubricated with straight mineral oil the tooth surfaces of these gears fail because, under high loads, uncompounded mineral oil does not prevent contact of the metal of one tooth with the other; welding, scuffing, seizure, and failure may occur in a short time. Seizure is prevented by addition of chemically active additives to the petroleum oil; these react with the tooth surfaces at localized areas where high temperatures are generated by friction. The film formed on the tooth surface by reaction of chlorinated or sulfurized organic compounds, or both, prevents welding and scuffing. Sometimes lead soaps are also used in these lubricants to aid in reduction of friction. Typical additives for gear oils include chlorinated paraffin wax, sulfurized fish oils, sulfurized mineral oils, and lead soaps. In a test-bearing combination, a straight mineral oil may carry a negligible load above which failure will occur by scuffing. Addition of lead soap and active sulfur compounds may increase the load-carrying capacity of the oil to more than 550 pounds (*5*). Many gear oils contain antirust and antifoaming additives as well as extreme pressure agents.

Cutting Oils

The general use of cutting fluids dates from about the turn of the century, and since then not much improvement has taken place, because the real facts by which the chemist

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can be guided in formulation of oils are still lacking. During the past 50 years various kinds of tests have been invented and tried; these cover tests at exaggerated speeds, trick shape tools, measurements of chip cross-section change. The results show up about the same. In any test, at the same speed, depth of cut and feed, same tool shape, material, and cutting fluid, the tool life normally varies 500% in repeated tests and may in some cases vary 1000 or 2000%. Tests are difficult to interpret. What is wrong? Let us examine the mechanical situation.

For turning, in the great majority of cases, the cutting fluid is applied to the tool from above, either directly downward, or in a few cases, attempts are made to "flood" the tool by flow from two directions. But in all cases, the pressure and speed of the stream are low—3 to 5 feet per second.

The stream flows on top of the chip and over the shank of the tool between work and tool holder; but examination of the work face leaving the tool edge shows it to be bright and dry—no oil on it. Another proof that the tool edge is dry is found in build-up. Feathers and slivers from the cut collect on the upper edge of the tool and weld there. This build-up is responsible for much of the variation in tool life, since it varies greatly between tools.

From the foregoing, an important conclusion may be drawn. The cutting edge is not being lubricated appreciably with any kind of cutting fluid, and the cutting edge is being cooled only indirectly, through the chip and the tool shank. This means that straight mineral oils, fatty oils, sulfurized oils, and soluble oils (95% water) are adding tool life chiefly by cooling—there is no appreciable lubricating function. It follows then that all the materials used in the cutting fluid have had some effect on the cooling; they have not much affected the lubrication because they never reach the tool edge in any quantity, except at very low cutting speeds.

The authors have devised a new method of application that gives astonishing results. Instead of increase of tool life of 50 to maybe 150%—all they have hitherto been able to accomplish between different cutting liquids—increases of 500 to 800% at the same cutting speed are being obtained; or the cutting speed can be doubled with the same life.

This method is extremely simple and is based on two major objectives: (1) Wet the edge of the tool with cutting fluid to get lubrication; and (2) wash the tool directly with cutting fluid to increase cooling. To show the difference in cooling, by example, the overhead stream is 2.7 gallons per minute and accomplishes 30° F. cooling of edge; directed jet 0.13 to 0.20 gallon per minute, 75° cooling. Life data, giving only one or two examples: overhead stream 14 to 35 minutes; directed jet, 171 to 203 minutes. This was on 3150 S.A.E. normalized steel work, depth cut 0.150 inch, feed 0.011 inch, 110 surface feet per minute, high speed steel tool. A second example: overhead stream 1 to 10 pieces; directed jet, 70 to 150 pieces and higher on Inconel work material, using tungsten carbide tool. The increase of life is as much as 20 to 1.

Good lubrication is proved by several indications. First, all build-up is eliminated, indicating a wetted tool, so that welding does not occur. Secondly, the tool nose is last to fail, and finish roughness decreases from 200 to 50 microinches (practically a finish cut, ready for grinding); lubrication is evidently now supplied. Thirdly, the work diameter does not change more than 0.001 to 0.002 on 2.5 to 4 inch diameter, until an inch or so from failure. There is almost no tool wear.

The spread of test results is greatly reduced; generally it does not exceed 25% of average value. As a result, a test method has been acquired that will allow the chemist a reasonable chance to select the materials to improve a cutting fluid on the basis of firm and provable facts and not on guess work. Since the new method of application introduces better cooling and, for the first time, lubrication, it appears probable that cutting oils may need a fairly complete restudy after this method is generally adopted.

In the effort to provide adequate lubrication of the tool and the metal being machined, many cutting and grinding oils contain additives similar to the sulfurized and chlorinated hydrocarbons used in lubricants for hypoid gears. This practice has become widespread during the last 25 years; before this a large proportion of metal-working oils were either uncompounded or contained lard oil (*19*). In machining ferrous metals, the sharpness of the cutting tool is maintained for relatively long periods by these additives, and the finish of the work is improved. Such chlorinated or sulfurized additives are believed to form a chloride or sulfide film on the work, at the point where high temperatures are generated by contact with the tool. The film of chloride on sulfide prevents localized welding, improves finish, and delays dulling of the tool.

Soluble cutting oils are mineral oils containing 10 to 50% emulsifiers such as sodium petroleum sulfonates, sodium naphthenates, or sodium rosinates. These compounds allow emulsification of 5 parts or less of the oil in 95 parts or more of water. The emulsion acts as a coolant and, to some extent, as a lubricant (*11*).

Recently it has been possible to use soluble oils for lubrication of some machine tools as well as for lubrication and cooling the cutting tools and the work.

Synthetic Oils

Synthetic lubricating oils of apparently high quality were manufactured in the early thirties by polymerization of cracked wax distillates (95% paraffin wax) (*12, 31, 32*). The thermal stability of these oils apparently was inferior to that for conventional petroleum oils and the demand for wax for other uses precludes its use in synthesis of lubricants. During World War II the Germans were successful in augmenting their meager supply of petroleum oils by polymerization of ethylene to a synthetic bright stock (*16*). This oil was successfully used for lubrication of aircraft engines and motor vehicles.

More recent developments in this country have included synthesis of relatively stable oils of low volatility, low pour point, and high viscosity index by esterification of octyl alcohols, such as 2-ethylhexanol, with dibasic acids such as adipic acid and sebacic acid (*3*). Octyl alcohols may be synthesized from petroleum hydrocarbons via the oxo process. Although of relatively high cost, these synthetic oils find general application in making greases for lubrication of antifriction bearings and instruments in aircraft.

Other synthetics derived from petroleum, having high viscosity index, low volatility, and low pour point, include polyoxyethylene and polyoxypropylene monohydroxy compounds (*22*). These can be made by an addition reaction between a monohydric alcohol and an alkylene oxide.

The unusual properties of silicones make them useful for some special applications as lubricants (*20*). They are relatively resistant to deterioration by heat or oxidation, and have the desirable properties of high viscosity index, low pour point, and low volatility. They may promote wear in steel-to-steel bearing surfaces under conditions of sliding friction, and are not generally useful for such applications. Silicones are satisfactory lubricants in antifriction bearings and in some bearing combinations other than steel sliding on steel.

Greases

The greases are in a less scientific position (or perhaps the term should be, rational) than the oils, chiefly because they can be classed as heterogeneous mixtures; they are not Newtonian liquids. It is certain that greases have greatly improved in the last generation. The adoption of a variety of different base soaps other than sodium and calcium, and the use of additives, have given great improvement in oil-retention, water-resistance, corrosion prevention, and stability. Most of the improvement in greases has come from chemical skill and has had little to do with engineering changes. But better test methods are needed; penetrometer and consistometer values mean little because the readings cannot be used in a formula to calculate working results; they are relative measurements only.

The engineer needs to be able to calculate the load capacity of a grease-lubricating bearing, so he can design rationally. A relatively new instrument is now available that leads to this solution—a continuous viscometer, one step further than the Standard Oil Development instrument, that yields apparent viscosity at any required rate of shear; measures the work per pound to reduce the grease from unworked to fully worked condition; and also shows recovery of unworked condition. Of course grease exhibits a combination of viscosity and plasticity, but the "apparent" viscosity serves perfectly well for substitution in hydraulic formulas for bearings and allows calculation of load capacity.

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Prior to 1925, lubricating greases were generally made by saponifying animal fats or rosin in mineral oil (*21*). The lime base greases (cup greases) are not generally usable above 180° F. because the small percentage of water necessary for holding these greases together is lost at higher temperatures. Soda soap greases require no water to maintain their consistency. Not being dependent on water as an essential constituent, they are usable at much higher temperatures. Aluminum stearate or oleate are the thickeners in some chassis lubricants and semifluid oils.

Recently new soaps have been found to improve greases with respect to melting point, adhesiveness, resistance to the washing action of water, and utility at both high and low temperatures. The newer thickeners are soaps of lithium (*25*) or barium (*24*). Certain properties of greases may be improved by saponification of the alkali with fats or fatty acids which have become available fairly recently; these products include hydrogenated fats and pure fatty (*13*) acids such as 12-hydroxystearic acid.

Greases made with lithium stearate and synthetic oils, such as 2-ethylhexyl sebacate or adipate, are especially applicable to lubrication of bearings that are subjected to both high and low temperatures. An important application is lubrication of antifriction bearings and instruments in aircraft which may encounter temperatures as low as −100° F. at high altitudes.

The resistance of greases to deterioration has been markedly increased by selection of well-refined petroleum oils and suitable soaps of saturated fats or fatty acids, and powerful antioxidants such as diphenylamine, octylated arylalkylated diphenylamines, or other organic amines. These antioxidants protect the grease against oxidation during storage but appear to have little influence on the rate of oxidation of greases during operation in bearings (*2*).

Recently, greases have been developed in which chemically altered bentonite is used as a thickener instead of soap (*10*). The bentonite is purified by removal of silica and is altered chemically by reaction with alkyl amines.

Manufacture of some greases has been improved by introduction of continuous processes (*7*) to replace the old batch methods, and by milling to shorten the manufacturing cycle and improve the consistency of the product.

Conclusion

Because of the brevity of this paper, it is possible to outline only the more important developments. Hundreds of petroleum-base lubricants are available, each of which is suitable for one or more applications. Most of these lubricants contain additives to modify or improve their properties. Pure iron is rarely satisfactory for fabrication of structures and machines. Its performance is improved by regulation of the amount of carbon present, and by addition of carefully controlled amounts of other metals such as manganese, chromium, and nickel. Similarly, striking improvements in the performance of lubricants are obtained by addition of modifying chemicals in proportions of less than 0.001 to 25% or more. At present there appears to be little promise of improving the performance of lubricants through development of new methods of refining. It seems probable that the development of additives will be the major effort for some years.

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Domestic Fuel Oil

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During the past 25 years the use of distillate fuel oil for residential heating has increased more than 23-fold. Whereas in 1926 domestic fuel oil represented only 1.1% of the crude oil refined, in 1950 it represented 11% and has become a major petroleum product to be reckoned with. Today about 16% of the fuel oil supplied for homes with central heating plants is fuel oil No. 1, a straight-run product similar to kerosene. The other 84% is supplied as fuel oil No. 2 or heavier to homes equipped with burners which can satisfactorily burn a heavier and higher B.t.u. product. This latter fuel now incorporates large percentages of stocks from catalytic cracking and has a higher heat content than straight-run fuel. The only real problem in using catalytic or other cracked stocks has been in sludge-forming tendency, and this has been satisfactorily solved by refinery treatments or the use of additives.

Twenty-five years ago the domestic fuel oil business was no more than a healthy infant; in fact, if we go back another five years, we are hardly aware of its existence. But in 1926 the 200,000 domestic oil burners in this country consumed 9,715,000 barrels of fuel oil, or about 1.1% of the crude petroleum run to stills. The oil burner was recognized as here to stay, and the oil industry was giving quite a bit of thought to its future. That thought was justified. As of the end of last year (1950) there were 5,146,354 domestic oil burners, and they consumed during the year 228,000,000 barrels of fuel oil, or 11% of the crude petroleum run. The infant has really grown up (Figure 1).

The three principal fuels for domestic central heating systems are coal, fuel oil, and gas. The growth of fuel oil has been mostly at the expense of the hand-fired coal furnace. One of the main attractions of fuel oil was automatic heat, and the automatic coal stoker was for a time a lively competitor. Lately its popularity has very much declined. Within recent years the extension of natural gas lines has resulted in increased popularity for gas heating, and in 1950 the sales of gas burners actually surpassed the sales of oil burners, as shown by the following percentage figures on sales of automatic heating equipment: gas burners, 56.3%; oil burners, 42.6%; and automatic stokers, 1.1%.

The estimated 1950 figures for fuel consumed, on a B.t.u. percentage basis, compared with the immediately postwar year of 1946, are as follows:

	1946	1950
Coal, %	65.7	49
Fuel oil, %	19.9	28
Gas, %	14.4	23

The rapid growth of the new fuel oil industry to its present size has not, of course, been unaccompanied by problems, both to the burner industry and to petroleum refiners.

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Advances in Chemistry; American Chemical Society: Washington, DC, 1951.

Fortunately, the two industries have listened to each other and have been able to work together.

Any discussion of the development of fuel oil requires a preliminary discussion of the types of burners which have been developed and which are in use. The burner and the fuel must be adapted to each other just as the automobile engine and its gasoline must be adapted. There are, however, very much wider differences in types of burners than in types of automobile engines.

While this paper is primarily concerned with fuels and burners for domestic central heating systems, it must not be forgotten that there are about 7,000,000 oil-burning, space-heating units in use that consume a large volume of fuel, not included in the graphs in Figure 1. These units vary all the way from the portable, unpiped, wick kerosene stove to the larger piped heating stoves in common use.

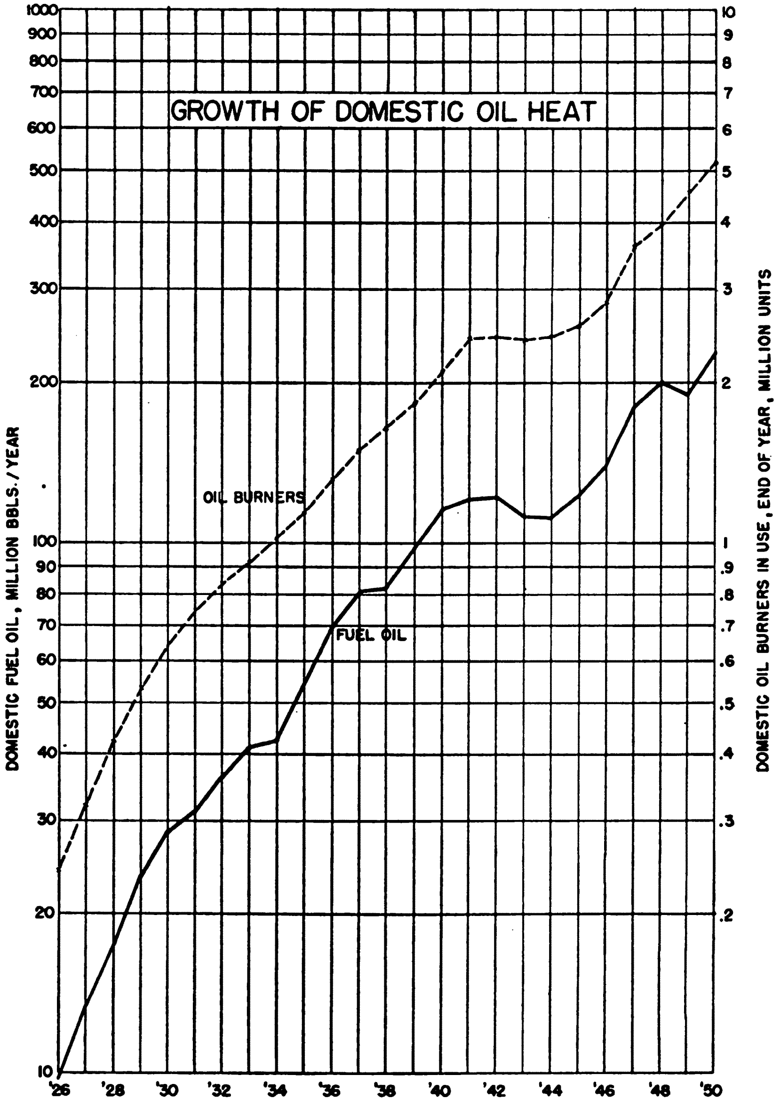

Figure 1. Growth of Domestic Oil Heat

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Oil burners are usually classified into the following groups and subgroups:

- I Vaporizing burners (pot-type)
  - Natural draft
  - Forced draft
- II Atomizing burners (gun-type)
  - Low pressure
  - High pressure
- III Vertical rotary burners
  - Wall flame
  - Suspended flame

The vaporizing-type burner vaporizes the fuel on a hot surface, or by radiant heat, and burns it as a gas. The simplest type uses natural draft and requires a fairly volatile, clean-vaporizing, and clean-burning fuel. While the trend has been away from the natural draft burner, large numbers of them were installed in low cost housing under the construction program following World War II. Most vaporizing burners are equipped with mechanical draft, which not only improves their functioning but somewhat widens their tolerance to heavier fuels.

The common atomizing burners are of the gun type. The oil is atomized either by a high pressure (40 to 200 pounds) solid injection nozzle spraying the oil into the air stream, or by mixing the oil with air at low pressure and obtaining air atomization at the nozzle. High pressure burners are the more prevalent, although the low pressure burners are increasing in popularity, particularly in the smaller sizes. Atomizing burners are much more tolerant of heavier and lower volatility fuels than are the vaporizing type.

The wall flame rotary burner is actually a vaporizing burner in which fuel is thrown from a distributing head, rotating at moderate speed, as a coarse spray. This fuel strikes a vaporizing ring located along the walls of the combustion chamber where it is vaporized, ignited, and burned. Combustion takes place upward from the vaporizing ring along the walls of the combustion chamber.

The suspended flame rotary burner produces atomization of the oil by throwing it off as a spray from a cone, cup, or disk, rapidly revolving about a vertical axis. The spray is supported by the air stream and burns in a flat, circular flame.

In 1950 the comparative sales of burners of the various types were as follows: vaporizing, 5.1%; high pressure atomizing, 70.9%; low pressure atomizing, 13.4%; and vertical rotary, 10.6%.

Domestic fuel oil originally was almost exclusively a straight-run or virgin fraction from petroleum, with a boiling range like kerosene or somewhat higher. It was sold under such names as "distillate," "straw distillate," or even as kerosene. The variations, however, in the burning qualities of the fuel supplied, and the different quality demands of different types of burners, early led to a classification of fuels by the American Oil Burner Association into three classes, and these were adopted in 1929 as a commercial standard of the U. S. Department of Commerce. Although there have been numerous modifications of burner units between 1929 and the present, the revisions in fuel oil No. 1 and No. 2 specifications have been relatively minor, as shown in Table I. This table presents a comparison of the 1929 and most recent, or 1948, specifications. The No. 3 fuel oil classification, which had never been generally accepted, has been dropped.

Table I. Comparison of Commercial Standards Specifications of 1929 and 1948

	No. 1		No. 2		No. 3
	1929	1948	1929	1948	1929
Flash, ° F.	100–165	100	125–190	100	150–200
Water and sediment, max.	0.05	Trace	0.05	0.10	0.1
Pour point, max., ° F.	15	0	15	20	15
Carbon residue (10% res.), max.	...	0.15	...	0.35	...
Distillation, ° F.					
10% max.	420	420	440	...	460
90% max.	...	...	620	675	675
End point	600	625	...	...	...
Viscosity/100° F., centistokes	...	1.4–2.2	...	...	...
Saybolt Universal, max.	...	...	...	40	55
Gravity, ° API, min.	...	35	...	26	...

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Under the 1948 commercial standard CS 12-48, fuel oil No. 1 is defined as "intended for vaporizing pot-type burners and other burners requiring this grade," whereas No. 2 is defined as "for general purpose domestic heating for use in burners not requiring No. 1." The No. 1 fuel is therefore specified to have a low 10% point in the ASTM distillation to ensure quick starting, and a low end point and low carbon residue to ensure clean vaporization.

Since the No. 2 fuel is burned as an atomized spray, these qualities are given much wider latitude. The viscosity specifications on both grades are to ensure proper mechanical functioning of the burner. The gravity specifications are an indirect measure of the carbon to hydrogen ratio and of the chemical composition. This property is important since it is related to burning quality. The low API gravity fuel contains a greater proportion of the nonparaffin hydrocarbons—olefins, naphthenes, and particularly aromatics. It has a higher B.t.u. content per gallon but burns more slowly with a longer flame and requires more air for combustion. It is therefore less suitable for the pot-type burner than is the high gravity fuel.

In accordance with these specifications fuel oil No. 1 has continued to be a straight-run fuel approaching kerosene in its properties. As a matter of fact, on the East Coast, where there has been a much more complete shift of fuel oil customers from No. 1 to No. 2 than in other sections of the country, No. 1 is substantially kerosene. In sections where the utilization of No. 1 is greater, more advantage is taken of the greater specification tolerance over kerosene. In refining, the fuel is usually sweetened and sometimes soda- or acid-treated, or even solvent-refined. Where it is sold as "range oil" for space heaters, especially pipeless, it is important that it be free from objectionable odors, both in the fuel itself and in its combustion products, and more drastic refining is required.

Fuel oil No. 1 is also a high grade Diesel fuel and has to compete with its use for that purpose. Furthermore, it is also an excellent cracking stock and therefore competes with gasoline. The question of how popular it will remain is consequently entirely one of economics, and certainly the burner that can handle all qualities of No. 2 has a distinct economic advantage over that requiring No. 1. In 1950, fuel oil No. 1 represented 16% of the total domestic fuel oil business.

In the case of fuel oil No. 2, refiners early recognized the competition of straight-run oil with its use as a cracking stock, and started to incorporate cracked stocks into this product. This trend has become increasingly pronounced, particularly since the advent of catalytic cracking, which produces a fuel well suited to modern burners. While actual figures are not available, it is probably safe to say that cracked stocks make up at least 70% of the No. 2 oil sold today. The cracked oils are of lower API gravity and, as a result, the customer is getting more B.t.u.'s for his money, but the burner manufacturer has to design for slower burning and longer flame.

The use of cracked stocks in No. 2 has meant additional problems for the refiner. Besides having to refine for odor and color, he is also faced with a stability problem. While catalytic cracking as a rule produces a more stable oil than does thermal cracking, there are still compounds present which on aging will form insoluble sludge. This sludge, if permitted to form, clogs burner screens, and eventually results in trouble.

Little has so far appeared in the scientific literature on the chemistry of sludge formation in these oils. The work of Thompson, Druge, and Chenicek (*8*, *9*) shows that sludges are much richer in sulfur and nitrogen than are the oils from which they are precipitated and that some of the typical compounds of these elements increase the amount of sludge formed in a given time. There is other evidence that oxygen compounds present in the oil may play a part. Unpublished work of the Du Pont Co. (*2*) shows that the sludges have molecular weights of about 300 to 400; this indicates that condensation or polymerization does not play a conspicuous part in the chemistry of sludge formation. Many laboratories are working on this chemistry, and the next few years will doubtless see other important contributions to its literature.

The steps which are being taken by refiners to ensure against any sludge trouble are varied. Since many cracked stocks do not show the tendency to form sludge, those that do can sometimes be sorted out and eliminated from the blend. In most cases chemical treatment, such as with caustic soda or sulfuric acid, is resorted to. The proper treatment to effect adequate stability improvement depends on the particular stock and must be determined by the individual refiner.

The most interesting recent development to avoid sludge troubles is the use of additives. For this purpose the common antioxidants are usually comparatively ineffective. The patent literature indicates that the attack on the sludge problem is along two lines. The first of these is to inhibit the reaction which forms sludge by means of a stabilizing additive. Prominent among these additives are amino compounds of various degrees of complexity (*3*, *4*, *6*, *7*). The second is to peptize the sludge in such a way that it does not plate out on the screens and eventually plug them. Metal soaps are prominent in this class (*1*, *5*).

Any prediction of the future growth of domestic fuel oil requires a better crystal ball than any of us have. Oil has won its present popularity by its greater convenience over the hand-fired coal furnace. With the rapid rise in our standard of living, the American householder has become thoroughly allergic to stoking a furnace, particularly when it gets him out of bed earlier in the morning. Other competitors, natural gas and liquefied petroleum gas, which also give automatic heat, are increasing in popularity. Coal might even stage a comeback by the development of a fully satisfactory automatic system for burning it. The interest of the oil-heat industry is to be sure that the technology of oil burning is made as simple and convenient for the householder as possible. Continuance of the existing cooperation between the equipment manufacturers and petroleum refiners should ensure this.

Acknowledgment

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Natural Gas Liquids

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In the quarter century since 1926 production of natural gas liquids in the United States has increased 597%, while crude oil production has increased only 152%. Better automotive engines and better fuels have resulted in larger, faster, and more luxurious cars. The refinery processes used in producing high octane fuels have caused increasing production of volatiles from destructive decomposition of crude oil fractions, at the time that natural volatiles have become increasingly plentiful as the fruits of conservation in America's oil and gas fields. Natural gas ethane, propane, and butanes are important chemical raw materials principally through conversion to olefins, or through controlled oxidation to yield aldehydes, etc. Economically, their most important chemical reaction is the simple exothermic combustion reaction, which attains its highest economic value in the engine of a moving vehicle. The amount of natural butanes, etc., which can be blended in conventional motor fuel is limited by automotive design, while in the present state of recovery technology our natural gas liquids production could be increased by an amount equal to over 14% of America's motor fuel. Utilization of these liquids as direct motor fuel in special services (tractors, trucks, busses) will realize their maximum combustion utility and will conserve America's less plentiful crude oil reserves, at the expense of its more plentiful and less valuable gas reserves. The "octane era" may be approaching its end, in which case the clean-burning paraffinic natural gas liquids may once again become the premium fuels which they were in the "high-test" days.

To limit the scope of this paper we may define natural gas liquids as liquid hydrocarbons normally recovered and recoverable from natural gas by physical processes only. Customarily these include propane, butane, and heavier hydrocarbons, but to a limited extent ethane is also recovered as a natural gas liquid.

As this paper reviews 25 years of progress in the technology of natural gas liquids, we may first adjust our thinking to the conditions in 1926, so that the progress made since then may be appreciated more fully. In 1926 total U. S. crude oil production was about 771,000,000 barrels; total motor fuel demand, something over 268,000,000 barrels; and highway motor vehicles in use, 21,000,000 (Table I).

It is usual to think of the highway motor vehicle as the dominant factor in petroleum demand. In 1950 the average number of highway motor vehicles in use was 46,500,000 (*12*), a gain of 122% over 1926. Turning to crude oil production, the gain over 1926 was 152% (*2*) and motor fuel demand increased by 272% (*12*). Obviously some other factors besides the number of highway motor vehicles have affected developments during the

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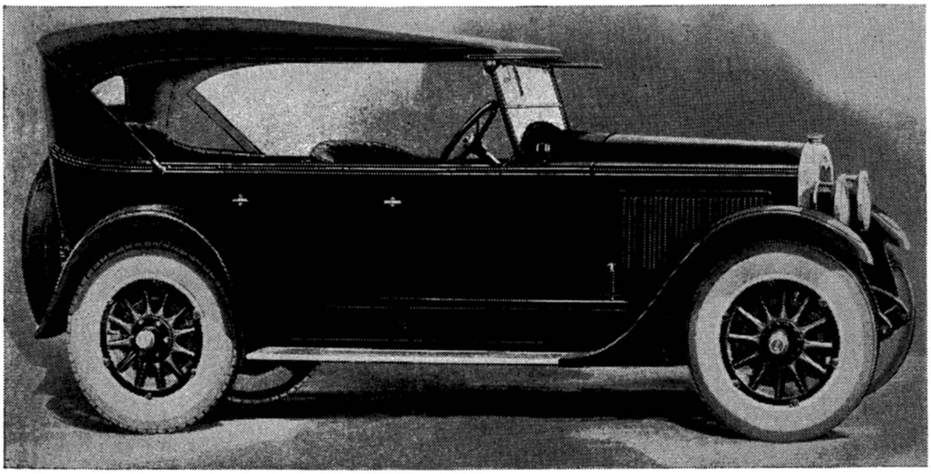

Figure 1. Car of 1926

25 years in question. Use per vehicle has increased and farm and industrial uses of motor fuel have grown from small amounts to a sizable volume. Over 3,500,000 farm tractors are an important factor in today's demand for motor fuel.

Natural gas production has grown from 2 trillion cubic feet in 1926 to 6.9 trillion in 1950 (*2*), an increase of 245%. Production of natural gas liquids has multiplied from 30,000,000 to 207,500,000 barrels (*3, 20*), an increase of 597%. This production of natural gas liquids has been an important factor in meeting the growing demand for motor fuel. Another important factor has been increased yields due to changing refining processes, including the introduction of catalytic cracking about the middle of the period under review.

The highway motor vehicle has been a dominant factor in the petroleum picture during all this time. Comparison of the typical personal car of 1926 (Figure 1) with the typical personal car of today (Figure 2) (*9*) is indeed interesting: From slightly less piston displacement the 1950 engine gets 111 hp. as against 61 for its ancestor of 1926 (Table II). The increased horsepower per cubic inch comes largely from higher compression ratio, so the 1950 car has a more finicky appetite. It requires a gasoline of 83 to 92 octane number, whereas the 1926 car used anything available, 55 octane being a reasonable estimate based on the known possibilities of the refining methods then in use. To get 111 hp. from the same displacement that formerly produced 61 is a notable development. Petroleum and automotive technologists can be truly proud of it. This development in motor car and refining technology is said to represent conservation of our petroleum resources and this is true, if we apply the criterion of ton-miles per gallon of fuel. However, the improvement has been utilized to provide larger, faster cars and not to conserve petroleum. Had petroleum conservation been the sole objective of this 25 years of progress, today's passenger car engine would attain a maximum horsepower of 61 from 136 cubic inches of piston displacement rather than 245. (Two 1950 production models were rated, respectively, 60 and 72 hp. from a displacement of 134 cubic inches.) To attain today's 111 hp. an engine using the design and fuel conditions of 1926 would have a piston displacement of slightly over 450 cubic inches, probably too heavy and expensive for use in any but a few very high-priced motor cars.

Table I. Gas and Oil Production (*2, 3, 6, 12, 16, 20*)

	1926	1950	% Increase
Motor vehicles in use[a]	21,000,000	46,553,000	122
Crude oil production, bbl.	770,874,000	1,943,776,000	152
Motor fuel demand, bbl.	268,128,000	997,000,000	272
Natural gas production, million cu. ft.	2,000,000	6,892,678	245
Natural gas liquids production, bbl.	30,000,000	207,500,000	597

[a] Motor vehicle figures represent averages in use rather than year-end registrations.

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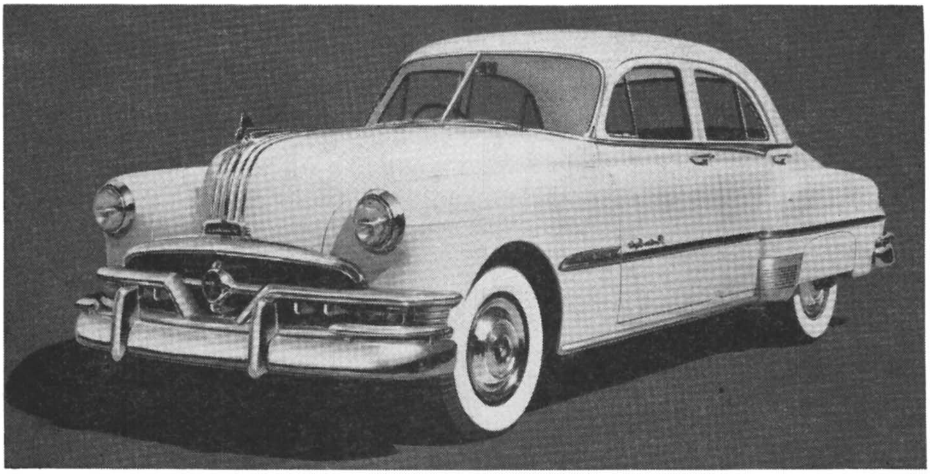

Figure 2. Modern Car

Chemistry of Natural Gas Liquids

From an economic standpoint the most important chemical reaction of the natural gas liquids (butane) is:

$$C_4H_{10}(l) + 6^1/_2O_2 = 4CO_2 + 5H_2O, \Delta H = -1{,}230{,}000 \text{ B.t.u.}$$

This reaction attains its highest economic value in the internal combustion engine of a moving vehicle, although, in this situation, the reaction does not proceed to the ideal completion shown here. To illustrate this concept quantitatively, compare the therm values of some petroleum fuels at the points of utilization:

	Cents/Therm (100,000 B.t.u.)
Natural gas, industrial	3.0–4.0
Natural gas, house heating	6.0–7.0
Distillate fuel, house heating	9.5–10.0
LPG, miscellaneous domestic and farm use	8.0–12.0
Motor gasoline (tax free)	15.0–18.0

Under present supply conditions, and bearing in mind the economic law of marginal utility, combustion still establishes the market values of natural gas liquids and other primary petroleum products. Still there are other chemical reactions of major importance in the utilization of natural gas liquids.

Controlled dehydrogenation of the light paraffins—ethane, propane, and butane—changes their chemical aloofness by changing them to olefins. From this starting point butylenes, for instance, may be further dehydrogenated to butadiene, on which the bulk of our synthetic rubber manufacture is based. In 1950 this usage accounted for 5,000,000 barrels of mixed butanes and refinery butylenes. The dehydrogenation reaction applied to propane and ethane yields the corresponding olefins, but propane may also be decomposed to yield ethylene.

Through reactions with acid and subsequent hydrolysis these olefins are converted to the corresponding alcohols. The isopropyl and *sec*-butyl alcohols yield the corresponding ketones through dehydrogenation or controlled oxidation.

Table II. Progress in Passenger Car Design (9)

Average Engine Data	1926 Car	1950 Car
Displacement, cu. inches	247.8	245.3
R.p.m. at maximum hp.	2629.0	3681.0
Compression ratio	4.44	7.03
Hp. per cubic inch	0.246	0.452
Maximum b.hp.	60.8	110.9

Averages are not weighed for varying sales of different makes and models.

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Ethylene is the basis for a large number of chemical reactions leading to styrene, acrylonitrile, Orlon, and other synthetic fibers. Large scale production of ethylene for chemical raw material has recently been announced by one major oil company. Part will be made from natural gas ethane.

In considering the chemical reactions based on the light olefins it is obvious that natural gas liquids are at a disadvantage in comparison with the corresponding refinery cuts. These contain varying but substantial percentages of olefins as such—the results of thermal and catalytic decomposition of the heavier petroleum molecules. But refinery olefins are also in demand for synthesis to premium motor fuels. It is fortunate that there are abundant supplies of natural gas paraffins for conversion to provide adequate raw material for our olefin chemistry.

In the manufacture of oxygenated compounds, natural gas liquids can be used in an entirely different type of chemical reaction (*14*). Controlled oxidation applied to propane gives the following indicated reactions:

$$C_3H_8 + O_2 \longrightarrow CH_3OH + H_2O$$
$$C_3H_8 + O_2 \longrightarrow CH_3CHO + H_2O$$
$$C_3H_8 + O_2 \longrightarrow HCHO + H_2O$$

and to a lesser degree,

$$C_3H_8 + O_2 \longrightarrow C_2H_5OH + H_2O$$
$$C_3H_8 + O_2 \longrightarrow C_3H_7OH$$

About equal weights of products from the first three reactions are contained in the reaction mixture. Separation of these reaction mixtures is no easy matter; however, it is being done successfully. At present about 1,800,000 barrels of propane and butane annually are processed by controlled oxidation, and this amount will be doubled when plans now under way are completed.

Natural gas liquids do not contain olefins—at least not in any appreciable amount. Bearing in mind that "Entropy strives toward a maximum," it is not surprising that these comparatively unstable hydrocarbons are not present after a few geological ages of time. It is rather surprising to find fairly large amounts of aromatics and naphthenes in many of the natural gasolines and natural gas condensates. We might expect that reservoirs of a younger geological age—e.g., the Cenozoic pays of the Gulf Coast—would yield natural gas condensates and natural gasoline relatively high in aromatics and naphthenes and that the older pays of the mid-continent areas would yield more highly paraffinic hydrocarbon mixtures. Considerable analytical data available to the writer, however, do not support this generalization. It is true that geologic age is only one factor in the diastrophic processes which have produced the hydrocarbons our gas and oil wells yield. With respect to natural gas liquids, perhaps the best generalization is that those areas and fields which yield naphthenic crude oils will also yield natural gasolines and condensates relatively high in naphthenes and aromatics. The petroleum technologist who seeks such raw materials for some special refining problem can be guided by this in selecting samples for actual laboratory investigation.

Recovery Methods

The physical processes by which natural gas liquids are recovered include phase separation, cooling, compression, absorption, adsorption, refrigeration, and any combination of these. Obviously the definition already stated excludes refinery light volatiles produced by the destructive decomposition of heavy petroleum fractions and it also excludes liquids that may be produced synthetically from natural gas. These distinctions are of economic importance in considering our basic energy reserves. Both the refinery volatiles and the synthetic liquids represent conversion products from other hydrocarbons and the conversion is usually attended by a considerable loss. Thus it has been stated that only about 47% (*17*) of the energy of natural gas is realized in the liquid hydrocarbon products of the Fischer-Tropsch type of synthesis.

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While the recovery processes used in extracting natural gas liquids from our gas production have improved enormously in the past 25 years, there has really been no new fundamental development in this period. Use of higher pressures and lower temperatures has permitted higher levels of recovery. Thus in today's technology recovery of 70 to 80% of the propane contained in the gas is a common attainment and higher recoveries are known. Similarly, 95% of the butanes may be readily recovered as liquid and substantially 100% of the pentanes and heavier volatiles.

The complexity of today's recovery plants results from the difficulty of selectively recovering a high percentage of the available propane and butane as liquid while rejecting to the gas stream unwanted methane and ethane (*15*). Thus, we have multistage flashing or stripping of the high pressure fat oil with a low pressure reabsorber. Or perhaps the two functions are combined into one column and dignified by the rather ponderous term "demethanization." Two-stage distillation systems are sometimes used to attain the otherwise conflicting objectives of high propane condensation and complete stripping of hexanes-plus from the lean oil.

Perhaps the hypersorption process (*7*) of recent years may be thought new and it is new in applying the mechanical principle of continuous operation to charcoal adsorption, but such adsorption on a batch process was in use more than 25 years ago and became obsolete in competition with absorption. Now the continuous hypersorption method appears to be finding a real field of usefulness, especially in making very high recoveries of propane and in recovering substantial amounts of ethane. Recovery of ethane is beginning to be important, in connection with its use as a chemical raw material for the reactions mentioned previously in this paper.

There are four basic sources of natural gas liquids: (1) gas field plants, (2) oil field plants, (3) cycling plants, and (4) gas wells.

Gas field plants are those installed for the primary purpose of processing natural gas to permit satisfactory transportation and use of such gas as a fuel. Such plants produce natural gasoline or condensate, depending on the type of gas reservoir that supplies the raw gas being processed (Table III). They also produce propane and butane. Oil field plants are those that process gas produced as an incident to the production of oil. Cycling plants produce condensate and, usually, butane and propane from high pressure reservoirs in which the gas and liquids exist as a homogeneous single phase at conditions beyond the critical. As implied by the term "cycling," the gas is returned to the reservoir after removal of the liquids. Gas wells, so-called, which tap such reservoirs produce a mixed stream of gas and liquid due to the formation of two phases incident to the reduction of pressure and temperature when the reservoir fluid is brought to the surface. The liquid separated from the gas at the wellhead is usually referred to as lease condensate.

Lease condensate is much the same as condensate produced in cycling or gas field plants, except that the plant product contains more pentanes and hexanes. Mere separation of the well stream from a high pressure gas zone does not effect complete recovery of the lighter liquids.

No discussion of natural gas liquids recovery would be complete without some reference to the conservation problems involved. Formerly considerable volumes of oil well gas were flared without processing. The liquid content of this rich gas was lost entirely.

Table III. Comparison of Reservoir Fluid Compositions – Low Pressure *vs.* High Pressure Gas Reservoirs (*21*)

	Low Pressure		High Pressure	
Reservoir pressure, lb./sq. inch absolute	467		4250	
Reservoir temperature, ° F.	88		202	
	Mole %	Gal./M cu. feet	Mole %	Gal./M cu. feet
Methane and inerts	85.49	..	82.66	..
Ethane	6.90	..	6.21	..
Propane	4.95	1.36	3.83	1.05
Isobutane	0.53	0.17	0.90	0.29
n-butane	1.27	0.40	1.83	0.58
Isopentane	0.33	0.12	0.57	0.21
n-pentane	0.30	0.11	0.43	0.16
Hexanes-plus	0.23	0.10	3.57	1.83
Totals	100.00	2.26	100.00	4.12

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Table IV. Natural Gas Liquids—Unit Production Data (2, 3, 20)

	Natural Gas, Billion Cu. Feet	Natural Gas Liquids, Million Gal.	Gal./M Cu. Feet
1946	4943	4830	0.98
1947	5630	5838	1.04
1948	6008	6913	1.15
1949	6245	7434	1.19
1950	6893	8713	1.26

In the years since the end of World War II authorities of the more progressive oil-producing states—Texas, in particular—have become increasingly critical of this practice. A greater percentage of total gas production is now being processed and by more efficient methods. Over-all recovery per unit of gas volume increased by 28% in the 5 years from 1946 to 1950 (Table IV). The increasing availability of these light hydrocarbons has resulted from: greater gas production, a greater percentage of the production processed, and more efficient process methods.

Utilization of Natural Gas Liquids

With the foregoing explanation it is now possible to study a little more closely the composition of the various streams of natural gas liquids which make up 10% of the total petroleum supply of the United States. Of the total 207,500,000 barrels produced in 1950, approximately 35,000,000 barrels were propane; about 53,500,000 barrels, butanes; and about 107,500,000 barrels, isopentane and heavier, up to the gasoline end point; and perhaps 11,500,000 barrels represented products heavier than gasoline (Table V). About 124,000,000 of the total production moved to market through oil refineries. This represents less than 60% of the total. The natural gas liquids taken by refiners are classified:

Propane and butane	12,270
Gasoline and other plant products	85,945
Lease condensate	25,905
	124,120

Somewhat over 40% of the total 1950 production moved directly to market either as liquefied petroleum gas or as conventional motor fuel. It is worthy of note that in 1950 the direct marketing of conventional motor fuel from natural gas liquids amounted to over

Table V. Analysis of Natural Gas Liquids Production, 1950 (2, 3, 20)

(Thousands of barrels)

	Propane	Butanes	Pentanes through Gasoline E.P.	Heavier than Gasoline	Totals
Reported					
LPG, etc.	35,244	35,629			70,873
Natural gasoline		15,769	63,075		78,844
Finished gasoline and naphtha		998	18,965		19,963
Raw condensate (plant)			7,142	1,786	8,928
Other products				2,950	2,950
Lease condensate		1,036	18,134	6,735	25,905
Totals	35,244	53,432	107,316	11,471	207,463
Potential recovery (100% basis) from 6,892,678,000 M cu. feet					
Gal./M cu. feet	1.14	0.65	0.80		2.59
M bbl.	187,087	106,672	131,289		425,048
% actual recovery	18.8	50.1	90.4		48.8
Practical recovery based on present technology, %	70	90	96		
M bbl./year	130,961	96,005	126,037		353,003
Increase over 1950 recovery, M bbl./year	95,717	42,573	7,250		145,540

Compositions estimated by author:
Blended LPG: 30% propane, 70% butane.
(Other LPG as reported by Bureau of Mines).
Natural gasoline: 20% butanes, 80% pentanes-plus.
Finished gasoline, etc.: 5% butanes, 95% pentanes-plus.
Raw condensate (plant): 80% gasoline, 20% heavier.
Lease condensate: 4% butanes, 70% gasoline, 26% heavier.

21,000,000 barrels, or approximately 20% of the pentanes—gasoline end-point components contained in the year's production.

Use in Conventional Motor Gasoline

Roughly speaking, this use includes all of the pentanes and heavier hydrocarbons distilling up to gasoline end point plus some of the butanes, totaling about 70% of the recent annual production of natural gas liquids.

The changes in motor car design and fuel technology have affected the use of natural gas liquids for motor gasoline in two ways. First, increasing octane number has deprived the naturally occurring pentane-plus fractions of the antiknock advantage they once had. Refiners find that these fractions can frequently be used in regular grade motor fuels of about 84 octane number without any disadvantage (Tables VI and VII). Some natural gasolines and condensates, however, may fall short of the current requirements for regular grade. In spite of an unusually good response to the addition of tetraethyllead, most natural gasolines fall short of the current octane requirements for premium grade gasoline. Second, and more important, the processes which the refiner uses to increase motor fuel octane number yield increasing volumes of light hydrocarbons. In the early 1920's cracking operations were undertaken to convert heavy petroleum products into lighter materials of gasoline boiling range. In more recent years, and all too frequently, the urge for higher

Table VI. Inspection Data—Typical Natural Gasolines from Oil Well Gas (*21*)

	E-Texas	N-Texas	S-Oklahoma	New Mexico	Illinois
Gravity, ° API	81.7	84.4	85.9	81.0	80.9
Vapor pressure, Reid	14.0	18.0	22.0	16.0	14.0
ASTM distillation, ° F.					
I.b.p.	94	80	70	86	84
10% rec.	106	96	78	101	100
20%	110	100	84	107	107
30%	113	105	92	112	114
40%	117	110	100	119	120
50%	122	117	111	128	129
60%	130	126	124	140	140
70%	142	138	142	158	160
80%	164	160	166	184	182
90%	196	195	205	222	220
E.p.	289	290	294	334	306
Recovery, %	97.5	97.5	97.0	97.0	97.0
Loss, %	1.5	1.5	2.0	2.0	2.0
Octane number, motor[a]					
− clear	79.2	74.0	77.0	77.0	70.0
+ 1 ml. TEL/gal.	84.6	83.6	81.4	81.8	78.0
+ 2 ml. TEL/gal.	87.4	88.0	82.8	84.9	82.3
+ 3 ml. TEL/gal.	87.8	90.2	84.6	87.4	85.1

[a] Blending octane No. Motor method in 50-50 blend with 72 octane No. reference fuel blend.

Table VII. Inspection Data—Condensate and Condensate Products (*21*)

	Motor Fuels from Plant Condensate		Lease Condensate	Kerosene from Lease Condensate
	A	B		
Gravity, ° API	64.9	68.7	56.4	42.8
Vapor pressure, Reid	7.5	8.0	...	...
ASTM distillation, ° F.				
I.b.p.	113	106	94	392
10% rec.	140	136	141	414
20%	149	149	180	421
30%	160	164	222	426
40%	175	185	251	432
50%	189	206	282	438
60%	204	231	323	447
70%	221	259	395	454
80%	248	293	476	465
90%	281	328	568	479
E.p.	367	386	652 (92%)	496
Recovery, %	97	98	92	98.2
Loss, %	2	1	1.2	0.6
Octane number, motor				
− clear	67[a]	59[a]	...	
+1 ml. TEL/gal.	76	70	...	
+2 ml. TEL/gal.	81	77	...	
+3 ml. TEL/gal.	...	79.4	...	
Flash point, ASTM D 56-36				168.5
Yield, % of condensate	70–80	70–80		15.5

[a] Research method octane numbers are usually 1 to 2 higher than Motor method on these products.

octane number has forced destructive processing of naphthas already in the gasoline boiling range. Such processing has yielded such by-products as: (1) gas having only refinery fuel value, (2) propane that must compete in liquefied petroleum gas markets with already abundant supplies of this hydrocarbon available in natural gas liquids, and (3) butanes that compete with the corresponding fraction from natural gas liquids for blending motor fuel, or for liquefied petroleum gas sales. Because of their olefin content refinery C_3 and C_4 fractions have a limited special utility as raw materials for chemicals and synthetic fuels, but this applies to only a part of these products.

Table VIII. Propane and Butanes Supply and Demand, 1950 (*18, 20*)

	M Bbl
Supply	
From natural gases	70,873
From refinery gases[a]	28,893
Total	99,766
Disposition	
Natural gas products used as refinery raw materials (propane and butanes)	12,270
Exports	258
Synthetic rubber[b]	5,000
Reported LPG sales	79,357
Total accounted for	96,885
Discrepancy and losses (2.89%)	2,881
Reported LPG sales	
Domestic and rural	51,025
Chemical	15,476
Industrial and miscellaneous	7,142
Gas manufacturing	5,714
	79,357

[a] Does not include refiners' own uses, or large pipeline sales to affiliated chemical plants.
[b] Not included in LPG marketing statistics.

As a result of by-product volatility produced while pursuing the elusive octane number many refiners have tended to recognize only one raw material—crude oil—while during the 25-year period natural gas liquids have grown from less than 4% to about 10% of total petroleum liquid supply. The problem of growing supplies of volatiles, however, has received considerable attention in recent years from both automotive engineers and fuel technologists. The recent action of the American Society for Testing Materials (*4*) in establishing a permissive maximum vapor pressure limit of 15 pounds Reid for winter gasoline is a constructive development. It has been estimated that this one change in gasoline specifications will permit the upgrading of 10,000,000 barrels of butane annually from gaseous fuel value to motor gasoline value, and it will permit progressive refiners to improve the starting and warm-up qualities of their winter gasolines. Unfortunately, the increased use of butane in winter gasolines competes with the peak seasonal demand for liquefied petroleum gas. However, butanes withdrawn from this supply can, in general, be replaced with comparatively plentiful propane. A still more constructive development would be an even moderate increase in the actual vapor pressure limits of summer grade gasolines. It is, perhaps, true that many refiners and marketers of gasoline are overly sensitive to the probability of vapor lock in a few obsolete or very poorly designed cars. Any large increase in summer vapor pressure limits must, in all probability, await improvement in automotive design (*10*).

Other Uses

The 25-year period under review has been characterized particularly by a phenomenal growth of what is known as the liquefied petroleum gas industry. Utilization of propane and butane for light, heat, and power was almost negligible in 1926. There are now said to be 7,500,000 domestic and rural customers (*18*) for these products and, of course, there has been parallel development in chemical use and in gas manufacture (Table VIII). These light hydrocarbons have also found a considerable outlet for industrial fuel, although in recent years this usage has tended to level off with increasing competition from natural gas due to its greater availability in the industrial areas of the Great Lakes states and the eastern seaboard.

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However, the domestic and rural uses of liquefied petroleum gas have by no means been fully developed. Because of temporary shortages due to inadequate transportation or lack of storage in consuming areas in the years since the end of World War II, there has been some tendency to think that supplies of propane and butane might become short within the next few years. As an instance of this, an executive of a large motor manufacturer told the writer in 1949 that his company had lost interest in developing truck engines for butane because it felt that fuel supplies could not be relied upon.

The writer recently has made an investigation of potential recoveries of liquefied petroleum gas and other natural gas liquids (*8*), based on a study of a large number of representative gas analyses from principal producing areas in the Mid-Continent and Gulf Coast. The data derived from this study have been applied in preparing a revised study based on the full year of 1950, results of which are shown in Table V. The conclusion is that recoveries of natural gas liquids could readily be increased by about 145,000,000 barrels annually, or about 71% over present levels. This increase can be attained well within limits of present methods for the recovery of these liquids; this potential increase does not include possible additional propanes and butanes to be recovered as liquid by more efficient processing of refinery gases and vapors. Other students of this problem have reported that a very much greater potential is available whenever the demand may justify (*1*, *13*). It is recognized that this increased recovery will be attended by higher costs than present recoveries. These higher costs must be reflected in higher prices, presenting a peculiar problem under controlled economy conditions. Price ceilings based on liquefied petroleum gas utilization might actually prevent the production of motor fuel propane and butane at prices lower than those for conventional gasoline. However, in the event of a shortage of motor fuel, as under wartime demands, the increased recovery could readily be justified and, indeed, this extra liquid fuel would in all probability be available at materially less cost than that of conventional gasoline. There is no question that it would be available at a saving compared with synthetic gasolines or gasolines from shale.

There has already been a notable trend in the past three or four years toward the utilization of propane and butane directly as motor fuel. In 1950 over 100,000 farm tractors (*18*) were converted to these fuels, and a number of urban bus operators announced the purchase of busses to be fueled with propane. It is felt, too, that the nonitinerant trucking operator will in many cases find it advantageous to convert to propane or butane when assured of engines that can take full advantage of the superior quality of these fuels, and once he realizes that an adequate supply can be had.

In considering propane and butane as motor fuel it is recognized that the B.t.u. value per gallon is from 17 to 24% below the B.t.u. value for gasoline. One manufacturer of urban busses has claimed that this disadvantage can be offset by the increased efficiency from the higher compression ratio possible with propane. To accomplish this, the propane engine must have a fuel efficiency 30% greater than a conventional engine using today's regular gasoline and must, accordingly, operate at a compression ratio of 10 to 12. Bearing in mind that propane has an octane number of 99 and based on the data reported by Kettering (*11*), it appears that with proper engine design this attainment is quite within the range of possibility. Of course, old engines converted to propane or butane will not attain the same fuel economy and may prove unsatisfactory.

In comparing propane and butane as direct motor fuels we may also remember that no penalty has been paid in the way of refining losses (*19*) to realize the high octane numbers which these fuels have. Neither has the cost of expensive catalytic processes for upgrading been incurred. From an over-all economic standpoint it is felt that these considerations can well offset the small extra cost of handling these volatile liquids under pressure.

Current Trends

For the immediate future it is clearly evident that natural gas liquids will constitute an increasing portion of America's petroleum supply. In 1946 these light hydrocarbons provided 6% of total petroleum liquids. By 1950 the corresponding figure was about

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10%. This is not surprising, considering that the proved reserves of natural gas liquids constituted 14.4% of all petroleum liquid reserves at the end of 1950. In short, the production of natural gas liquids is still not in equilibrium with the relative reserves. Furthermore, present reserve estimates are adjusted to present levels of recovery. If utilization should catch up with present recovery technology, our recovery of these liquids could be 2.15 gallons per 1000 cubic feet of gas instead of 1.26 gallons as now realized. Adjusting the current reserve estimates accordingly shows a total of 7,270,000,000 barrels of natural gas liquids instead of the 4,267,000,000 barrels reported by the American Petroleum Institute and the American Gas Association (Table IX). Expressed in another way, this nation can—whenever the need becomes apparent—transfer about 12 trillion cubic feet of its comparatively plentiful gas fuel reserve to liquid fuel having mobile combustion utility. The cost of the transfer, while appreciable, can be small compared with the differences in economic values.

Table IX. Total Proved U. S. Petroleum Reserves—December 31, 1950 (2)

	M Bbl.	Years' Supply	Therms (100,000 B.t.u.)	% of Total Therms	Therms per Unit
Crude oil	25,268,398	13.0	1,465,567 × 10^6	40.6	58
Natural gas liquids	4,267,663	20.6	198,446 × 10^6	5.5	46.5
Gas, million cu. feet	185,592,699	26.9	1,948,723 × 10^6	53.9	10.5
Totals			3,612,736 × 10^6	100.0	
Adjusted for Possible Increased Recovery of Natural Gas Liquids (Table V)					
Crude oil	25,268,398	13.0	1,465,567 × 10^6	40.6	58
Natural gas liquids	4,267,663	20.6	198,446 × 10^6	8.9	46.5
added	3,003,000		124,625 × 10^6[a]		41.5
Gas, million cu. feet	181,556,667	25.2	1,824,098 × 10^6	50.5	10.1
Totals			3,612,736 × 10^6	100.0	

[a] Equivalent to 11.9 trillion cu. feet in terms of gas at 1050 B.t.u. per cu. foot.

Years' supply computed on 1950 production. These figures do not signify—especially as to oil production—that present production rates could be continued for stated number of years from present known reserves.

The trend toward direct motor fuel use of propane and butane will be accelerated in the near future, particularly if the defense emergency should tend to create an over-all scarcity of petroleum products. Propane and butane can advantageously supply certain special needs, such as those of farm tractors and urban busses, of nonitinerant trucks, and of contractors' earth-moving equipment. The conventional motor fuel so released can help to take care of increased military needs.

The seasonal characteristic of the liquefied petroleum gas industry has created serious transportation and storage problems. In part these problems will be eliminated in future years as motor fuel uses of these gases tend to create a uniform year-round demand. Inexpensive underground storage will be developed to conserve off-peak production. Transportation of liquefied petroleum gas in vapor phase with pipeline gas and extraction of the liquid near points of heavy consumption may become a more important factor where large volumes of propane and/or butane are needed for chemical purposes. One such large scale operation is under way. There should be a continued healthy growth for many years in the miscellaneous domestic and rural uses of liquefied petroleum gas. Use of these liquids for industrial fuel will not grow so rapidly because of competition from increasingly available supplies of pipeline natural gas. The provision of large supplies of natural gas liquids for basic fuel needs will assure adequate raw materials for a growing petrochemical industry using the light paraffins.

Current trends appear to discourage slightly the use of pentanes-plus from natural gas in conventional motor gasoline, but a period of tight petroleum supply could change this situation just as it changed during World War II. Furthermore, we may be approaching the end of the octane era in automotive development and a more long-range trend promises the possibility of engines that are not sensitive to ignition characteristics: such developments as the combustion turbine and, in the conventional reciprocating engine, the use of fuel injection combined with spark ignition and other special design conditions (*5*). These developments are bound to favor the clean-burning paraffinic materials which constitute the bulk of the heavier natural gas liquids. Indeed, the time may come when the "high test" (high API gravity) of the early 1920's will again become a criterion of superior internal combustion engine fuel.

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Asphalts and Waxes

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Asphalts and waxes, initially by-products of petroleum refining, have attained important industrial status; asphalts because of their unique suitability for paving, roofing, and numerous miscellaneous applications; waxes primarily for waterproofing paper. During the past three decades significant advances in the processing of both materials have resulted in marked product improvement. These process improvements are reviewed, as are advances in the colloidal, organic, and physical chemistry of both materials. Also directions are indicated in which future technological improvements may be expected.

There is much evidence (*1*) that naturally occurring asphalts were valued for their cementitiousness, inertness, and waterproofing qualities as early as 3800 B.C. But it is only since they became readily available from petroleum sources that asphalts have been widely used on a large scale. The first modern asphalt pavements were constructed about 1852 near Paris, France, of a rock asphalt mastic (*2*). From 1870 to 1876 several pavements, using rock asphalts and Trinidad lake asphalt were laid in eastern cities of the United States (*3*). The demand for such pavements was relatively small and was filled by natural asphalts imported from Trinidad and Bermudez lakes during the next 35 years.

Petroleum Asphalts

Blown, or oxidized, petroleum asphalts were first produced commercially by Byerley about 1894. But neither blown nor residual asphalts from the early crudes enjoyed very good repute in the United States, partly because of the nature of the crudes and partly because of insufficient care in manufacture. Discovery of sources of asphaltic and semi-asphaltic crudes made possible the production of residual petroleum asphalts suitable for paving, and improvements in the blowing process led to products well suited for the manufacture of prepared roofings. In fact, the early growth of the roofing industry corresponded closely with the production of petroleum asphalts (*26*).

By 1911 the tonnage of domestic petroleum asphalts exceeded the importations of Trinidad and Bermudez asphalts. Starting about 1920, and coincident with the rapid expansion in rural road building, the production of petroleum asphalt has rapidly increased, as shown by Figure 1, so that it exceeded 9,000,000 tons in 1949. The ratio of petroleum to native and rock asphalt production in 1949 was approximately 8 to 1 (*126*).

U. S. Bureau of Public Roads figures (*125*) show that, as of December 31, 1948, there were 281,350 miles of bituminous pavements of all types in our state highway systems, as compared to 92,265 miles of concrete pavement. During 1948, 27,744 miles of new bituminous pavement and 1588 miles of new concrete pavement were constructed. Bituminous construction was almost 95% of the total. Paving needs consume about 64% of the total asphalt production (Table I). Significantly smaller, but still by far the next largest use is in the production of roofing materials of all types. Large quantities of asphalt are also used in dust-laying oils for roads, as binders in briquetting operations, as a waterproofing material, in paints, and for miscellaneous uses such as pipe-coatings, molding compounds, and paper lamination.

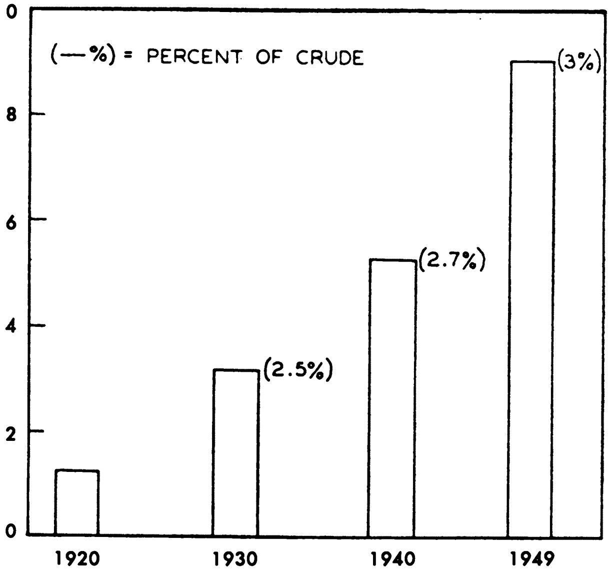

Figure 1. U. S. Asphalt Production by Decades (Millions of Short Tons)

Processing. Early asphaltic crudes, such as Panuco (Mexican) and Heavy Californian, yielded up to 65% asphalt (*4*), and were fairly readily processed in horizontal, direct-fired batch stills as shown in Figure 2. Usually steam was introduced to assist in the vaporization of the volatile constituents. The temperature at the termination of the process varied between 600° and 750° F., and the time of distillation was between 12 and 36 hours. These batch stills were replaced by continuous stills of similar construction. The oil flows from one still to another, with each still producing a predetermined grade of distillate.

Table I. Petroleum Asphalts Sold in the United States in 1949 (*126*)

Use	Short Tons	% of Total
Paving, all types	5,795,850	63.9
Roofing	2,351,471	26.0
Road oils	142,128	1.57
Briquetting	147,475	1.63
Waterproofing	127,093	1.4
Paints, enamels, lacquers, japans, other liquid products	90,098	1.0
Miscellaneous uses	409,107	4.5
Total	9,063,222	
Total value	$179,922,731	

During the past several years such stills have been largely replaced by tube or pipe stills because of their lower initial cost, greater throughput, and economy of operation. A common type of operation utilizes a two-stage atmospheric and vacuum distillation unit (*13*). This type of operation has an important advantage—the asphaltic residue remains at the extreme temperature for only a fraction of a minute in the pipe stills as contrasted to several hours in shell-type stills.

One method of operation (*45*), particularly suited for paving asphalt production, produces residues of only two penetration grades, one hard and one soft, by straight distillation. By blending these two grades, and with solvents when required, the entire range of paving grade asphalts may be prepared. Another method of operation produces only a

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soft asphaltic residue which is hardened the required amount by air oxidation (*5, 29*). Roofing asphalts are produced almost exclusively by air oxidation of soft residues (*95*).

For air oxidation, the asphaltic residue from the vacuum tower is transferred to batch-type oxidizers. These are vertical stills fitted with air distributors in the bottom and arranged for blanketing the charge with steam. Air is passed through at 400° to 500° F. at the rate of 30 to 50 cubic feet per minute per ton of charge until the desired hardness is obtained. No addition of heat is necessary because the reaction is exothermic. The reaction is not well understood, but is chiefly dehydrogenation and condensation; about 80 to 90% of the oxygen is recovered as water (*92*). Part of the reacting oxygen is bound in the asphalt, with small quantities of carbon dioxide and other oxidation products being formed (*121*).

A recent processing development has been the continuous oxidizer, shown in Figure 3 (*91*). The charge is fed to the bottom of the column, where air is also introduced. At the top of the column the liquid overflows into a buffer tank. From this the oxidized asphalt is drawn off by means of a pump, provision being made for recirculation.

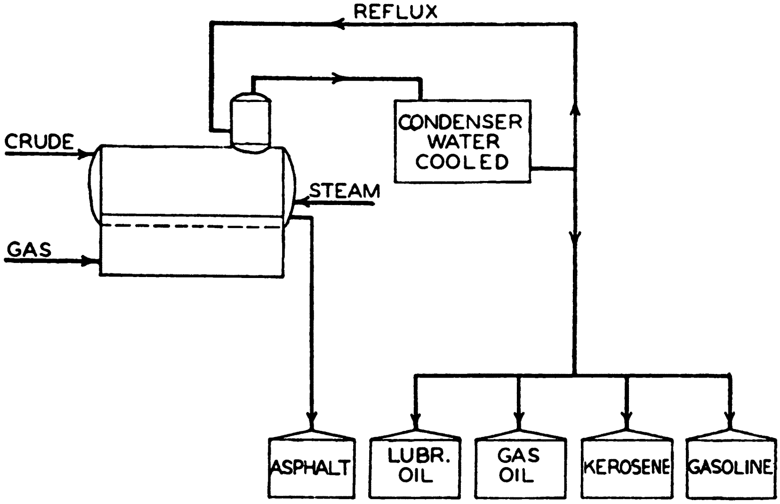

Figure 2. Diagrammatic Shell Still Installation

Whether an asphalt should be prepared by distillation or oxidation depends on the properties desired. If a given residue is distilled and the penetration of successive samples is plotted against their ring and ball softening points, the distillation curve of Figure 4 results. If the same residue is oxidized and sampling repeated, the blowing curve is obtained. Blown asphalts are characterized by greater pliability than steam vacuum-distilled asphalts of the same penetration from the same crude (*95*). By a combination of distillation and oxidation asphalt of any combination of properties lying between the two curves can be produced (*92*). Residues which have been distilled further than desired may be blended with heavy distillate before oxidation (*102*) in order to obtain the correct properties. The location of the curves and the area between them vary, of course, with different base stocks.

If asphalts having properties in the area above the blowing curve are desired, the producer may resort to the use of oxidation catalysts, which have been the subject of extensive study in recent years (*7, 12, 19, 36, 56, 77, 118*). The only catalysts known to be in large scale use are ferric chloride and phosphorus pentoxide (*36, 45*). Table II illustrates that asphalts of the same ring and ball softening point oxidized in the presence of these catalysts have markedly higher 77° and 32° penetrations than another prepared from the same base stock in the absence of catalyst.

Composition and Physical Properties. Advances in our knowledge of the con-

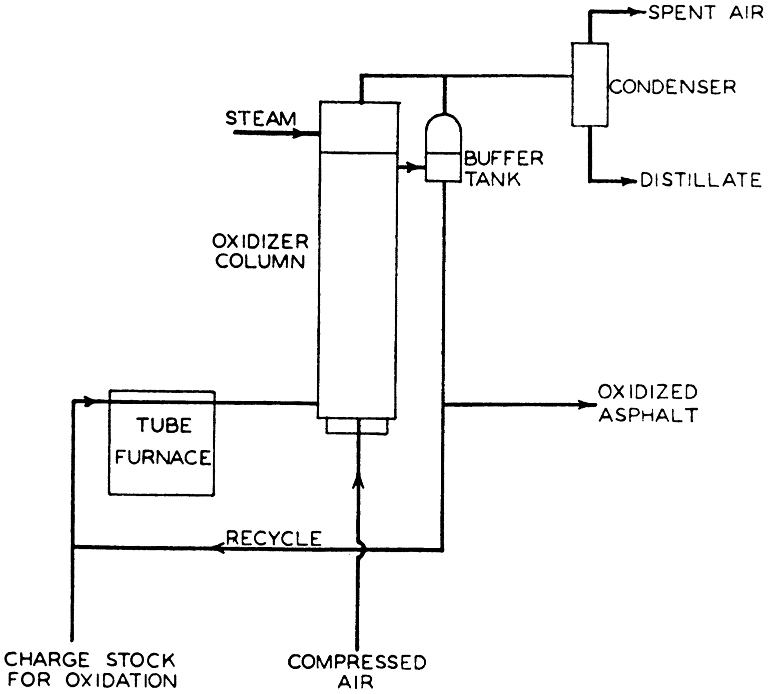

Figure 3. Diagrammatic Continuous Oxidizer Installation

stitution of asphalts have paralleled advances in processing. While predominantly hydrocarbon in character, with small amounts of nitrogen, sulfur, and oxygenated compounds present, asphalts are of such molecular weight and complexity that the usual chemical methods of analysis yield little information of value. A more productive approach has been the separation into fractions of distinctive character by means of selective solvents as first suggested by Richardson (*101*).

Table II. Effect of Catalyst on Properties of Asphalts from the Same Flux (*36*)

	Asphalt		
	A	B	C
Catalyst	0	0.5% $FeCl_3.6H_2O$	0.4% P_2O_5
Blowing time, minutes	140	49	110
Soft. pt. (R and B), ° F.	195	196	193
Penetration 77° mm./10	31	54	54
Penetration 32° mm./10	18	33	31
Penetration 115° mm./10	66	96	98
Ductility 77° F., cm.	4.4	3.8	4.6

When asphalts are diluted with low molecular weight solvents such as pentane, aromatic-free gasoline, ether, and others, a solid is precipitated. Its nature and quantity depend on the conditions of the experiment and the nature of the solvent (*34*, *89*). Table III, summarizing some of the characteristics of asphaltenes, shows them to be high molecular weight solids more readily soluble in aromatic than in paraffinic solvents. Specific gravities and carbon-hydrogen atom ratios indicate that asphaltenes are more aromatic than other petroleum fractions. Solutions of asphaltenes increase rapidly in viscosity with increasing concentration; gels form at very high concentration. Numerous studies (*23*, *34*, *58*, *59*, *93*, *105*) confirm and amplify the original suggestion of Nellensteyn (*72*) that, in an asphalt, the asphaltenes make up the micelles of a colloidal system. The dispersing medium, called petrolenes, is a liquid of molecular weight from 400 to 900 and of widely varying aromatic content.

Table III. Characteristics of Asphaltenes

	Range
Molecular weight	2500–5300
Specific gravity	1.01–1.24
C:H atom ratio	0.78–0.94
Fuses (decomp.), ° F.	340–460
Intrinsic viscosity, Tetralin, 20° C.	0.04–0.09
Solubility	
Aromatics	Complete
Paraffinics	Partial

Rheological investigations of asphalts by Traxler and associates (*123*, *124*), Lee *et al.* (*51*), Pfeiffer and Van Doormaal (*94*), Thelen (*117*), Mack (*60*), and others show the following to be characteristic colloidal properties.

Rapid increase of viscosity with increasing asphaltene concentration
Dependence of viscosity on rate of shear
Yield values
Elasticity
Age hardening of a reversible nature

While these are not all found for every asphalt, they constitute strong supporting evidence for the colloidal theory of asphalt structure.

Mack (*58*, *59*) points out that asphaltenes from different sources in the same petrolenes give mixtures of approximately the same rheological type, but sols of the same asphaltenes in different petrolenes differ in flow behavior. Those in aromatic petrolenes show viscous behavior and presumably approach true solution. Those in paraffinic media show complex flow and are considered to be true colloidal systems. Pfeiffer and associates (*91*) consider that degree of peptization of asphaltene micelles determines the flow behavior. Thus, a low concentration of asphaltenes well peptized by aromatic petrolenes leads to purely viscous flow. High concentrations of asphaltenes and petrolenes of low aromatic content result in gel-type asphalts. All shades of flow behavior between these extremes are observed.

In order to relate quantitatively certain flow properties to asphalt composition, Hardman and Hughes (*32*) found it necessary to introduce viscosity of the petrolenes as a controlling variable, in addition to the weight per cent asphaltenes and the aromatic

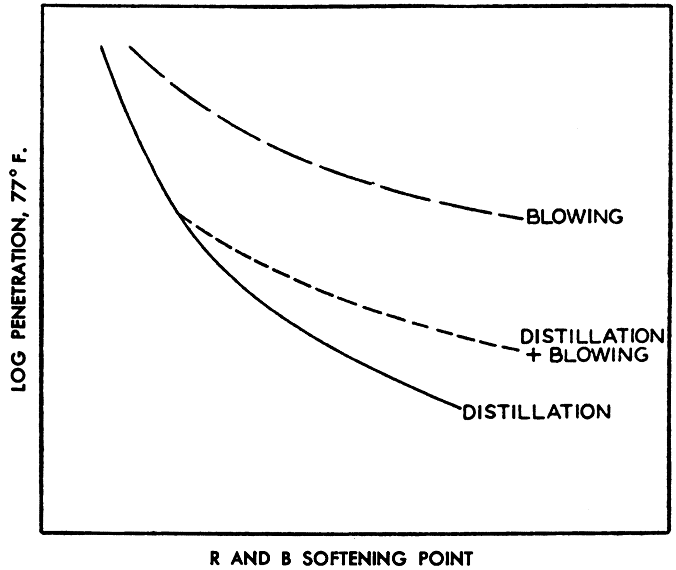

Figure 4. Comparison of Air Blown and Straight Run Asphalts from the Same Crude

content of the petrolenes. The latter is indicated by viscosity-gravity content, high values showing high aromatic content. Figure 5 is a composite plot relating penetration to these composition variables. Making the assumption that all asphalts from a given crude will contain petrolenes of the same viscosity-gravity constant, it is possible to predict from this plot the various compositions at which a given level of penetration will be obtained. Thus, as illustrated, dashed lines 1, 2, and 3 are drawn in the direction of the arrows from selected petrolene viscosity values to the viscosity-gravity constant line and thence to their intersection with line 4 drawn as indicated by the arrows from the desired penetration. The point of intersection indicates the per cent asphaltenes required. Having determined the possible compositions, corresponding values of the complex flow constant n and of the temperature susceptibility index, penetration 77°/penetration 32°, may be predicted from Figure 6.

In this manner the predicted curve of Figure 7, showing the effect of varying petrolene viscosity at constant level of penetration, was obtained. Other asphalts were prepared and analyzed for the above variables. The experimental points were placed on Figure 7. Agreement between the predicted curves and the experimental points is seen to be satisfactory. Figure 7 illustrates that in this penetration range, gel-type asphalts are obtained only from crudes of low aromatic content at low petrolene viscosities. As the petrolene viscosity is increased, asphalts from all crudes tend toward the viscous type. At lower penetrations, the curves are shifted upward, so that hard asphalts from the more aromatic crudes have rather complex flow properties.

Substantial variation (threefold) in the low temperature behavior of asphalts in paving mixtures is shown by Hughes and Faris (*41*) using extent of deformability of laboratory specimens as a criterion. Table IV shows that general correlation was found between the deformability value and the known field reputation of asphalts in the colder portions of the United States. Reasonable correlation, except for a California asphalt having petrolenes of very high viscosity, was also shown between deformability at 0° F. and the temperature susceptibility index, penetration 77°/penetration 32°, as indicated in Figure 8. Via these intermediate correlations, field performance under certain climatic conditions has been related to the composition variables discussed above—namely, weight per cent asphaltenes, viscosity of petrolenes, and viscosity-gravity constant of petrolenes.

Table IV. Relation of Deformability to Service Reputation

Asphalt	Service Reputation	Deformability[a], 0° F.
Trinidad	Excellent	10.8
Mid-continent	Good	10.0
Smackover	Good	7.9
West Texas	Fair	6.3
Cracked	Poor	3.1

[a] As % of sample thickness.

The effect of make-up of roofing asphalts on weathering properties, in terms of the fractions asphaltenes, resins, and oils, has been studied by Thurston (*120*). Increase of either asphaltenes or oils reduced resistance to weathering, while apparently an optimum content of resins aided permanence under exposure. Weathering properties were dependent not only on the quantities but also on the sources of these fractions, but the effect of source was not sufficiently clarified.

The use of cutback asphalts has increased remarkably from 130,000 tons in 1929 (*39*) to about 2,390,600 tons in 1949 (*126*). Since these consist of paving asphalt, temporarily liquefied by means of a volatile petroleum solvent to facilitate application and manipulation in construction, control of the rate of hardening by solvent evaporation is necessary. Normally, hardening characteristics have been determined and specified by means of a distillation test, but this procedure has come to be considered inadequate. Martin (*68*) has suggested the "evaporation index" as an improved method, and other methods are under consideration by Committee D-4 of the American Society for Testing Materials.

The interfacial relations between asphalt, aggregate, and water have been recognized as of considerable importance, particularly in the mixtures made with liquefied asphalts

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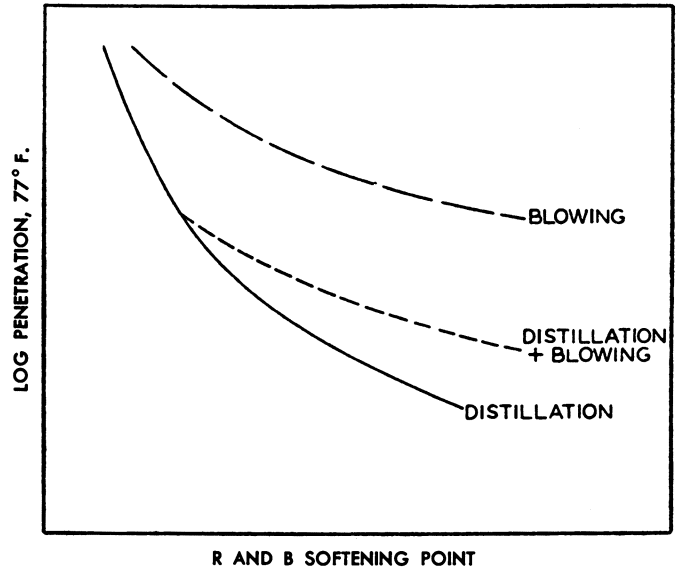

Figure 4. Comparison of Air Blown and Straight Run Asphalts from the Same Crude

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(*38, 55, 64, 79*). Because many aggregates are hydrophilic, difficulty may be experienced in obtaining or retaining a satisfactory asphalt-aggregate bond in the presence of moisture. This difficulty has been overcome in many instances by the use of special surface-active additives (*33, 42, 61, 64, 80, 98, 111, 116*). Certain of these have attained appreciable commercial significance, notably those of the cationic type.

Although they are a relatively small volume product—approximately 75,000 tons produced in 1949 (*126*)—interest in asphalt emulsion has continued at a high level. Abraham (*6*) has reviewed the patent literature relative to the types of emulsifying agents used, while commercial practice has been discussed by Day (*16*). The most common emulsifiers are sodium or potassium soaps of tall oil, abietic acid, or Vinsol resin, or colloidal clays such as bentonite for adhesive base emulsions. Lyttleton and Traxler (*53*) studied the flow properties of asphalt emulsions, and Traxler (*122*) has investigated the effect of size distribution of the dispersed particles on emulsion viscosity. A decrease in particle size uniformity was found to be accompanied by a decrease in consistency because particles of various size assume a more loosely packed condition than do those of the same size.

Future Research Lines. Several independent studies (*40, 52, 96, 97*) clearly indicate that asphaltic pavements deteriorate badly whenever the penetration of the contained asphalt drops to about 25. Such decrease in penetration results from oxidation during preparation of the paving mixture and from weathering and slow oxidation within the bituminous carpet itself. Similar deterioration from weathering contributes to eventual failure of asphalt roofings also. It would seem obvious therefore that discovery of ways of preventing such deterioration would add years to the life of bituminous pavements and roofings, with large economic savings. A fruitful approach should be that of the use of additives.

Because they become brittle at low temperatures, another opportunity exists for substantial improvements of both paving and roofing asphalts. Severe winters cause unusual damage to pavements and precautions must be taken in the application of prepared roofings in such weather. A practical solution to this problem would be of considerable value to the industry.

Perhaps the greatest gap in our present knowledge is that we know in only a few instances precisely the properties an asphalt must have for successful use in its specific application. This situation stems from the early development and widespread use of empirical tests, still of uncertain interpretation. There remains a need for practical methods of measuring in scientific units such properties as yield value, elasticity, and viscosity over the extremely wide range of temperatures and rates of shear to which asphalts are subjected during use. Further, methods are needed for measuring interfacial tensions or work of adhesion between asphalts and solid surfaces. Following the development of these and other methods, there will remain the sizable task of correlating service requirements with values of these properties. With this asphalt technology may progress from "black art" to "black science."

Petroleum Waxes

Our industry's first technical report was made in 1851 by Silliman of Yale. He made the following statement concerning the distillation of crude:

> This last product, which came off slowly at about 750° Fah., is thicker and darker than the original oil, and when cold is filled with a dense mass of pearly crystals...This substance may be separated and obtained as a white body, resembling fine spermaceti, and from it beautiful candles have been made (*110*).

As soon as crude was produced, wax became an important product. Along with kerosene it helped in the first big job of petroleum, that of lighting. Even as late as 1939 candles accounted for 64% of the world-wide use of wax (*31*). In this country particularly, this use has now been subordinated to that of waxing paper, for which 80% of the United States production is used (*17, 47*).

In 1916 about 193,000 tons of wax were produced annually. In the United States in

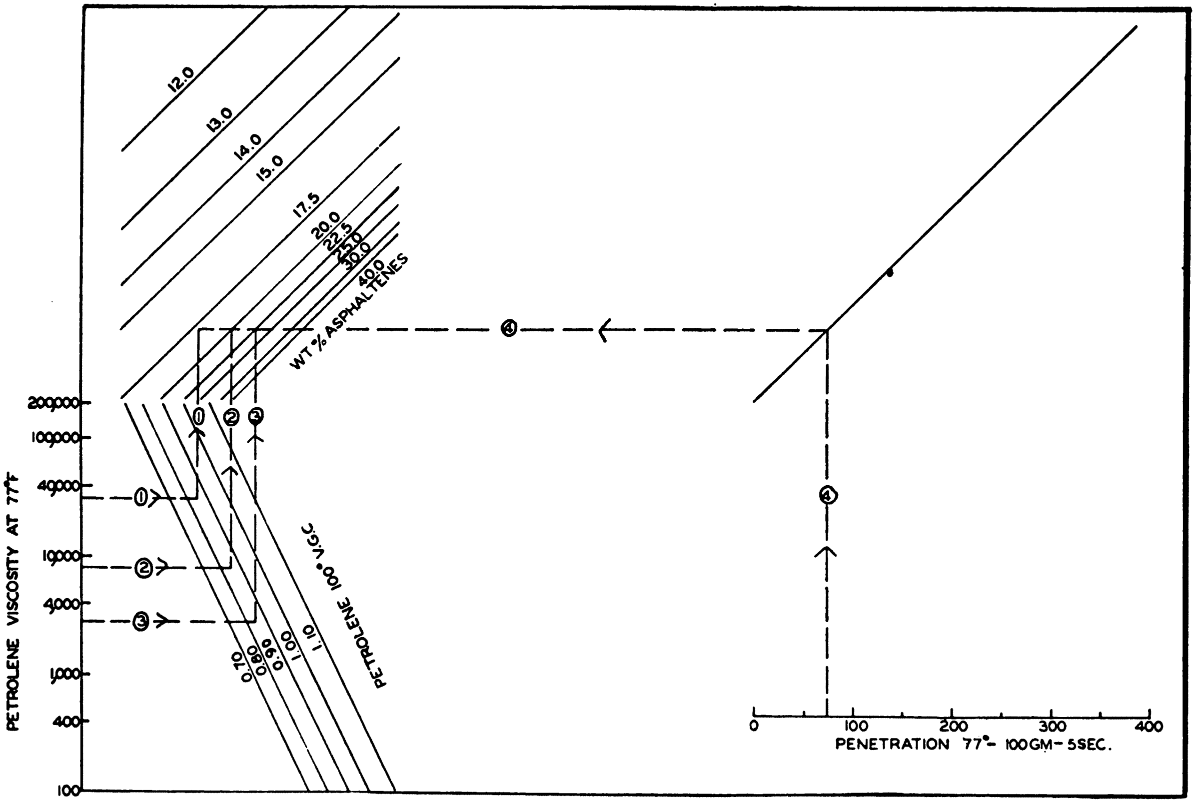

Figure 5. Correlation of Penetration and Composition

1946 there were 350,000 tons of paraffin waxes and 70,000 tons of microcrystalline waxes used (*18*). Besides paper coating and candle manufacture, wax is used in matches, rust preventives, fruit and vegetable coatings, electrical and communication equipment, dental wax, cosmetics, printing inks, engraving accessories, textile and leather treating, ceramics, polishes, pharmaceuticals, lubricants, carbon paper, photographic preparations, fuel briquets, and rubber blooming (*17, 31, 47, 67, 114*).

The source of paraffin wax is the lighter lubricating oil fractions after distillation from the crudes. The wax content of these is commonly 10 ± 5% (*103*). These oils set to gels due to crystallization of the wax and therefore wax removal is a necessity for lubricating-oil manufacture. Wax is a true by-product, yet one of such great value that at times it is prepared as a primary product and the oils are cracked.

The extraordinary resistance of wax to penetration by water has made it unusually useful. The clean, nonsmoky character of its flame makes it an ideal candle ingredient, although it is necessary in their making to include high melting, debrittle waxes or stearic acid (*22, 31*).

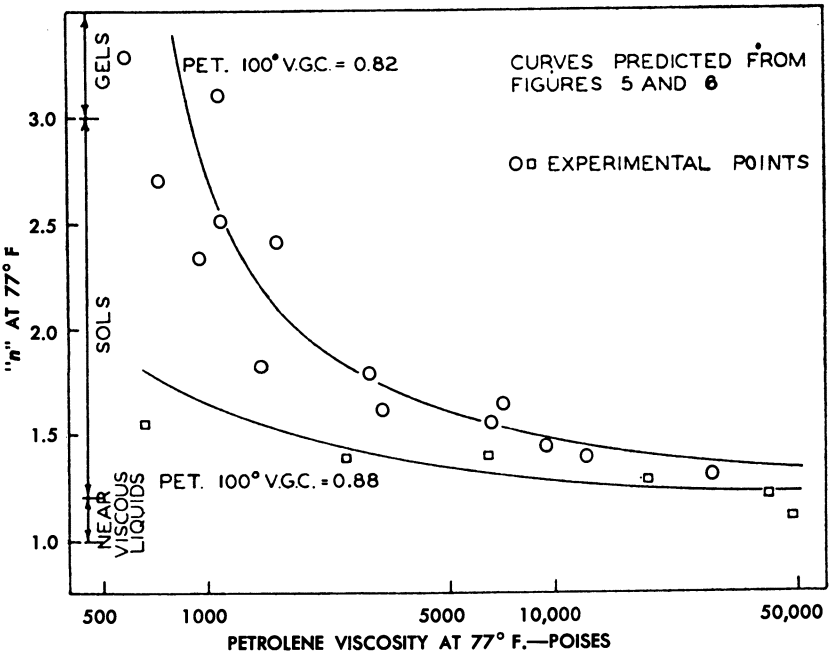

Figure 7. Effect of Petrolene Viscosity on "n" (Penetration at 77°: 70/80)

Processing. The separation of paraffin wax from oil was first carried out in plate and frame presses. This is still an important process (*76*). A special crude fraction, paraffin distillate, is segregated in a vacuum still. This is fractionated to avoid the inclusion of amorphous wax which would render the wax unpressable. The fraction is cooled in tubular, scraped chillers to 0° to 15° F. and fed at pressures up to 350 to 500 pounds per square inch to the presses (*48, 106*). The recovered slack or crude scale wax is melted and charged to sweaters where it is frozen and fractionally melted to remove oil and soft waxes (*82*). It has always been a problem to reduce the oil content low enough to maintain good wax yields from sweaters. Many ideas have been tried, one of the latest being an interesting "emulsion deoiling" process (*85, 107*). The sweaters are even more sensitive to small amounts of amorphous wax than the presses. Treatment with sulfuric acid and clays or bauxite is often used to finish the product to color and odor specifications (*21, 43*). The products of this operation are paraffin waxes melting in the range of 90° to

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160° F. (*31*, *74*). The oil contents are reduced to 0.3 to 1% (*22*) for refined wax and such wax is usually colorless (*31*).

It has never been possible to apply the above process to the higher boiling fractions of the crudes. The filters would block or the wax would pass through (*20*). The viscosity of the oils made by this process seldom exceeds 500 S.U.S. at 100° F., and there has long been a requirement for more viscous oils. These oils were made by diluting the heavier oils with naphtha and settling the wax in large cold tanks. The Sharples centrifuge process (*109*) devised in the twenties replaced this cumbersome settling. The Weir process of this period using naphtha and filter-aid was the first solvent process using filtration (*28*). These provided a fair microcrystalline wax, but little or no use was developed for it.

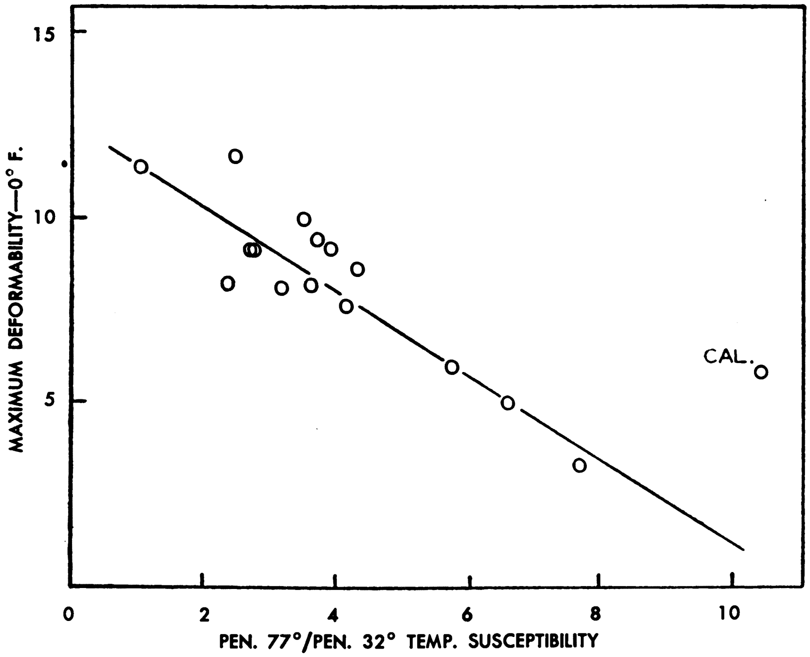

Figure 8. Relation of Deformability to Temperature Susceptibility

In the late twenties many other solvents were investigated for diluting both paraffin distillate and higher boiling fractions to aid in the filtration. It was very desirable to produce both light and heavy motor oils with better low temperature performance. As little as 1 to 2% of wax can keep the cold test as high as 10° to 20° F. (*104*), and lower pressing temperatures for paraffin distillate lead to very poor filtering rates.

The first nonhydrocarbon solvent dewaxing plant was devised by Govers of the Indian Refining Co. (now part of The Texas Co.) (*30*). It employed acetone mixed with benzene as the solvent in a ratio of 35% acetone to 65% benzene. Methyl ethyl ketone (*27*, *83*), trichloroethylene (*88*), and ethylene dichloride–benzene (*8*) have been utilized, the first being employed in the majority of plants. Propane is another popular solvent (*84*, *127*). The filter rates are high and relatively small rotary presses of low pressure design are used. The solvent processes work well on all fractions of crude as long as asphaltenes are absent. During the past fifteen years there has been a rapid change to solvents, so that in 1947 the world capacity for producing waxes was about 1040 tons per day (*75*).

The wax cake obtained from paraffin-distillate solvent dewaxing sweats more readily than that obtained from pressing, because the former has less oil. The amorphous wax recovered from the more viscous oils will not sweat, and therefore solvent processes for deoiling have to be installed. These usually involve a repulping or resolution of the wax in

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fresh solvent. Another process adds solvent while cooling (*35, 86*) to enable utilization of the favorable crystal structure obtained during the initial crystallization.

These processes have made available a variety of microcrystalline waxes of low oil content and valuable properties (*44*). Neutral and bright stock lubricating oils with pour points of −30° to 0° F. have also become available commonly as a result of this notable advance in technology.

Chemistry. Mabery showed early in this century that paraffin wax consists mainly of normal paraffins of $C_{23}H_{48}$ to $C_{29}H_{60}$ (*54*). This work has been amply substantiated by combined fractional distillation and fractionations (*11, 25, 62, 71*) and recently by urea adducting (*128*). Most investigators also find that commercial products contain small amounts of naphthene-containing and possibly branched-paraffin molecules (*65, 69–71*). These types of molecules melt lower than the normal paraffins for a given boiling point. They have been called soft waxes (*11, 70*).

The microcrystalline or amorphous waxes separated from the crude fractions boiling above paraffin distillate are predominantly of the naphthene-containing paraffin structure (*62, 70*). Thus urea adducting of 149° to 165° F. melting point wax (Superla of Indiana) isolated but 15% of adductive material assumed to be normal or terminally branched paraffins. The microcrystalline waxes consist mostly of hydrocarbon with 34 to 60 carbon atoms (*70*) and have a melting range from 140° to 200° F. (*15*).

The Fischer-Tropsch process, as operated in Germany, produces normal paraffin wax also. These waxes melt in the range of 122° to 243° F. and the molecular size extends up to 150 carbon atoms (*50*). A United States plant employing iron catalyst does not expect to produce these.

Both types of wax are readily oxidized (*24*) and halogenated (*115*). The latter is an important commercial outlet, the products of which are used as extreme pressure additives for oil (*112, 113*) and as intermediates in Friedel-Crafts condensations (*119*). Air oxidation leads to carboxylic acids, for which considerable use has been found both here and abroad. Sulfonates can be made by reaction of waxes with chlorosulfonic acid (*37, 104*) or with sulfur dioxide and chlorine (*46, 99*).

Melted wax has the typical property of the normal paraffins, that of having the lowest viscosity for a given boiling point of any hydrocarbon type. The solid properties are, of course, the most important and have received extensive study. Some typical waxes have properties shown in Table V.

Table V. Properties of Typical Waxes

	Macrocrystalline Waxes				Microcrystalline Waxes			
	1[a] (*78*)	2 (*49*)	3 (*49*)	4 (*49*)	5 (*49*)	6 (*78*)	7 (*78*)	8[a] (*78*)
Melting point, ° F.	127	132	140	163	140	156	163	187
Needle penetration, 0.01 cm.	18	21	11	18	40	40	25	4
Contraction, %	13.3	13.3	13.7	13.9	9.8	10.3	11.4	11.4
Plastic point, ° F.	100	..	..	..	..	13	55	118
Tensile strength, lb./sq. inch	140	..	..	..	..	78	116	300
Compressive strength, lb./sq. inch	216	..	..	..	..	78	120	720
Ductility, cm.	0	..	..	..	..	1.6	1.6	0
Flexibility, No. of bends	0	..	..	..	..	164	150	0
Viscosity at 210° F., S.U.S.	..	39	40	50	84	..	..	..

[a] Wax contains no oil.

Dimorphism certainly is exhibited by the solid (*14*), and four crystalline forms have been observed by some investigators (*70*). Normal paraffins and some commercial waxes show transition points or bands below the melting points in cooling curves. Microscopic observations support these crystallographic changes (*14*). A close-packed, hexagonal, needlelike form is typical of the paraffin waxes in the narrow temperature range of about 25° F. between the transition and melting points (*14, 104*). It is the form which is essential to satisfactory sweating, because it allows the oil to drain from it (*104*). Rapid precipitation or the presence of impurities such as resins will cause the formation of needle crystals at any temperature (*9*). Crystals coming out of solution below the transition temperature have a platelike form (*14, 104*). These platelike crystals are best for filtration, because they pack down to a porous structure in the presses but needles do not (*76, 104*).

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Many commercial waxes do not show a measurable transition point (*108*), yet it is believed that this is often due to the mixture of paraffins spreading the point to a band. Mazee (*69*) has shown this phenomenon with pure compounds and their mixtures. Kinsel and Phillips (*49*) show the abnormal contraction of paraffin wax in the range of 10° to 20° F. below its melting point. This could be due, at least partly if not wholly, to a change in crystal form. Viscosity measurements below the melting point with a Stormer viscometer for a paraffin wax give evidence of a relatively plastic condition for about 10° F. below the melting point (*55*). Extrusion is easily conducted in this temperature range. This result might also be an indication of a transition to another crystal form of more rigid nature.

Microcrystalline waxes show much less contraction and their addition to macrocrystalline wax substantially reduces this effect (*49*). No transition points have been observed for the microcrystalline type (*70, 108*).

The needles of the paraffin wax are typical of many organic crystals in which the molecules are in staggered position to each other as in Type I of Figure 9. The plate type is the side-by-side alignment of the molecules (*66*).

The higher degree of symmetry (crystallinity) of Type II leads to lower energy and more dense crystals (*66*). It is attainable by normal paraffins and by a series of the American Petroleum Institute Project 42 hydrocarbons of branched or naphthene containing paraffins. Type I has infinite possibilities for disorganization of the crystals, thus accommodating multiple branching by both alkyl and naphthene groups. The presence of rather small amounts of such molecules built into the crystal might well retard the formation of Type II crystals. Microcrystalline wax has the needle form and substantial amounts of it in paraffin wax cause the whole to have Type I structure (*22*). Pour depressants such as aluminum stearate (*10*), wax alkyl naphthalene, benzene (*22*), or phenol (*100*), reduce crystal size drastically but do not necessarily change types of crystallization. Davis and Zimmer (*22*) attribute this phenomenon to an adsorption of the additive on the crystal face where it not only prevents growth but changes the wetting character of the surface.

Figure 9. Alignment of Paraffin Wax Needles

This indicates that waxes change rapidly in physical properties with temperature in the valuable range of 0° to 110° F. Hardness (*70*), pliability, and tensile strength (*69*) change manyfold even in the range of 50° to 100° F. The change of tensile strength with temperature is shown in Figure 10 (*87*). By reducing crystal size and possibly crystal form with microcrystalline wax it has been possible to increase pliability substantially without loss of tensile strength (*74*).

Differences in physical properties are also caused by the presence of oil in the wax. Minchin found pure paraffins to be substantially harder than commercial products (*70*). MacLaren (*63*) shows the bad effects which relatively small amounts of oil—for example, less than 2%—can have on the desired properties of wax. Even 0.1% of apparent oil is undesirable. The oil segregates between the crystals. This does not improve pliability, but rather makes the product crumbly.

Future Problems. Since the work of recent investigators has shown that oil-free wax has superior properties, new manufacturing techniques must be devised to provide it. Substantial increases in strength and hardness might well bring wax into competition with some plastics for structural uses.

The occurrence of pour reversion necessitates a fundamental review of the action of

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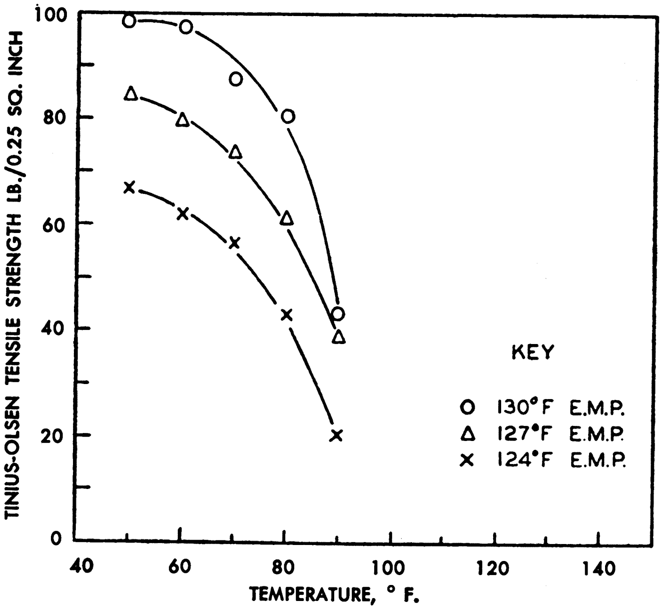

Figure 10. Effect of Temperature on Tensile Strength of Commercial Grade Waxes

the synthetic pour depressants on wax. Recent attempts to explain this, on the basis of desorption of the pour depressants followed by failure to readsorb, do not fit in well with equilibrium concepts of colloid chemistry. Possibly the idea of the building in of the pour depressant followed by a recrystallization and expulsion of the extraneous molecule from the crystal would serve as another hypothesis.

Knowledge of the structure, crystal form, reactions, etc., of the microcrystalline waxes must be worked out in as full detail as the paraffin waxes before we reach an understanding of the whole subject. In fact, the type of work recently reported by Mazee (*69*) would indicate that much can still be learned about paraffin wax, particularly through close study of pure paraffins and their mixtures.

While much valuable research has gone into the crystallography of nice crystals one can get out of solution, there remain large and important fundamental studies to be made of the characteristics of waxes in films and on paper. These could well upset our ideas derived from the single-crystal work and lead to improvements in the waxes used in this way.

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Petroleum Coke and Coking

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During the past 25 years United States petroleum coke production has increased from less than 1,000,000 tons per year to 3,400,000. Most of the 1,000,000 tons were produced in externally fired shell stills and manually removed from the stills. Almost all of the 3,400,000 tons were produced in large "delayed coker" type coke drums and removed mechanically. As was true 25 years ago, the major use for petroleum coke is as a fuel, although the proportion so used is declining. Its use in aluminum production is growing rapidly and currently takes about 18% of the production.

In trying to assess the growth of the petroleum coke industry during the past 25 years, two things have been attempted: to picture the industry as it was 25 years ago and as it is today. The difference between these two represents the progress made. This apparently simple operation is more complex than it seems. Twenty-five years ago the petroleum industry was in a state of flux because of its rapid growth. It is in the same state today. Petroleum coking, as a part of the petroleum industry, exhibits this same state of flux. Lacking precise pictures, the best possible cross sections of the industry 25 years apart are described here along with the technical features that have contributed to the progress of the industry.

Growth of Coking

According to reports by the U. S. Bureau of Mines, the petroleum coke production in the United States was 980,000 tons during 1925. During 1949 it was 3,392,000 tons with an estimated 3,420,000 tons for 1950. This represents an average growth of 5.5% per year. Actually the growth was irregular, since the period includes an economic depression and a war.

Using the 5.5% per year growth for looking into the future, one obtains 4,200,000 tons per year by 1955 and 5,500,000 tons per year by 1960. Both of these figures neglect any effect due to an intervening war or depression.

Future coke production can be approached in an independent way. The yield of coke (weight per cent of the crude oil produced) has been as low as 0.65% and as high as 1.65%. Recently it has been around 1.2%. Using 2.738 billion barrels as the 1955 crude oil production figure and 3.102 billion barrels as the 1960 figure (*8*) one gets 4,700,000 tons for 1955 and 5,300,000 tons for 1960 as the future production of petroleum coke. These figures are consistent with those obtained from the growth curve.

The technical development of petroleum coking has been inseparable from the development of thermal cracking. Untold millions have been spent on research and development trying to eliminate the formation of petroleum coke. Added millions have been spent learning how to prevent coke from forming in heating coils and making the coke deposit where it could be removed most conveniently (*18*).

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Coking Operations Twenty-Five Years Ago

Shell Stills. At the beginning of the period under review, large quantities of crude oil were processed in "tower stills." These were cylindrical vessels 10 to 15 feet in diameter and about 40 feet long. The vessels were mounted horizontally and arranged so that a fire could be applied to the underside (*10, 35*). The stills were charged with crude oil and the appropriate fractions removed by distillation. The residue was then destructively distilled or coked. Heating was continued until the bottom of the still was at a dull red heat (*35*).

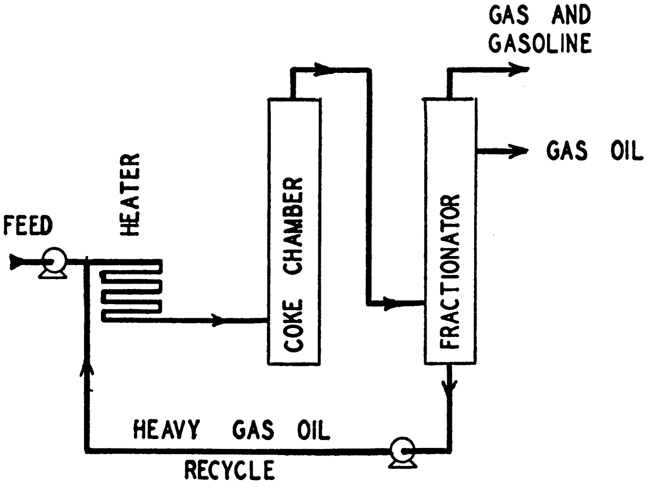

Figure 1. Delayed Coker

The high temperatures applied to the bottom of the tower stills damaged them so that they had to be replaced frequently. This was relatively expensive. As a result, special coke stills were used. Similar to the tower stills but smaller, the bottoms of these stills were cheaper to replace. The crude oil was reduced in the tower still to about 20° to 25° API gravity and transferred to the atmospheric coke still. This still was then heated rapidly to effect the cracking and coking. The entire coking operation required about 40 hours (*35*). Twenty-five years ago, a major part of petroleum coke was made in such shell stills.

Coke from Thermal Crackers. Not all coking processes were as crude as those described above. The coking process as we know it today had made its appearance in embryonic form. The oil was pumped through heated pipe coils designed so that the velocity was high enough to prevent the deposition of coke in the coils. The hot oil, under pressure, was passed to an insulated reaction chamber and the coke accumulated there. This chamber was away from the heated zone, so there was no danger of burning out a "bottom" (*35*).

After 2 days to 3 weeks of operation the reaction chamber was filled with coke. The unit was shut down and the coke cleaned out (*35*). Multiple units were used, so that some units would be on stream at all times (*42*).

Some refiners used atmospheric coke stills to prepare "clean" charging stock for the thermal cracking units. The clean stock formed less coke, so the thermal cracking units could stay on stream longer without shutting down to clean out the coke (*18*).

Modern Coking Operations

From the humble beginnings described, coking operations have been developed that can be considered modern processes, for some are still operating today.

Delayed Coking. Almost every crude oil contains high molecular weight hydrocarbons that cannot be distilled without cracking. Coke formation accompanies this cracking. It is the primary object of the delayed coking process to limit the cracking to the minimum necessary to convert the high molecular weight residual hydrocarbons into distillable hydrocarbons and coke, depositing the coke where it can be removed conveniently. This primary object may be altered in some operations to give more than the minimum thermal cracking, so that appreciable yields of thermally cracked gasoline are produced.

The feed stock, usually topped or reduced crude oil, is heated in pipe coils (Figure 1) from about 900° to 950° F. The oil is then fed to one of two or more vertical, insulated coke drums. The coke drums are connected by valves so that they can be switched on-stream for filling, then switched off-stream for coke removal. The temperature in the drum will ordinarily be 775° to 850° F. and the pressure 4 to 60 pounds per square inch gage. Hot, coke-still vapors from the coke drum pass to a fractionator where gas and gasoline, intermediate gas oil, and heavy gas oil are separated. More or less of the heavy gas oil is recycled. The ratio of recycled heavy gas oil to fresh feed is usually less than 1 but may go up to about 1.6 (*5*, *15*, *28*, *40*).

The transfer line from the heating coil to the coke drum may enter near the bottom of the coke drum (*15*) or near the top of the coke drum (*40*).

The early units used coke drums 10 feet in diameter by 40 feet high (*40*). More recent units use drums as large as 17.5 feet in diameter by 80 feet high (*4*). The capacity has increased correspondingly. An early unit with three drums, 16 feet in diameter by 35 feet high, had a daily capacity of 2860 barrels (*15*). A more recent unit using six drums, 17 feet in diameter by 80 feet high, has a capacity of over 15,000 barrels per day (*28*).

Similar progress has been made in operating cycles as the following comparison shows:

Operation	Hours Employed in	
	Early unit (*15*)	Recent unit (*28*)
Filling with coke	36	24
Standing or "soaking"	24	0
Steaming	0.25	0.75
Water cooling	1	2
Removing heads, decoking and replacing heads	33	10
Steaming	2	0.75
Vapor heating	12	6

Delayed coking was originally used to convert heavy fuel oil into lighter oils for use as such or for use as feed stock to thermal cracking units. More recently, delayed coking has gained favor as a means of preparing feed stock for catalytic cracking (*5*, *28*).

The yields and product distribution obtained in delayed coking are functions of the character of the feed stock and the operating conditions. Gas oil yields of 60 to 85 volume % with coke yields of 10 to 30 weight % of the feed are reasonably representative (*5*).

Coking plus Thermal Cracking. It is possible to combine coking and thermal cracking to maximize thermally cracked gasoline production. A simplified flow chart is given in Figure 2. Its relationship to delayed coking can be seen by comparing it with Figure 1. A light gas oil is heated to temperatures as high as 1100° F. at pressures up to 500 pounds per square inch. The hot gas oil is mixed with fuel oil or residuum and the mixture fed to one of several vessels that serve both as reaction chambers for thermal cracking and as coke chambers. The temperature in the coke chamber is 800° to 875° F. and the pressure 25 to 250 pounds per square inch. A clean reaction chamber is switched into the circuit when one becomes full (*5*, *40*).

Polyforming plus Coking. In Polyforming, a naphtha is mixed with C_3 and C_4 hydrocarbons and reacted by passing through a heated coil. The reaction is stopped at the exit of the heating coil by quenching. The products are then fractionated. By using a fuel oil or tar as quench oil and inserting coke drums between the heater discharge and the fractionator, coking can be carried out in the unit (Figure 3). The heater outlet temperature is between 1020° and 1125° F. The pressure on the coke drums is 300 to 400 pounds per square inch (*31*).

Knowles-Type Ovens. The Knowles-type oven is made up of an enclosed, heated, refractory floor together with ports for introducing the feed and exit vapor lines (*2, 9, 14, 19, 20, 23, 36*). The coke is heated to a higher temperature (1500° F. or higher) than in delayed coking units.

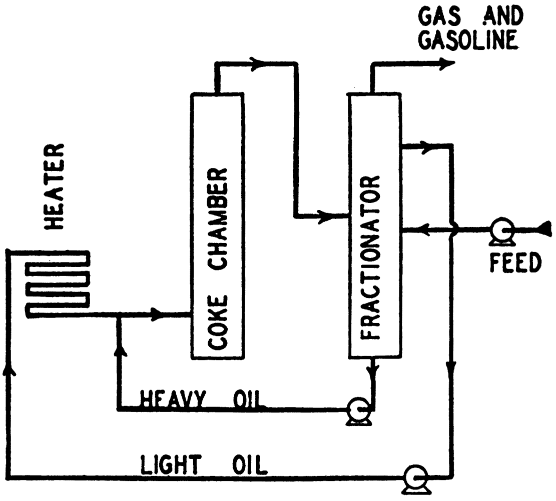

Figure 2. Thermal Cracking plus Coking

Two installations of this type have been built in the United States for processing petroleum (*2, 23*), but only one of these was part of a petroleum refinery operation.

Heavy fuel oils have also been coked in by-product coke ovens of the slot type used for coking coal, although this is not a customary operation (*22*).

Future Coking Processes

Many users of present coking processes have been unhappy with the multiplicity of coke drums, irregular operation, and intermittent discharge of coke. A coking operation that could be lined-out with continuous discharge of coke has been the dream of many. Technical advances made in catalytic cracking for handling the solid catalyst have given tools that are potentially applicable to coking.

Some of the principles used in Thermofor catalytic cracking have been applied to a coking operation. Coke itself, instead of catalyst, is the solid circulated. The coke is heated in the regenerator of the unit and more coke is deposited on the hot moving solid in the reactor of the unit. Appropriate proportions of the coke are removed continuously as the process proceeds (*34*).

The principles of fluidized solids so successfully used in catalytic cracking are applicable to the coking operation. Again the coke itself is the solid circulated. It is heated in the regenerator and coke is deposited on it in the reactor (*24*).

Both types of operation are in pilot or semicommercial stages of development (*24, 34*).

The desire and the need for a truly continuous coker are so great that a commercial unit of this general type is sure to be built in the not too distant future.

Decoking

Decoking means the removal of the coke from the drum or vessel where it was formed.

Manual Decoking. Early atmospheric coke stills were manually decoked. Men went into the stills with hand tools, broke up the coke, and removed it manually. Because of the heat and the dirt, it was not a desirable job (*35*).

Cable Decoking. With the advent of vertical coke drums, cable decoking came in as a vast improvement over manual decoking. A coiled steel cable, placed inside the coke drum, is supported on hooks. At the end of the coking cycle the bottom of the

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coke drum is removed. The end of the cable is located, attached to a winch, and pulled. As the coiled cable comes out it brings much of the coke with it. Residual coke is removed manually. The cable is then replaced for the next run (*5, 15, 26, 40, 42*).

Decoking by Drilling. For this method of decoking, a hydraulically controlled, rotating drill stem is mounted in a well below the coke drum. At the end of the cycle, the bottom from the coke drum is removed and a hole is drilled upward through the coke bed. The drill is then removed from the stem and "knocker-bars" are mounted in its place. The knocker-bars swing out from the drill stem when it is rotated, hit the coke, and break it loose from the drum. The coke falls out and is recovered (*5, 40*).

Hydraulic Decoking. One of the major contributions to the technology of coking made during the quarter century under discussion is hydraulic decoking. Water does the work at pressures around 1500 pounds per square inch. At the end of the coking cycle the heads are removed from the coke drum and a hole is bored downward through the coke with mechanical boring tool about 18 inches in diameter. This revolving tool is powered from the reaction of water jets discharging horizontally (*12*).

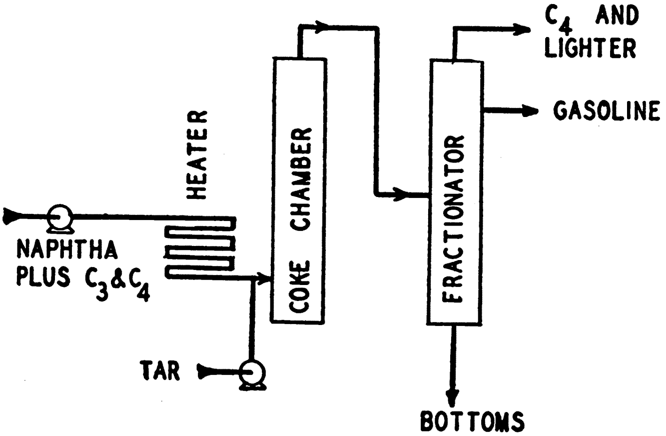

Figure 3. Polyforming plus Coking

When a hole has been bored from top to bottom of the coke bed, the boring tool is removed. It is replaced by cutting nozzles that are horizontal, so that the water jets penetrate and cut the coke bed. The nozzles are offset so the reaction rotates the nozzle assembly. The jets cut the coke bed into layers as the revolving jets move through the bed. The coke breaks away and falls to the bottom of the chamber. The diameter of the effective cutting stream is about 1.75 inches at a distance of 8 feet from the nozzle. The jets clean all of the coke from the chamber, so that it is not necessary for a man to enter the chamber at all. Furthermore, the action is fast; over 150 tons of coke have been removed from a drum in 2 hours (*12*).

Petroleum Coke

Drum or Chamber Coke. Volatile matter in coke ranges from 8 to 18% or slightly higher. Sulfur will range from 0.2 to 4.2% or higher—i.e., a little higher than sulfur in the oil being cracked. Ash will run from 0.05 to 1.6% or higher, depending on the ash in the crude oil used and whether lime or other inorganic substances were added during processing. The true or real density of the coke ranges from 1.28 to 1.42. This is appreciably different from the true density of 2.25 of graphite or 3.5 of diamond. It is, however, consistent with the concept that petroleum coke is not carbon but highly condensed hydrocarbons. In fact, some of the hydrocarbons can be extracted by solvents. One petroleum coke having a real density of 1.28 was extracted with carbon disulfide. The insoluble part had a real density of 1.41 (*30*).

The electrical resistivity of a petroleum coke having a real density of 1.39 was 9 × 10^6

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ohm-inches. This is more nearly an electrical insulator than an electrical conductor. It contrasts with graphite which has resistivity of the order of 0.0004 ohm-inch (*6*). These differences also are consistent with the concept that petroleum coke is hydrocarbon rather than carbon.

Strength of Coke. Petroleum cokes vary in strength, depending on the volatile matter content. A coke containing 8 to 10% volatile was strong and hard enough to give 73 to 94% plus 2-inch lumps in the ASTM shatter test, while a coke with 14 to 18% volatile was so soft that it gave no 2-inch lumps in the same test (*30*).

The nature of coke varies somewhat throughout the coke drum. In the lower section, the coke is dense and the volatile matter content is low. At the higher levels the coke becomes softer, more brittle, and the volatile matter content increases. The volatile matter in the coke at the top of the drum may be 2 to 3% higher than in the coke from the bottom of the drum (*15*).

Frequently a coke is desired that will be strong enough to form the maximum amount of lump coke. The principal operating factors that control the coke hardness are (*15*):

Heating coil outlet temperature. An increase from 910° to 925° F. gave a 12% increase in the yield of lump coke.

Length of time the coke is allowed to remain at an elevated temperature before cooling. "Soaking" for 12 to 20 hours before cooling also gave about 12% increase in lump coke.

Nature of the feed stock to the unit. Adding 10 to 15% cracked residuum to a reduced crude feed increased the lump yield 10 to 15% at constant temperature and constant soaking time.

Atmospheric Coke Still and Knowles Oven Coke. The volatile matter in atmospheric still coke runs about 7 to 11% while Knowles oven coke runs lower—i.e., up to about 7% (*10*). These cokes are harder and the lumps are stronger than the drum or chamber cokes.

Correlation of Coke Properties. This discussion has given qualitative trends in coke properties. More quantitative relations have been obtained from a series of cokes prepared in the laboratory from a constant feed material. Figure 4 summarizes the results. The friability (units are arbitrary), the per cent soluble in trichloroethylene, and the per cent hydrogen all increase as the per cent volatile matter in the coke increases (*7*).

Uses for Petroleum Coke

Fuel. With a heating value of 15,300 to 16,400 B.t.u. per pound, petroleum coke is an excellent fuel (*30*). Of the 3,392,000 tons produced during 1949 approximately 60% (over 2,000,000 tons) was used as fuel. In 1928 approximately 80% of the 1,300,000 tons produced was used as fuel—most of it by the petroleum refineries themselves (*16*).

Most of the petroleum coke produced in the United States is drum or chamber coke. Much of it contains more than 10% volatiles, so it is relatively soft and friable. This, its high B.t.u. value, and low ash make it a desirable powdered fuel. Good results have been obtained over long periods of time using it in this form (*13, 27, 32, 33, 39*).

If petroleum coke is used on moving grate stokers rather than as a powdered fuel, it must be given close supervision and care. Unless this is done, the grate life may be unduly short (*33, 41*).

In many respects, however, petroleum coke is the ideal solid fuel for domestic use. The lumps make an excellent fireplace fuel and the smaller pieces make good domestic furnace fuel (*10*).

Fines from petroleum coke are too small to use alone for domestic heating. But petroleum coke fines have been briqueted successfully, and the briquets used as domestic fuel (*21, 38*). In one instance, briquets made with 5 to 10% of refinery acid sludge as the binder were roasted to 1100° F. The resulting briquets were clean, hard, strong, and smokeless and could be stored or shipped in any weather. Uncalcined briquets tend to soften and deform in hot weather (*16*).

Aluminum Production. Petroleum coke is one of the major raw materials for

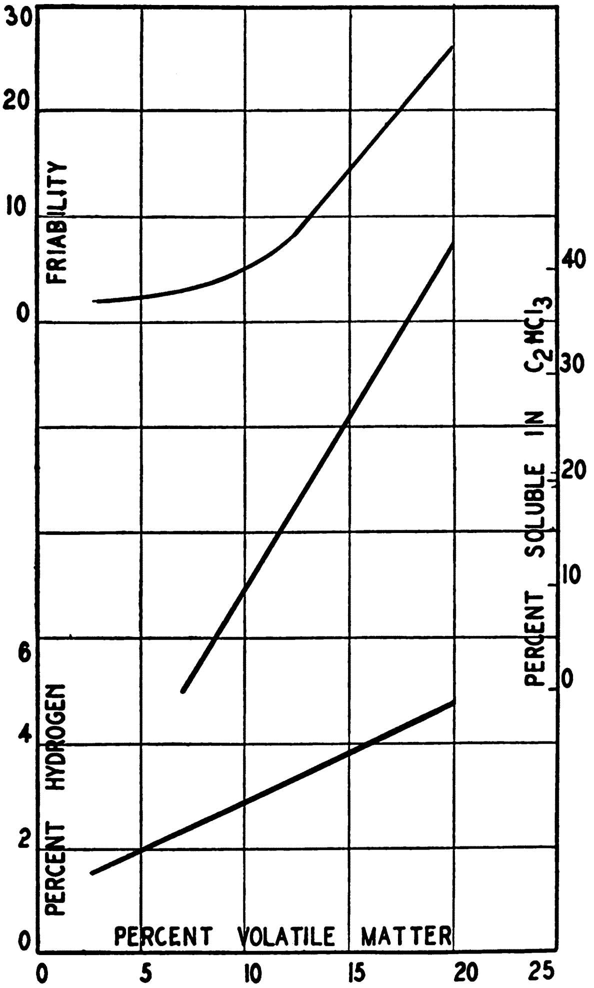

Figure 4. Relation between Volatile Matter Content and Other Properties of Petroleum

anodes for making aluminum. About 0.7 pound of petroleum coke, as it leaves the refinery, is consumed to make 1 pound of aluminum. The average yearly United States aluminum production for 1947–49 was 850,000 tons (*3*) which correspondingly used an average of 600,000 tons of raw petroleum coke. This is about 18% of the United States petroleum coke production and is its second largest use. Present plans call for an estimated 50% expansion of the United States aluminum industry by 1953 with a corresponding need for a total of about 900,000 tons per year of petroleum coke.

Before petroleum coke can be used for making anodes for making aluminum, it must be calcined. This converts it from an electrical insulator into an electric conductor. At the same time its real density is raised to about 2.0 (*17*). During the calcination, losses of 15 to 30% by weight are sustained (*25*). The volatile content is reduced to less than 0.5% (*17*). Calcination may be done in shaft kilns, electric calciners (*17*), or rotary kilns (*37*). In rotary kilns, temperatures up to 2700° F. may be used (*37*). Care must be taken in the electric calciners not to graphitize the coke; otherwise the thermal conductivity of the product will be too high for anode use (*17*).

Ash impurities in the petroleum coke should be as low as practical. Iron and silicon compounds in the coke are reduced and appear as alloying impurities in the metal. Lime and magnesia accumulate in the electrolyte and may cause undesirable effects there (*17*).

Synthetic Graphite. Petroleum coke is the major raw material for synthetic graphite electrodes and anodes in the United States. Taking the United States graphite production for 1950 as 100,000 tons, this corresponds to about 140,000 tons of petroleum coke at the refinery. This is equal to somewhat less than 5% of the production. The steel industry is the largest user of synthetic graphite and its capacity is scheduled to increase about 20% by 1953. Therefore, about a 20 to 25% increase in the amount of petroleum coke going into synthetic graphite may be expected.

The coke for synthetic graphite is also calcined before further processing. It is calcined until a sample of −35 + 100 mesh material shows an electrical resistivity of less than 0.05 ohm-inch. The same type of calciners are used that are used to calcine coke for the aluminum industry (*29*). The calcined coke retains a major portion of the sulfur present in the green petroleum coke (*1*). Low-sulfur, green coke is preferred.

Foundry Coke. Ordinarily petroleum coke is not strong enough for use as foundry coke (*35*). By processing it in gas retorts, however, it is possible to make a useful cupola fuel. The processed coke gave the following inspection properties: volatile matter, 2.1%; fixed carbon, 95.8%; ash, 1.5%; sulfur, 0.5%; 14,500 B.t.u. per pound; apparent density, 0.95; true density, 1.52; ASTM shatter test 89 to 93% + 2 inches (*11*).

This coke performed satisfactorily in the cupola. The silicon loss was 30 to 40% less than normal and for this operation was about 0.15%. The temperature at the iron spout was higher than when foundry coke from coal was used. There was no apparent saving in manganese when petroleum coke was used (*11*).

When the ratio of metal to coke got much below 10 to 1, "kish" appeared in the product. Adjusting the metal to coke ratio corrected this (*11*).

Bricks. When mixed with clay to make bricks, petroleum coke assists in burning the brick. It acts as a reducing agent for some of the colored oxides in the clay, giving a brick with improved color. When coal coke is used in the same way, the ash in the coke may flux with some of the clay, giving an undesirable product (*16*).

Other Uses. There are many lesser uses for petroleum coke, such as making dry cell battery carbons, carbon brushes, fuel in California smudge pots, etc. (*30*).

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Aliphatic Chemicals

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Production of aliphatic chemicals over the past 25 years has increased 16-fold in volume, to about 16 billion pounds per year; more than 75% of this is based on petroleum and natural gas raw materials. The most significant advances include synthesis of ethyl and isopropyl alcohols to supplement fermentation products; large scale production of chlorinated hydrocarbons for solvents, antiknock fluids, and plastics raw materials; manufacture of ethylene and propylene glycols for antifreeze solutions; development of oxygenated solvents; and production of synthetic glycerol to add to the supply from fats. Petroleum based olefins are manufactured in large volume for use in production of synthetic rubber, fibers, plastics, and detergents. Among the newer developments are the direct oxidation of hydrocarbons to produce aldehydes, acids, and alcohols; the partial combustion of methane for acetylene manufacture; and the Fischer-Tropsch and oxo syntheses employing carbon monoxide and hydrogen to yield oxygenated chemicals. Complicated interprocess and interproduct competition characterizes this field, and the concentration of their end use in the more rapidly expanding chemical product segments is pointed out as one of the causes for the rapid growth of aliphatic chemicals.

It is an economic truism, but one which bears repetition, that an abundant supply of raw materials provides a sure foundation for development of a large scale market in any commodity. This has been demonstrated most decisively by the expansion in the field of aliphatic chemicals during the past 25 years, roughly corresponding to the period in which petroleum and natural gas have become important as raw material sources. To be sure, brilliant chemical research, bold engineering strides, and vigorous market development have been necessary; but with all these, the widespread use of end-products based on the simple aliphatics would probably not have flourished but for the ready availability of the relatively inexpensive hydrocarbons which the oil industry provides.

This point was emphasized in a recent article (*21*) explaining why the United States had apparently lagged behind Germany in production of chemicals from acetylene:

> For one thing, our abundant supplies of natural gas and petroleum have given us shorter and cheaper routes to many of the same ends, while Germany is limited primarily to the raw material, coal, which is the backbone of its synthetic aliphatic chemical industry.

Although the continued importance of acetylene in contributing to the output of acetic acid, vinyl chloride, trichloroethylene, and other important commodities is recognized, it is indisputable that petroleum and natural gas represent the backbone of our synthetic aliphatic industry.

A phenomenal over-all growth has taken place in the field of aliphatic chemicals since 1925, when the Petroleum Division of the AMERICAN CHEMICAL SOCIETY was still young. The following statement was made in early 1924 in an otherwise shrewdly prophetic survey of the possibilities of petroleum as a chemical raw material:

> Popular writers have sometimes referred to the petroleum industry as a chemical industry, and have also stated, always in a very vague way, that petroleum is similar to coal tar and that by chemical research it is capable of yielding a wealth and variety of substances comparable to the number and commercial importance of the coal tar derivatives. There are several reasons for objecting to this kind of writing—it contributes nothing and arouses no interest among scientific men who can also see through such transparent stuff.

No one would suggest that the number of petroleum-based chemicals now rivals that of coal tar derivatives, but it cannot be denied that the commercial importance does loom large and that this field has grown even more vitally than the older aromatic one. Whereas 25 years ago the total volume of aliphatic chemicals produced in the United States was about one billion pounds per year, this class of chemical products, as reported by the Tariff Commission (*36*) now comprises nearly 16 billion pounds annually. And it can be estimated that a good 75% of this present output is derived from petroleum and natural gas, although the 1925 share from these same sources was under 1%. The aliphatics have long since overtaken and surpassed the cyclic chemicals, which amount to scarcely more than half as large a volume today. If the figure of 12 billion pounds of aliphatics from petroleum seems unbelievably large, it can be shrunk into credibility when it is recalled that less than 0.5% of the total crude oil and natural gas production constitutes the raw material for this aliphatic production (*11*). The petroleum industry will feel no strain in providing the basis for this growing stream of chemicals which flows into the very vitals of U. S. industry.

Time would not allow a complete detailed description of the developments which have taken place in the past 25 years in this field. Whole volumes have been devoted to this topic, and such excellent contributions as the older work of Ellis (*13*), and the recent publications of Brooks (*4*) and Goldstein (*16*) might be cited for further details.

Only a few of the major developments can be traced here, yet these should give a fair idea of the magnitude and importance of the aliphatic petrochemical growth. It is well to remember that some of the chemistry involved in this industry is old. Four Dutch chemists, otherwise unrecalled today, prepared ethylene dichloride by addition of chlorine to ethylene in 1795, and the synthesis of ethyl alcohol from ethylene via sulfuric acid absorption was studied by Berthelot in 1855 (*3*). Of course, this was coal-gas ethylene, and the commercial application of this synthesis did not occur until 75 years later, in 1929, when ethylene produced from natural gas was first converted into ethyl alcohol on a practical scale (*34*).

Prior to this time, other ventures had already been operating to produce commercial quantities of aliphatic chemicals from petroleum sources. Truly commercial production of ethylene glycol had been achieved by 1925 (*10*) using natural gas fractions as a starting material, and even earlier (about 1920) there had been the manufacture of isopropyl alcohol from cracking plant propylene (*20*), which may be termed the pioneer operation on a successful, continuing basis in the sphere of aliphatic synthesis from petroleum.

Alcohols and esters, made not from olefins, but from saturated hydrocarbons in this case, pentanes, were next on the scene, with the production in 1926 of amyl alcohol by chlorination and caustic hydrolysis. And shortly thereafter the intentional chlorination of ethylene was undertaken to expand the output of ethylene dichloride, formerly obtained as a by-product of glycol manufacture.

So, at the beginning of the 25-year period here commemorated, alcohols, glycols, aldehydes, and ketones, chlorinated hydrocarbons, esters, and ethers—all so vital in their direct uses or as chemical building blocks—were beginning to be produced by synthesis from hydrocarbons provided by the already well-grown petroleum and natural gas industries. Subsequent developments came in rapid succession, with remarkably little in-

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hibition by the depression of the early thirties. Butyl alcohols, the newer chlorinated solvents (trichloroethylene and perchloroethylene), solvent ketones, acetic acid, and a growing list of glycol ethers and esters, all testified to the continued advances in the aliphatic industry, with petroleum hydrocarbons coming more and more into use as raw material. This swing toward oil and natural gas sources is most significantly pointed up by the moves made in the years immediately preceding our entry into World War II, when several of the major chemical companies established plants along the Gulf Coast, where they would be close to their preferred raw material. Since 1936, nearly $2 billion worth of plant investment has been made in that area for petrochemical production, and about three quarters of that is in aliphatics. A most important accomplishment was the completion of a plant in 1945, where propane and butanes undergo direct oxidation to yield aldehydes, acids, ketones, and alcohols; this fulfills the promise of the first small scale hydrocarbon oxidation venture started in 1926.

The more recent developments in fibers and plastics have opened up new markets for aliphatic chemicals, such as vinyl chloride and acrylonitrile, as starting materials, although the glory here must be shared with the cyclic compounds, among which polystyrene is expanding most rapidly. Even glycerol, once producible only as a by-product of soapmaking from natural fats and oils, has been synthesized from propylene, and is meeting military and civilian demands as they reach beyond the soapmakers' production. This has indeed been a most amazing quarter century of progress.

Chlorinated Hydrocarbons

Although a great variety of chlorinated hydrocarbons of the lower carbon numbers had been well known and produced in small quantities for many years, the large scale manufacture and use of such compounds other than chloroform and carbon tetrachloride is a fairly recent development. And although synthesis, particularly of the two-carbon derivatives, has in great measure depended on acetylene from calcium carbide, more and more reliance has been placed on petroleum raw materials in this field in the last few years.

The chlorinated solvents have in great measure replaced the conventional petroleum naphthas in extraction, degreasing, and dry-cleaning operations, essentially because of their nonflammability and consequent freedom from fire hazard in open-vat operations or in enclosed areas. This advantage is somewhat offset by generally higher toxicity, but some of the members of this series, particularly perchloroethylene, are relatively harmless. The superior solvent power of these chlorinated compounds for fats, oils, and waxes makes them especially desirable oil-seed extractants and suitable for the removal of greasy soil in metal finishing procedures and in garment dry cleaning.

Carbon tetrachloride represents an example of the change to petroleum raw materials in this field. The traditional source of this widely used product has been the chlorination of carbon disulfide, either directly or through the use of sulfur dichloride. Military requirements in World War II caused an increase in demand, and in addition to expansion of the older operations, a new process (*23*) was introduced in 1943; it involved direct chlorination of methane at 400° to 500° C. and essentially atmospheric pressure. This apparently straight-forward substitution of halogen for hydrogen in the simplest paraffin hydrocarbon was still a difficult technical accomplishment, requiring special reactor construction to avoid explosive conditions. There is also the fact that disposal of by-product hydrochloric acid is necessary here, though this does not enter the carbon disulfide picture. That these problems have been settled successfully is indicated by the report (*32*) that the chlorination of methane is the predominant process in use in the United States today, and it is estimated that more than 100,000,000 pounds of carbon tetrachloride were so produced last year.

Carbon tetrachloride is still important as a fire-extinguishing agent and as a general solvent and extractant; it has particularly found new growth as a precursor of the Freons, so widely used as aerosol propellants and as refrigerants. But carbon tetrachloride has lost considerable ground in solvent uses, especially in metal degreasing and in garment dry cleaning, to the newer chlorinated derivatives, trichloroethylene and perchloroethylene, and this trend appears to be continuing.

In the process of methane chlorination; coproducts of lower chlorine content than carbon tetrachloride—namely, methyl chloride, methylene chloride, and chloroform—may be produced and recovered. Methanol remains the major source of methyl chloride ($CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$) and acetone a favorable route to chloroform ($CH_3COCH_3 + 3NaClO \longrightarrow CH_3COCCl_3 + 3NaOH$; $CH_3COCCl_3 + NaOH \longrightarrow CHCl_3 + CH_3COONa$), but the natural gas route contributes substantially to the nation's output of these two commodities and is responsible, as well, for a good share of the methylene chloride. Methyl chloride is interesting at the present time, since in addition to its refrigeration use it is vital in the Butyl rubber process, acting as solvent in the polymerization of isobutylene at −150° F.

Among the chlorinated ethanes and ethylenes, the original syntheses from acetylene or from alcohols have been partially displaced by production from petroleum sources, though in some cases this is not a displacement but rather supplementation. It is apparent, however, that dependability of supply, relative stability of price structure or at least predictable economic behavior, and generally more favorable economics are swinging a larger share of the manufacture to the petroleum hydrocarbons. Ethyl chloride is an instance of this change. More than 400,000,000 pounds of this material will be used this year in the production of tetraethyllead and ethyl cellulose. Whereas the reaction of ethyl alcohol and hydrochloric acid was first used and still finds a minor place, direct addition of hydrochloric acid to ethylene in the presence of halide catalysts and substitutive chlorination of ethane today are responsible for by far the greatest portion of U. S. output.

In halogenating ethylene, the simple addition of chlorine or bromine at moderate temperatures in the vapor phase, using metal halide catalysts, or in liquid-phase solvent systems at low temperatures with similar catalysts, yields ethylene dichloride or ethylene dibromide. These materials are used with tetraethyllead as scavengers to remove lead residues from internal combustion engine cylinders and thus reduce undesirable deposit formation. Ethylene dichloride was first marketed in this country in 1925, when its use as a solvent was promoted in order to aid the disposition of this by-product of the ethylene glycol synthesis. Shortly thereafter it was recognized that this compound had better characteristics as a scavenger than the aromatic halides first used in lead fluids, and its manufacture by chlorine addition became necessary in order to meet the growing antiknock fluid demand. It also became clear that bromide scavenging was required, and brine-produced bromine was inadequate to this new use. Thus resulted that bold depression-born venture of recovering bromine from sea water (1933–34) and the synthesis of ethylene dibromide turned out to be the major use for this halogen, of which more than 100,000,000 pounds are now made each year.

Meanwhile a new use for ethylene dichloride had arisen. When treated with alkali at moderate temperatures, hydrochloric acid is split off to form vinyl chloride. This compound, of course, is also produced and was first commercially made from acetylene by hydrochloric acid addition in the presence of catalysts such as mercury salts. Large scale production by this latter route had been undertaken as early as 1933 (*37*), and the development of vinyl resins was begun. Today, vinyl chloride production is believed to be close to 300,000,000 pounds per year, and of this volume nearly half is supplied via ethylene (*5*). This is a rapidly growing commodity and one which will call for further large quantities of petroleum ethylene during the coming years. With the lead fluid demand and various solvent and extractant uses, as well as some application in the fumigant field, ethylene dichloride requirements must also be pressing close to 300,000,000 pounds.

The substitutive chlorination of propylene at 400° to 600° C. gives high yields of allyl chloride (*19*), valuable for various syntheses including glycerol. Allyl chloride has been produced commercially in this way since 1945 and glycerol since 1948. Chlorination of C_4 hydrocarbons has not been of commercial significance, but the production of mixed amyl chlorides by vapor-phase chlorination of pentanes has been practiced since 1926 (*1*) and remains a major source of amyl alcohols, which with their esters are valuable as surface-coating solvents. In all these halogenation operations, the attainment of favorable yields required extensive research to develop adequate reactor designs, and the extensive

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literature bears witness to the combined efforts of chemists and chemical engineers in bringing these processes to practical use.

Another chlorinated compound which, like vinyl chloride, is used only in its polymeric form, is chloroprene (2-chloro-1,3-butadiene), which is polymerized to make neoprene, first produced in 1940. As far as is known (*17*), the monomer is made commercially only from acetylene via addition of hydrochloric acid to monovinylacetylene in the presence of cuprous chloride, but syntheses from butylenes or butadiene have been described. The production of chloroprene exceeded 100,000,000 pounds per year at the wartime peak and has been somewhat lower since then, but in view of the many valuable properties of the neoprene rubber it will continue to be important.

Chlorinated kerosene fractions, preferably those of highly paraffinic nature, have been widely used as intermediates in the manufacture of so-called keryl benzene detergents. The volume of chlorinated hydrocarbons so used represents an appreciable contribution to the important alkyl aromatic sulfonate detergent output.

Another group of chlorinated hydrocarbons comprises those made from paraffin wax. Major applications are in extreme pressure lubricants and as extenders and plasticizers in surface coatings and in vinyl plastics. The chlorinated waxes were also widely applied in flameproofing cotton fabrics, which led to large consumption by the military. It is believed that current military requirements for flame-resistant fabrics will be met by vinyl sheeting of vinyl-coated textile products, so that the World War II demand for the halogenated waxes will not be repeated.

The large volume solvents, trichloroethylene and perchloroethylene, are still chiefly made from acetylene, but appreciable amounts of the former are derived from ethylene. The competitive situation between these source materials runs through the whole chlorinated hydrocarbon picture, and extends on to other compound classes as well—for example, acrylonitrile is just on the threshold of a severalfold expansion, as demand grows for synthetic fibers based thereon. Acrylonitrile can be made either from ethylene oxide and hydrogen cyanide, from acetylene and hydrogen cyanide, or from allylamines. The ethylene oxide route is reported to be the only one in current commercial use, but new facilities now under construction will involve the addition of hydrogen cyanide to acetylene (*27*).

Acetylene is usually thought of as a coke-derived product via calcium carbide. But acetylene, used for vinyl resins manufacture, has been made by partial oxidation of natural gas methane for over a year now in a major installation in Texas, which is now being expanded (*6*). Moreover, another Gulf Coast plant now under construction will also produce acetylene from natural gas, utilizing this product for acrylonitrile as well as vinyl chloride production (*28*). These moves represent a momentous advance, pointing to the future entry of natural gas to an even greater degree into aliphatic syntheses.

Oxygenated Aliphatic Chemicals

Twenty-five years ago the only oxygenated aliphatics produced in important quantities were ethyl and *n*-butyl alcohols and acetone made by the fermentation of molasses and grain, glycerol made from fats and oils, and methanol and acetic acid made by the pyrolysis of wood. In 1927 the production of acetic acid (from acetylene) and methanol (from synthesis gas) was begun, both made fundamentally from coal. All these oxygenated products are still made from the old raw materials by the same or similar processes, but the amount so made has changed very little in the past quarter century. Nearly all the tremendous growth in the production of this class of compounds has come from petroleum hydrocarbons.

As a group the oxygenated aliphatics find their largest use as solvents and raw materials for synthetic resins applications. These include protective coatings, synthetic fibers, adhesives, and other plastics and resins products such as sheeting and film, moldings, laminates, and plasticizers. The next largest end-use field is products related to the petroleum and automotive industries, especially antifreeze but also including hydraulic fluids, petroleum additives, and processing solvents. Drugs and cosmetics plus a number of smaller end uses are of considerably less importance.

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In the following paragraphs the developments of the past 25 years are reviewed primarily on the basis of the various processes whereby the basic oxygenated compounds are produced from the original petroleum raw materials:

Hydration of Olefins. The earliest and still the largest production of chemicals from petroleum hydrocarbons was based on the hydration of olefins to produce alcohols by the employment of sulfuric acid. The addition of olefins to sulfuric acid to form alkyl sulfates and dialkyl sulfates takes place on simple contact of the hydrocarbons with the acid. To keep down polymerization and isomerization of the hydrocarbons, the temperature is kept relatively low, usually below 40° C. and commonly considerably lower than that (*18*). The strength of the sulfuric acid used depends on the olefin to be absorbed. Absorption of ethylene requires an acid concentration higher than 90%, whereas propylene and butylenes are readily absorbed in 85% acid or less. The alkyl and dialkyl sulfate solutions, on dilution and heating, are hydrolyzed to the alcohols plus small amounts of by-product ethers. After distilling off the organic products, the dilute sulfuric acid is reconcentrated and re-used.

Isopropyl alcohol production in 1950 exceeded 800,000,000 pounds, all made from petroleum. This alcohol is used mainly as a raw material for the production of acetone and also as a solvent. Acetone is made by the catalytic high temperature dehydrogenation or air oxidation of isopropyl alcohol. A much smaller part of the total acetone supply comes from fermentation and from hydrocarbon oxidation. Like isopropyl alcohol, part of the consumption is for solvent uses, but most serves as a raw material for other oxygenated compounds.

The largest offtake of acetone is its conversion into solvents, used mainly in lacquers and other synthetic resin applications. These solvents include diacetone alcohol, methyl isobutyl ketone, methyl isobutyl carbinol (methyl amyl alcohol), and methyl amyl acetate. The following equations (*22*), in each of which the raw material is the product of the previous reaction, show a possible procedure by which these solvents may be made:

$2(CH_3)_2CO \longrightarrow CH_3COCH_2C(OH)(CH_3)_2$ Diacetone alcohol

$CH_3COCH_2C(OH)(CH_3)_2 \longrightarrow H_2O + CH_3COCH{:}C(CH_3)_2$
Mesityl oxide

$CH_3COCH{:}C(CH_3)_2 + H_2 \longrightarrow CH_3COCH_2CH(CH_3)_2$
Methyl isobutyl ketone (MIBK)

$CH_3COCH_2CH(CH_3)_2 + H_2 \longrightarrow CH_3CHOHCH_2CH(CH_3)_2$
Methyl isobutyl carbinol (MIBC)

$CH_3CHOHCH_2CH(CH_3)_2 + CH_3COOH \longrightarrow H_2O + CH_3CH(OCOCH_3)CH_2CH(CH_3)_2$
Methyl amyl acetate

The diacetone alcohol reaction is a catalytic liquid-phase aldol condensation. The subsequent reactions involve dehydration, hydrogenation, and esterification.

For some years acetone has been converted to ketene ($CH_2{:}CO$) by high temperature decomposition. The ketene is reacted with acetic acid to give acetic anhydride. Since the mid-1930's acetone has also been one of the basic raw materials for methacrylate plastics. The first step in this process involves the addition of hydrocyanic acid to acetone to produce acetone cyanohydrin: $(CH_3)_2CO + HCN(CH_3)_2C(OH)CN$. The methacrylate ester monomers are then made by reacting with methanol or another alcohol in the presence of sulfuric acid or some other dehydrating agent.

Ethyl alcohol has been made by the hydration of ethylene (*9*) since 1930. Like isopropyl alcohol, part of the output is used as a solvent, but most is converted to other oxygenated chemicals. Its most important raw material use is conversion to acetaldehyde by catalytic air oxidation. Acetaldehyde, in turn, is the raw material source of acetic acid, acetic anhydride, pentaerythritol, synthetic *n*-butyl alcohol (via aldol condensation), butyraldehyde, and other products. Butyraldehyde is the source of butyric acid, polyvinyl butyral resin, and 2-ethylhexanol (octyl alcohol). The last-named eight-carbon alcohol is based on the aldol condensation of butyraldehyde and is used to make the important plasticizer di-2-ethylhexyl phthalate. A few examples of the important reactions of acetaldehyde are as follows:

$CH_3CHO + {}^1/_2O_2 \longrightarrow CH_3COOH$ Acetic acid

$3CH_3CHO + 1{}^1/_2O_2$ (approx.) $\longrightarrow (CH_3CO)_2O + CH_3COOH + H_2O$ Acetic anhydride

$2CH_3CHO \longrightarrow CH_3CH{:}CHCHO + H_2O$ Crotonaldehyde

$CH_3CH{:}CHCHO + H_2 \longrightarrow CH_3CH_2CH_2CHO$ Butyraldehyde

$CH_3CHO + 4HCHO + NaOH \longrightarrow C(CH_2OH)_4 + HCOONa$ Pentaerythritol

Other important raw material uses of ethyl alcohol are conversion to esters and ethers, vinegar, ethyl chloride, butadiene, styrene, and chloral (for DDT). Nearly all the new developments in chemicals from ethyl alcohol, particularly the four-, six-, and eight-carbon derivatives are based on alcohol derived from petroleum. The butyl alcohol and butyl acetate so made supplement the production by fermentation and from oxidation of hydrocarbons and synthesis gas operations. The consumption of ethyl alcohol for all industrial uses (denatured alcohol) exceeded 1.2 billion pounds (100% basis) in 1950. More than 700,000,000 pounds of this were made from petroleum.

One of the newer developments in the production of alcohols is the direct catalytic hydration of ethylene to ethyl alcohol. Temperature and pressure must be higher than in the conventional process, but the use and reconcentration of large amounts of sulfuric acid are avoided.

The hydration of acetylene produces acetaldehyde which then can be converted to acetic acid and other derivatives. The process is similar to olefin hydration employing a sulfuric acid solution containing also a mercurous sulfate catalyst.

sec-Butyl alcohol is another important product made by olefin hydration. It is used as a raw material for methyl ethyl ketone (MEK, analogous to acetone, produced by catalytic high temperature dehydrogenation of the alcohol) and *sec*-butyl acetate. These derivatives are used primarily as solvents for resins for protective coatings.

A major limitation on the production of alcohols by olefin hydration is the fact that the products consist almost solely of secondary or tertiary alcohols (excepting, of course, ethyl alcohol). The normal or primary alcohols are made by other means (but also from petroleum hydrocarbons). It appears more difficult to prepare C_5 and higher alcohols by the hydration of olefins since they are produced commercially by other means. One of the problems encountered (*31*) is excessive polymerization of the higher olefins when contacted with aqueous sulfuric acid.

Direct Oxidation. Direct oxidation of petroleum hydrocarbons has been practiced on a small scale since 1926; methanol, formaldehyde, and acetaldehyde are produced. A much larger project (*29*) began operating in 1945. The main product of the latter operation is acetic acid, used for the manufacture of cellulose acetate rayon. The oxidation process consists of mixing air with a butane-propane mixture and passing the compressed mixture over a catalyst in a tubular reaction furnace. The product mixture includes acetaldehyde, formaldehyde, acetone, propyl and butyl alcohols, methyl ethyl ketone, and propylene oxide and glycols. The acetaldehyde is oxidized to acetic acid in a separate plant. Thus the products of this operation are the same as those (or their derivatives) produced by olefin hydration and other aliphatic syntheses.

Synthesis Gas Operations. Among the latter developments in the production of oxygenated aliphatics from petroleum sources are synthesis gas operations, which involve reactions of carbon monoxide and hydrogen. The first important process of this nature was the production of synthetic methanol (*15*) by passing a CO-H_2 mixture over a metal oxide catalyst at high temperature and high (over 3000 pounds per square inch) pressure. Prior to World War II the U. S. production of methanol came largely from synthesis gas made by the reaction of steam with coke. Since the war there has been a rapid shift to use of natural gas as the source of the carbon monoxide and hydrogen, produced by reacting the methane with steam or oxygen. Production by hydrocarbon oxidation and the old wood distillation process accounts for only a small fraction of the total. Methanol is used for radiator antifreeze, as a solvent, and as a raw material for formaldehyde and other chemicals. The 1950 output was more than 900,000,000 pounds. Most of the companies that make methanol also make ammonia, which of course is not an or-

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ganic aliphatic chemical but deserves mention because it is another product based on synthesis gas. The hydrogen component of synthesis gas is reacted with nitrogen from air in equipment similar to or the same as that used for methanol.

In Germany prior to World War II it was found that by using a cobalt-thoria catalyst, at lower pressure and temperature than required for methanol, an almost exclusively paraffinic hydrocarbon product was obtained. This was the basis of the German synthetic oil plants. In this country the synthesis has been modified (*12*) to give an intermediate product containing about 75% hydrocarbons and 25% oxygenated aliphatics. This variation of the Fischer-Tropsch synthesis uses an iron-alkali catalyst. The first U. S. plant has now been constructed, and in addition to much larger amounts of liquid hydrocarbons will produce annually up to 150,000,000 pounds of aliphatic oxygenated compounds. The major portion of the output is ethyl alcohol, acetaldehyde, acetic acid, and acetone, which are all produced in larger amounts by other processes. About 25,000,000 pounds of normal propyl derivatives may also be produced to greatly augment the present small supply made by hydrocarbon oxidation and as a by-product of the methanol synthesis. All of the oxygenated products, 20 or more in number, are produced as one mixture, and a complex series of processes is necessary for their separation.

Another fairly recent development based on synthesis gas is the oxo process, in which olefins are reacted with carbon monoxide and hydrogen to produce aldehydes and alcohols. Octyl and nonyl alcohols have been made on a commercial scale since 1948. These long-chain alcohols are used mostly as raw materials for plasticizers.

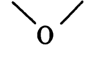
Another oxo plant, now being constructed, will make butyl compounds (*38*). These may be the source of butyl alcohol, butyl acetate, butyric acid for the manufacture of cellulose acetate butyrate and other products, butyraldehyde for polyvinyl butyral, and the eight-carbon compounds including 2-ethylhexanol. All these will add to the present production of the same compounds made by the older methods from acetaldehyde via aldol condensation.

The oxo reaction (*31*) is carried out in the liquid phase at high pressure using a cobalt catalyst. A mixture of aldehyde isomers is always produced, each isomer being one carbon number higher than the starting olefin. As a group the oxygenated products of the hydrocarbon synthesis (Fischer-Tropsch) process and the oxo process are primary compounds and thus (except, of course, the methyl and ethyl derivatives) differ fundamentally from the products based on alcohols made by the hydration of olefins, which are always secondary or tertiary in structure.

Ethylene and Propylene Oxides. Ethylene oxide (*26*) and its derivatives are among the important aliphatic chemicals; the 1950 production amounted to between 400,000,000 and 500,000,000 pounds. The chlorohydrin process was introduced in the early 1920's and the direct oxidation process in the 1930's, both based on ethylene. In the older process, the one most used today, the ethylene reacts in solution with hypochlorous acid at room temperature.

$$CH_2{:}CH_2 + HOCl \longrightarrow CH_2OHCH_2Cl \qquad \text{Ethylene chlorohydrin}$$

Ethylene dichloride is a by-product of this reaction. On treatment with alkali, the ethylene chlorohydrin is converted to ethylene oxide. In the oxidation method, ethylene and air are mixed and passed over a silver-containing catalyst at elevated temperature.



$$CH_2{:}CH_2 + {}^1/{}_2O_2 \longrightarrow \underset{\diagdown\;O\;\diagup}{CH_2\text{—}CH_2}$$

The most important use of ethylene oxide is as a raw material for ethylene glycol. Hydration of the oxide with a weak acid solution at high temperature and pressure conditions produces ethylene glycol and by-product di- and triethylene glycols. Ethylene glycol can also be produced directly from ethylene chlorohydrin by hydrolysis with a sodium bicarbonate solution. This saves a reaction step, but introduces difficulties in purifying the product. Propylene glycol is made from propylene by the chlorohydrin process, and its uses are also similar to those of ethylene glycol.

Ethylene glycol has also been made since 1939 by an entirely different process (*14*). Formaldehyde is reacted with carbon monoxide and water to form glycolic acid. After esterifying the acid with methanol, the resultant methyl glycolate is hydrogenated to form methanol and ethylene glycol. The principal use of the glycol is antifreeze. Other uses include incorporation in cellophane and other products and employment as a raw material for industrial explosives, resins, polyglycols, esters, and other chemicals.

Acrylonitrile is made from ethylene oxide by combining it with hydrogen cyanide and dehydrating the resultant cyanohydrin. Acrylonitrile is now used mostly for nitrile rubber. The new synthetic fibers Orlon, Dynel, and Chemstrand will be large consumers of acrylonitrile. However, a large part of the expanded output of this derivative may come from the addition of hydrogen cyanide to acetylene.

Other derivatives of ethylene oxide are the polyglycols, amines, detergents, and glycol ethers. Among the polyglycols, a broad range of molecular weights is made, including di-, tri-, and polyethylene glycols. Some of the higher derivatives have been used as synthetic lubricants. Ethanolamine derivatives are made by reacting ethylene oxide with ammonia. Nonionic detergents are made by combining ethylene oxide with an oil-soluble molecule such as an alkylphenol or fatty acid derivative. The glycol monoethers widely used as solvents are made by reacting ethylene oxide with methyl, ethyl, or butyl alcohol.

Hydrolysis of Chlorinated Hydrocarbons. The production of oxygenated aliphatics by the hydrolysis of chlorinated hydrocarbons includes the synthetic glycerol process and the amyl alcohols process. Glycerol (*7*) is made from propylene via allyl chloride ($CH_2{:}CHCH_2Cl$), and competes with glycerol made from fats and oils for use in dynamite and alkyd resins, as a tobacco humectant and cellophane plasticizer, in cosmetics and pharmaceuticals, and for other applications. Amyl alcohols have been made since 1926 by the alkali hydrolysis of a mixture of amyl chlorides, made by the chlorination of pentanes from natural gasoline. Production from this source far exceeds the supply from the fusel oil by-product of fermentation processes. Amyl alcohol and its derivatives are used mainly as solvents.

As indicated, any given aliphatic chemical is likely to be made by a number of processes from several raw materials. Important examples are acetic anhydride and acetic acid (*2*); production of the former was about 900,000,000 pounds in 1950 and that of the latter was about half as great. The large demand for these related products is primarily the result of the requirements of cellulose acetate rayon for acetic anhydride. The economic complexities in the production of the aliphatic oxygenated chemicals are probably best illustrated by these two products.

Twenty-five years ago the domestic supply of acetic acid came from the distillation of wood. This, in the form of calcium acetate, was reacted with acetyl chloride to produce acetic anhydride to satisfy the wants of the infant cellulose acetate rayon industry. Shortly thereafter a better process came on the scene utilizing the reactants sodium acetate, sulfur dichloride, and chlorine.

In the mid-1930's, it was found that acetic acid itself could be catalytically dehydrated to ketene, which when absorbed in fresh acid gave the anhydride. Soon after this process became commercially established, the older processes of making the anhydride were discontinued. By this time synthetic acetic acid was being made from acetylene via acetaldehyde oxidation, from synthetic ethyl alcohol also via acetaldehyde, and by the direct oxidation of fermentation ethyl alcohol. The ketene route to acetic anhydride, in addition to starting from acetic acid, later employed acetone as raw material.

In the 1940's, in addition to these operations, two other processes became important. Acetic acid was made by reacting methanol with carbon monoxide, and acetic anhydride was being made by the ethylidene diacetate process, which in effect is the dehydration of acetic acid to the anhydride by the use of acetylene. Fermentation ethyl alcohol was converted to acetic acid via acetaldehyde as well as by the direct oxidation of ethyl alcohol. A new operation on the Gulf Coast was also based on acetaldehyde. However, the acetaldehyde is made by the direct oxidation of liquefied petroleum gas. A further process for the production of these materials, in which acetaldehyde is oxidized in one step to a mixture of anhydride and acid, was also begun.

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Thus, in 1948, acetic acid and anhydride were being made on a large scale commercial basis by at least ten producers using at least ten different processes and converting at least six different raw materials. Since that time some operations have been curtailed, but the situation remains exceedingly complex. Probably no one can say which processes are the most economical or predict what developments will occur in the future.

Hydrocarbons

Another group of materials in the aliphatic chemicals field comprises hydrocarbons as such. In this one would not include, of course, the basic raw materials, the lower paraffins and olefins, which form the fundamental starting points for all the manifold syntheses so far described. Butadiene, on the other hand, although it is only a starting material going into synthetic rubber, is sufficiently varied in its origin so that it has been classed among the aliphatic chemicals. When synthetic rubber demands were at their highest level in World War II, during 1944 and 1945, annual butadiene production reached 1.25 billion pounds, with petroleum sources accounting for the major portion (*35*). Dehydrogenation of normal butane and normal butylenes over metal-oxide catalysts at temperatures in excess of 600° C. with steam dilution was most widely employed (*30*), but some minor use was made of the high temperature pyrolysis of petroleum naphthas (*25*). The wartime butadiene produced from other than hydrocarbon sources was made from ethyl alcohol (*33*) by condensation with acetaldehyde (in turn produced from alcohol) over a tantalum oxide–silver catalyst, at 350° C., which converts the intermediate crotonaldehyde to butadiene. Use of ethyl alcohol in this manner was terminated at the end of World War II and has only recently been resumed as the defense production of GR-S has been expanded. Butadiene purification methods included extractive distillation as well as absorption in cuprous salt solutions.

A new commercial use for butadiene is its employment in the nylon synthesis joining furfural, benzene, and cyclohexane as raw materials for nylon salt components. Another olefinic hydrocarbon, which has found large scale application in recent years, is propylene tetramer, widely employed in reaction with aromatic nuclei to yield an alkylated aromatic base used in synthetic detergent production.

Purely aliphatic materials that have assumed important positions among polymeric products are polyethylene, polyisobutylene, and Butyl rubber. These will not be discussed here, since in industrial practice their production generally passes from the raw material stage right on to the plastics and elastomer segments, without pausing in the aliphatic chemicals field. However, these products have reached considerable volume—for example, Butyl rubber output is pressing toward 150,000,000 pounds as its use in inner tubes and other specialty applications grows; polyethylene capacity is currently undergoing rapid expansion from its 1950 level, estimated (*8*) at 75,000,000 pounds, with molding, sheeting, and electrical applications increasing. An interesting point in connection with plastics and resins in general is that before World War II there was only a minor development of aliphatic materials in this field. Today, however, with the great expansion in the vinyl resins, nylon, polyethylene, and the acrylic plastics as well as the newer acrylonitrile fibers, the entry of petrochemical formaldehyde as a plastics component, and the use of aliphatic chemicals as synthetic rubber precursors, it appears that the contributions of the oil industry to the resins and plastics segment indeed loom large.

General Discussion

If the foregoing discussions have seemed somewhat complex, it must be noted that the complications are not those of chemistry or technology; the reactions and processes are generally simple and straightforward, and the number of successive steps in the path of most of these syntheses is usually small. The essential complexity, however, arises from the fact that in this field of aliphatic chemicals superimposed on the vigorous competition between companies, one encounters multifold technical competition: there is the competitive production of a single commodity from different raw materials (usually this also involves different processes); secondly, there are alternate process routes which may be taken from a single raw material to yield a single major product; and, lastly,

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there exists product versus product competition, where two or more commodities may be used practically interchangeably in a given end use.

An example of the first situation is methanol, which is made today from the three main chemical raw material sources: plant matter (by wood distillation); coal (via carbon monoxide and hydrogen in water gas); and natural gas hydrocarbons (both by direct oxidation and through CO-H_2 synthesis, where the synthesis gas is made from methane).

To exemplify the second relationship, process competition, there are the two alternate routes from ethylene to ethylene oxide—direct oxidation and chlorohydrination. Even more involved is the acetic acid picture, in which, as has been described, at least ten processes have been in use at the same time in commercial competition with one another.

An interesting case of interproduct competition is that of the four original lacquer solvents—ethyl alcohol, butyl alcohol, ethyl acetate, and butyl acetate. These were once produced mainly by fermentation processes, but today all are also produced by synthesis from petroleum hydrocarbons. Moreover, in the past 30 years solvents have been developed from petroleum sources which are competing successfully with these materials even though the new compounds are not identical in all properties: isopropyl alcohol competes with ethyl alcohol; methyl isobutyl carbinol and *n*-propyl alcohol can replace butyl alcohol; methyl ethyl ketone to a large extent supplants ethyl acetate; and methyl isobutyl ketone can be substituted for butyl acetate. Thus, petroleum aliphatic chemicals have served both by displacement of source and replacement of end product to supplement and to compete with the fermentation solvents.

There is also an apparent trend in manufacturing operations toward simplification by direct processing. Examples of this include the oxidation of ethylene for direct manufacture of ethylene oxide; the direct hydration of ethylene to produce ethyl alcohol; production of chlorinated derivatives by direct halogenation in place of round-about syntheses; and the manufacture of acrolein by olefin oxidation. The evolution of alternate sources, varying process routes, and competing end products has given the United States aliphatic chemical industry much of its vitality and ability to adjust to varying market conditions.

Considerations of ample supply of raw material and economies in using petroleum sources as against synthesis from agricultural products, for instance, have been important factors in the development of aliphatic chemicals from petroleum hydrocarbons. There is, however, one other factor which completes the picture—the fact that aliphatic chemicals find their greatest application in those sectors of our economy which are relatively young and growing rapidly. It was pointed out in an analysis (*24*) of the 1945 usage of nearly six billion pounds of aliphatic chemicals that their consumption was concentrated to the extent of almost 85% in the following five fields of application: automotive (not the manufacture of automobiles but rather the chemicals consumed in operation thereof—namely antifreeze, antiknock compounds, and brake fluids), synthetic rubber, synthetic fibers, plastics and resins, and protective coatings. Certainly in the first four of these categories and even to some extent in the protective coatings, rapid expansion is still taking place, and it is believed that an end-use analysis for the present time would show a similar picture. The vigorous growth of these chemical product segments goes far to explain the rapid expansion in the demand for synthetic aliphatic chemicals.

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Aromatics from Petroleum

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The historical development of aromatics production from petroleum is outlined, and the methods employed during World War II for the production of nitration grade toluene are described. Included is a discussion of methods of synthesizing and purifying benzene, xylenes, and aromatics of higher molecular weight both as mixtures and as pure compounds. Data are presented on the composition of the aromatic hydrocarbons available from typical hydroformates. Aromatics and mixtures thereof currently available from petroleum are listed. Some of the problems facing the industry in the field of aromatics production are discussed and the probable trend of future research is indicated.

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The petroleum industry entered the field of aromatics production largely because the unprecedented demand for toluene for the manufacture of TNT at the outbreak of World War II in 1939 could not be met by other sources. As a result of its efforts, the industry supplied 75 to 85% of all the toluene which was nitrated for TNT production during the latter years of World War II. Since that time the petroleum refiners have remained in the field and at present they are major suppliers of toluene and xylenes. In Table I it is shown that in 1949 about 59% of the toluene and 84% of the xylenes produced in the United States were derived from petroleum sources. The petroleum industry has diversified its operations in the field of aromatics production until at present a variety of materials is offered. Table II presents a partial list of the commercially available aromatics, together with some of their uses. A number of other aromatics, such as methylethylbenzene and trimethylbenzene, have been separated in small scale lots both as mixtures and as pure compounds.

Aromatics of high purity were first derived from petroleum in the form of toluene for nitration to TNT during World War I. During that period, TNT assumed first rank among explosives because of its low melting point, safety in handling, and the ease with which its time of explosion can be controlled. The scarcity of toluene caused the price to soar from its normal value of 25 cents per gallon to a high of about $5 per gallon. The extreme shortage prompted separation of toluene from petroleum, even though expensive

Table I. United States Production of Aromatics in 1949[a]

Product	Production, Millions of Gallons/Year	%
Toluene, total	82	100
Petroleum sources	48	59
All other sources	34	41
Xylenes, total	58	100
Petroleum sources	49	84
All other sources	9	16

[a] From United States Tariff Commission Reports.

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processes were required. Narrow-cut virgin naphthas containing 25 to 35% toluene were subjected to thermal cracking conditions which decomposed a large percentage of the less stable nonaromatics to coke and light gases. The resulting liquid product, containing a high concentration of toluene, was then acid-treated to remove olefinic materials and redistilled to remove nonaromatic hydrocarbons boiling below and above toluene. Manufacture of toluene by this process was abandoned at the end of World War I because processing costs made the price prohibitive for peacetime uses. Between 1920 and 1940, small amounts of mixed aromatics were obtained for solvent purposes by the Edeleanu or liquid sulfur dioxide extraction process.

Table II. Uses for Petroleum Aromatics

Aromatic	Uses
Benzene	Manufacture of styrene, dyes, intermediates, phenol, solvent
Toluene	Manufacture of TNT, aviation gasoline, solvent
Xylene-mixed isomers	Solvent, manufacture of aviation gasoline
o-Xylene	Phthalic anhydride
p-Xylene	Terephthalic acid (for plastics)
Ethylbenzene	Styrene
C_9 alkylbenzene-mixed isomers	Solvent
C_{10} alkylbenzene-mixed isomers	Solvent
Naphthalene	Moth repellent, manufacture of phthalic anhydride, 2-naphthol, intermediate
300° to 550° F. boiling range aromatic mixture	Solvent
Catalytic tar	Carbon black manufacture
Lubricating oil extracts	Sulfonate manufacture

In the late 1930's, it was estimated that the toluene requirements for TNT production would be about 16,000 barrels per day if the United States were to become involved in a war. As the coal-tar industry could supply only about 2500 barrels per day, an extreme wartime shortage of aromatics was indicated. Increasing supplies by expansion of the coal-tar industry was impractical, because toluene was only a by-product from the manufacture of coke for the steel industry. Consequently, the Ordnance Department of the United States Army turned to the petroleum industry to produce toluene. Recovery of the naturally occurring toluene in crude petroleum appeared to be a practical method of increasing supplies, but was inadequate to supply the needed quantities. Therefore, a synthesis method was needed to supplement the naturally occurring toluene. Fortunately, the petroleum industry already had developed the hydroforming process for synthesizing aromatics by the catalytic dehydrogenation of cyclohexane and its homologs. Hydroforming had been developed for increasing the octane number of virgin naphthas by converting naphthenes of relatively low octane number to aromatics of high octane number.

At the outbreak of World War II in 1939, no commercial hydroforming units were in operation; construction was in progress, however, on one plant originally designed for motor gasoline production but subsequently converted to the production of toluene (*4*). Under the impetus of the war movement, seven additional installations were completed and placed in service in the United States prior to and during the period of United States participation in the war. Although these plants were designed primarily for achieving maximum production of nitration grade toluene, the ingenuity with which their operations were integrated with those of other refinery processing units enabled very substantial contributions to the supply of aromatics for 100-octane aviation gasoline. Products from the hydroforming process which boiled above and below toluene constituted valuable blending components for aviation gasoline, particularly because of the exceptionally good rich mixture antiknock characteristics of certain of the aromatics, such as the ethylbenzene contained therein. The design and construction of hydroformers with only meager process data and the adaptation of the process to the manufacture of toluene and aviation gasoline are regarded as outstanding technical contributions of the petroleum industry to the war effort.

The problem of concentrating toluene above the 50 to 70% value obtainable by fractional distillation of hydroformates was solved by the development of azeotropic and extractive distillation techniques and by improvement in the sulfur dioxide extraction

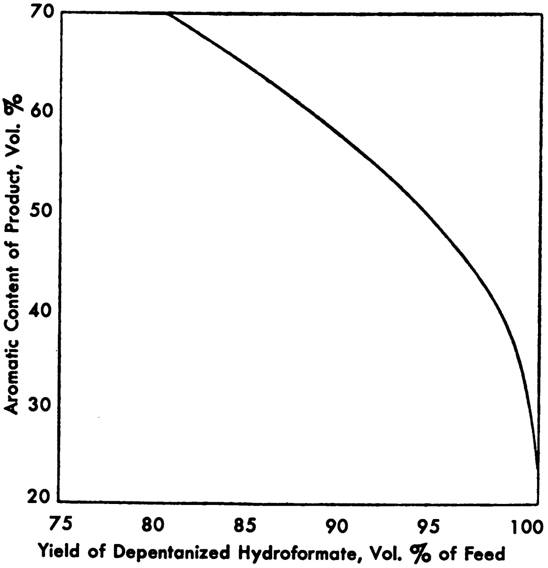

Figure 1. Effect of Yield on Product Aromatic Content

Reforming 250° to 330° F. virgin naphtha

process. Plants utilizing all three processes were constructed to purify toluene; the single installation of largest capacity was the Baytown Ordnance Works at Baytown, Tex., which employed sulfur dioxide extraction.

Following the cessation of hostilities of World War II, there was a short period of abundant supply of aromatics, particularly toluene, caused by the sudden decline in consumption of aromatics for nitration and for use in aviation gasoline. Soon, however, the peacetime uses for aromatics created a demand which could be satisfied only by the combined production of aromatics from petroleum and coal-tar sources. Consequently, many of the toluene plants were purchased from the Government by the petroleum refiners and utilized for manufacture of the many aromatic products available on the market today.

The current benzene shortage has presented a new challenge to the oil industry. It has been estimated that a shortage of 30,000,000 gallons will exist in 1951 and may increase to 100,000,000 gallons per year within 5 years (*18*). An expansion of coal-tar production by about 50% would have to be realized to supply the shortage. As this appears impractical, the increase is being sought in the petroleum industry. As early as the spring of 1947, benzene was produced from petroleum in commercial quantities on an experimental basis (*18*). In the early part of 1950 benzene from petroleum became a regular commercial operation at the Texas City refinery of the Pan American Refining Co. (*23*). Shortly thereafter, benzene production was initiated at the Wilmington refinery of the Shell Oil Co. Both companies synthesize benzene by dehydrogenation of cyclohexane.

Synthesis of Aromatics

Hydroforming. Hydroforming is the most widely used process for synthesizing aromatics for purification. The process consists of the catalytic reforming of naphthas in the presence of hydrogen; the primary conversion occurring is the catalytic dehydrogenation of six-carbon-atom naphthene ring compounds to the corresponding compounds containing benzene rings. The processing variables allow considerable control over the reactions involved and the products made—for example, varying yield affects the concentration of aromatics in the hydroformate as shown in Figure 1. Feed stock boiling range also has a marked effect on the yield of various aromatics. Thus, when a narrow boiling light virgin naphtha containing methylcyclopentane and cyclohexane is hydroformed at the Texas City refinery of the Pan American Refining Co., benzene is synthesized by isomerization of methylcyclopentane to cyclohexane and dehydrogenation of the cyclohexane (*23*). Another boiling range feed stock is needed for synthesizing toluene, whereas a third boiling range is needed for synthesizing C_8, C_9, and C_{10} aromatics, as shown in Table III.

Table III. Effect of Feed Stock Boiling Range on Relative Quantities of Aromatics Produced in Hydroforming

Feed stock boiling range, ° F.	200–275	250–350
Aromatics in product, vol. %		
Benzene	0.9	0.6
Toluene	29.1	3.6
C_8	9.3	25.4
C_9	0.7	16.6
C_{10} and higher	0.2	6.2

The above illustrates the fact that judicious selection of feed stocks and process conditions allows a wide range of the yield–aromatic production relationship and considerable control over the relative quantities of aromatics of given boiling range or molecular weight. Tables IV to VI show the composition with respect to the various isomers of the C_8, C_9, and C_{10} aromatics produced from hydroforming of virgin naphthas at normal hydroforming conditions.

Table IV. Composition of Eight-Carbon Atom Aromatics in Hydroformate

Compound	Boiling Point, ° F.	Freezing Point, ° F.	Wt. %, Based on Total C_8 Aromatics
Ethylbenzene	277	−139	19.3
p-Xylene	281	+56	16.4
m-Xylene	282	−54	42.9
o-Xylene	292	−13	21.4

Platforming. Within the past two years, announcement was made of a new catalytic reforming process called Platforming. The process, which employs a platinum catalyst, involves essentially the reactions listed above for hydroforming, except that the carbon deposition reactions are greatly reduced, thereby providing a catalytic process which does not include a regeneration step (*11*). The Platforming process is usually conducted at higher pressures than hydroforming but at approximately the same temperature. The yield-octane relationship for platforming is stated to be slightly better than that obtained with hydroforming under certain conditions. The Platforming process is comparable to the hydroforming process in the selection of feed stocks and operating conditions to control the yield and type of aromatics produced. Although only one Platformer was in commercial operation in 1950, and this unit was designed for improvement of motor gasoline octane, the Platforming process is a valuable additional tool for the synthesis of aromatics.

Other Methods of Synthesis. Huge quantities of aromatics are synthesized by thermal reforming and by catalytic and thermal cracking of middle distillates and

Table V. Composition of Nine-Carbon Atom Aromatics in Hydroformate

Compound	Boiling Point, ° F.	Freezing Point, ° F.	Wt. %, Based on Total C_9 Aromatics
Isopropylbenzene	306	−141	0.4
n-Propylbenzene	319	−147	5.7
m-Ethyltoluene	322	−140	21.0
p-Ethyltoluene	324	−80	9.6
1,3,5-Trimethylbenzene	329	−49	9.3
o-Ethyltoluene	329	−114	9.0
1,2,4-Trimethylbenzene	337	−47	34.8
1,2,3-Trimethylbenzene	349	−14	8.5
Indan	352	..	1.7
			100.0

Table VI. Composition of Ten-Carbon Atom Aromatics in Hydroformate

Compound	Boiling Point, ° F.	Freezing Point, ° F.	Wt. %, Based on Total C_{10} Aromatics
Isobutylbenzene	343	−61	0.0
sec-Butylbenzene	344	−104	0.0
m-Cymene	347	−83	0.5
p-Cymene	351	−90	0.3
o-Cymene	353	−97	0.3
1,3-Diethylbenzene	358	−119	2.3
1-Methyl-3-*n*-propylbenzene	360	..	1.8
1-Methyl-4-*n*-propylbenzene	362	−81	1.8
n-Butylbenzene	362	−126	1.8
1,3-Dimethyl-5-ethylbenzene	363	−120	4.8
1,4-Diethylbenzene	363	−46	0.8
1,2-Diethylbenzene	362	−25	0.5
1-Methyl-2-*n*-propylbenzene	363	..	1.5
2-Methylindan	367	..	7.3
1-Methylindan	369	..	
1,4-Dimethyl-2-ethylbenzene	368	−65	6.0
1,3-Dimethyl-4-ethylbenzene	371	−81	18.3
1,2-Dimethyl-4-ethylbenzene	374	−89	
1,3-Dimethyl-2-ethylbenzene	374	+3	1.3
1,3-Dimethyl-3-ethylbenzene	381	−57	4.8
1,2,4,5-Tetramethylbenzene (durene)	385	+175	8.5
1,2,3,5-Tetramethylbenzene (isodurene)	388	−11	13.5
5-Methylindan	395	..	11.1
4-Methylindan	395	..	
1,2,3,4-Tetramethylbenzene (prehnitene)	401	+21	5.2
1,2,3,4-Tetrahydronaphthalene (Tetralin)	404	−22	0.0
Naphthalene	424	+176	7.5

residua. However, these aromatics usually are present in low concentrations relative to the concentrations obtained from catalytic reforming; furthermore, the aromatics are associated with rather large concentrations of olefins and diolefins, and are therefore more difficult to purify. Aromatics from cracking and thermal reforming were recovered during the last war because of the over-all shortage of aromatics, but have not been recovered on an extensive scale since then because of economic considerations.

The Catarole process was developed in England during the past 10 to 15 years for the production of aromatics (*20*). Placed in commercial operation in 1948, the process charges naphtha or gas oil over a catalyst at a high temperature to obtain a 40 to 60% yield of a product containing up to 95% aromatics. A complete range of aromatic compounds from benzene to polycyclic aromatics is produced (*17*).

Some processes have been developed for the synthesis of particular aromatics starting with other aromatics, usually of different molecular weight, as charge stocks. Dealkylation of alkylbenzenes to produce benzene has been reported by Thomas *et al.* (*22*). Using a chromia-alumina catalyst at 750° to 950° F. and atmospheric pressure, the alkylbenzenes were dealkylated to give benzene with no toluene, styrene, etc., in the product. Bimolecular disproportionation can be accomplished by subjecting alkylbenzenes to cracking conditions in the presence of a silica-alumina catalyst (*9*). Thus, where xylene is cracked, toluene and trimethylbenzenes are produced in equimolar quantities. Alkylation of an aromatic compound with an olefin to yield an aromatic compound of higher molecular weight represents still another commercial synthesis. The production of ethylbenzene by alkylation of benzene with ethylene in the manufacture of styrene is a notable example of such an operation. Commercial application of any of these processes which use an aromatic compound as a starting material depends on the higher value of the product in relation to the starting material.

Separation of Aromatics from Hydrocarbon Mixtures

The separation of aromatics from complex mixtures of hydrocarbons may be effected to a considerable degree by distillation alone. For example, wide boiling (100° to 300° F.) hydroformates containing 40 to 50% aromatics can be fractionally distilled to obtain toluene and xylene concentrates of 70 to 80% aromaticity. Such an operation usually results in a recovery of only about 75% of the aromatics present, the balance being discarded in order to obtain high purity. However, when coupled with extraction processes, recoveries of 90 to 95% are realized. In this operation, the hydroformate is distilled into narrow-boiling fractions, some of which contain 60 to 70% aromatics for use as aviation blend stocks. Others contain only 40 to 55% aromatics; these latter streams are purified further by extraction to recover aromatics of 97 to 99% purity. Some of the narrow-boiling fractions of low aromaticity are discarded.

Another technique used for production of high purity aromatics without resorting to extraction involves the hydroforming of a feed stock prepared by precisely fractionating a naphtha so that it contains no hydrocarbon of higher boiling point than the naphthenes to be dehydrogenated. Thus it is possible to take advantage of a boiling point increase when naphthenes are dehydrogenated to the corresponding aromatics; examples of this shift in boiling point are shown in Table VII. The process can be illustrated by the production of by-product xylenes wherein a naphtha of 270° F. true-boiling end point is hydroformed. The naphthenes in the 240° to 270° F. boiling range produce xylenes which boil in the 270° to 300° F. range, while the unconverted naphthenes remain substantially in the boiling range below 270° F. Thus, when the 270° to 300° F. fraction is separated from hydroformate by distillation, xylenes of 90 to 95% aromaticity are produced. As the number of side chains increases, the magnitude of the boiling point shift increases, thereby enabling the production of higher molecular weight aromatics of purities in excess of 95%. In all cases, the purity of these by-product aromatics is reduced considerably if, because of poor fractionation, the hydroformer feed contains paraffinic material boiling in the range of the desired aromatic.

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Table VII. Boiling Points of Various C_8 and C_9 Naphthenes and Aromatics

Aromatic Compound	Boiling Point, ° F.	Boiling Point of Corresponding Naphthenes, ° F.
Ethylbenzene	277	266
p-Xylene	281	247–256
m-Xylene	282	249–257
o-Xylene	292	255–266
Isopropylbenzene	306	310
n-Propylbenzene	319	311
m-Ethyltoluene	322	301
p-Ethyltoluene	324	303
1,3,5-Trimethylbenzene	329	285
o-Ethyltoluene	329	309
1,2,4-Trimethylbenzene	337	289
1,2,3-Trimethylbenzene	349	293

The technique for purifying aromatics by thermally cracking the less stable non-aromatics to gas and coke, mentioned above, was used rather extensively during World War II to prepare aviation gasoline components. Unlike the earlier World War I case in which the available charge stocks contained only 25 to 35% aromatics, charge stocks containing as much as 75% aromatics were available from catalytic cracking and from hydroforming. Thermal treating of the catalytic naphtha fractions, followed by acid treating and rerunning, produced stocks containing as much as 96% aromatics with over-all yields of 85 to 90% of the aromatics charged. Rehydroforming of toluene concentrate in a blocked operation followed by acid treating and rerunning was employed to produce nitration grade toluene without extraction.

In 1907, Edeleanu described a batch process for refining kerosenes and similar distillates by extraction with liquid sulfur dioxide to remove aromatic compounds and thereby improve the burning qualities of the kerosene. By 1930 sulfur dioxide extraction had been developed into a continuous process and a plant was operated in California charging 7000 barrels per day of California kerosene distillate (*8*). Although the early operations were intended primarily to recover the refined paraffinic oil, the aromatic extracts were utilized as solvents after treatment to remove some of the impurities. In some cases, the extracts were subjected to hydrogenative cracking to produce aromatic solvents known as "hydro-solvents." By these methods petroleum refiners obtained stocks containing 75 to 90% aromatics, which found a ready market as commercial solvents. The technology of solvent extraction was developed subsequently to apply extraction processes to stocks having boiling ranges from that of benzene through that of the highest boiling hydrocarbon mixtures obtainable from petroleum. Furthermore, new solvents were introduced, each of which possessed virtues in specific fields. The development of the aforementioned

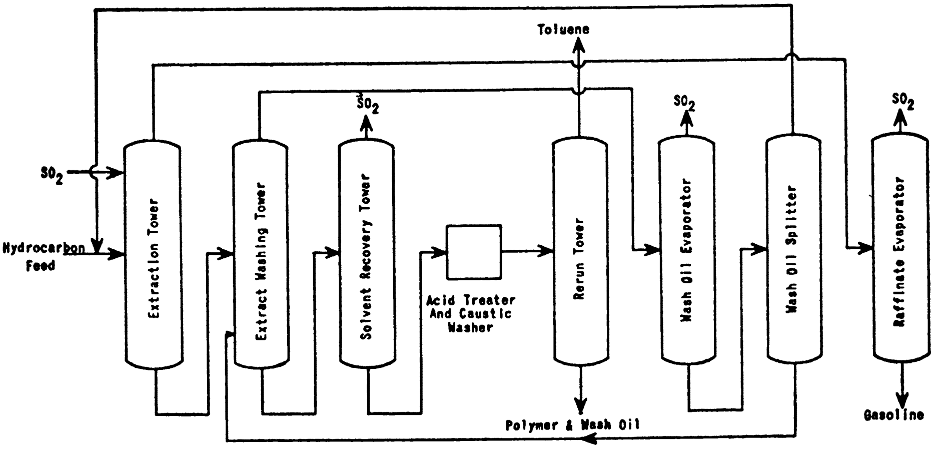

Figure 2. Solvent Extraction of Toluene

catalytic reforming processes for the synthesis of vast quantities of aromatics prompted great advances in the technology of aromatic separations.

The use of a double extraction operation formed the basis for a process to separate nitration grade toluene from hydroformer products at the Baytown Ordnance Works, which was operated by Humble Oil & Refining Co. during World War II. This operation is shown schematically in Figure 2. A toluene concentrate prepared by fractional distillation to contain 40 to 50% toluene is brought in contact with liquid sulfur dioxide at a temperature in the range of −20° to −30° F. This operation produces a sulfur dioxide extract phase containing hydrocarbons comprising about 65 to 70% toluene, the remaining hydrocarbons being nonaromatic impurities which distill near the boiling point of toluene. To remove these impurities, the sulfur dioxide extract is washed with heavy paraffins in the kerosene boiling range in a countercurrent operation to replace the lower boiling impurities with higher boiling paraffins. Removal of the heavy paraffins from the toluene by distillation is an easy matter. The washed extract is stripped of sulfur dioxide and finished by treatment with 10 to 20 pounds of 98% sulfuric acid per barrel of extract to remove small quantities of olefins present in the extract, followed by a distillation to remove the heavy wash oil and polymers formed during the acid treatment; small amounts of light paraffinic material and water are also removed in the distillation operation.

The Baytown Ordnance Works was the only plant which used liquid-liquid extraction for producing nitration grade toluene, and its successful operation is reflected by the increase in production rate from a design capacity of 2500 barrels per day to about 4700 barrels per day near the end of World War II. After the war, the plant was operated successfully for purifying xylenes and higher boiling aromatics in combination with the toluene operation and in separate blocked operations. The process has been operated experimentally for benzene production. Early difficulties with exchanger fouling from the formation of polysulfones with sulfur dioxide and olefins were minimized by gas blanketing (*15*) and inhibiting (*21*) feed stocks to the plant; this is thought to prevent formation of peroxides which act as initiators in polysulfone formation.

Extractive distillation was the basis of a process introduced commercially by the Shell Development Co. and put into operation in 1940 at the Houston refinery of the Shell Oil Co., Inc., for separating toluene from virgin stocks (*6*); subsequently it was used also on hydroformates and cracked naphthas. This process, shown diagrammatically in Figure 3, involves the production of a toluene concentrate by distillation to remove low and high boiling contaminants, which then is extractively distilled with phenol to separate the aromatics from the paraffin (*5*). The extract is obtained as a bottoms stream from the extractive distillation tower, and is further fractionated in a distillation tower to separate raw toluene from the phenol, after which the toluene is acid treated and redis-

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tilled to obtain nitration grade toluene. When diolefins are present in the charge stock, as when charging cracked naphthas, the phenol forms a sludge which is believed to be the result of its alkylation with diolefins. This difficulty is reduced in some instances by pretreating the toluene concentrate for diolefin removal prior to extractive distillation. This treatment is not necessary with virgin stock, but is desirable with hydroformate, and is necessary with cracked stocks. The pretreatment may consist of liquid or vapor phase clay treatment, vapor phase phosphoric acid treatment, or liquid phase sulfuric acid treatment. Contamination of the phenol with the sludge has no apparent harmful effect up to 30 or 40% concentration of sludge, except that the phenol circulation rate must be increased and the phenol stripper bottoms temperature must be raised.

During World War II, the phenol extractive distillation process was used for separating toluene from hydrocarbon mixtures by most oil companies, including the Shell Oil Co., Sinclair Refining Co., Standard Oil Co. (Indiana), Pan American Refining Co., The Texas Co., Gulf Oil Corp., and Continental Oil Co. The use of other solvents such as furfural, cresols, antimony trichloride, aniline, and methyl phthalate, has been demonstrated to be suitable for separating aromatics from hydrocarbon mixtures, but their use has not been accepted as universally as phenol in extractive distillation. Cresols are used as a solvent in the extractive distillation of benzene by the Shell Oil Co. at its Wilmington refinery (*5*).

Another process for producing toluene from hydrocarbon mixtures involved azeotropic distillation with methanol and with methyl ethyl ketone as applied by the Magnolia Petroleum Co. and the Union Oil Co., respectively, for recovering toluene from cracked naphthas and hydroformates. The flow plan for such an azeotropic distillation process is presented in Figure 4. In the distillation with methanol (*7*), a narrow-boiling toluene concentrate (215° to 240° F.) is charged to azeotroping towers with sufficient methanol to produce a bottoms fraction containing 96 to 98% toluene, which is finished to nitration grade by acid treating and redistilling. The azeotropic overhead, which contains 55 to 70% alcohol, is water-washed to remove the alcohol from the gasoline; the aqueous phase then is distilled to recover the methanol. A similar operation with methyl ethyl ketone is claimed to provide more efficient toluene recovery (*13*). The following table compares the toluene recovery from the best four of 25 azeotrope formers in comparable batch distillation using 20-plate fractionating columns at 20 to 1 reflux ratio:

Azeotrope Former	Toluene Recovery[a], %
Methyl ethyl ketone–water	100
Nitromethane	95
Methanol	93
Dioxane	84

[a] As 99% toluene based on toluene in feed.

Numerous patents have issued covering the separation of aromatics with other azeotroping agents, including acetone, methyl acetate, butyraldehyde, ethyl formate, 4-methyldioxolane, propionic acid, and the like, but their commercial application appears to be limited. Although the above processes were discussed with reference to separating toluene, they are generally applicable also, with minor modification, for separating other aromatics, such as benzene and xylene.

Aromatic Isomer Separation. Recent activity directed to producing pure aromatic hydrocarbons has been concerned primarily with separating isomers from aromatic mixtures. The problem does not arise with benzene and toluene, but is encountered first with C_8 aromatic mixtures; some of these isomers have been separated commercially since World War II to provide intermediates for chemical synthesis.

Chronologically, the production of *o*-xylene from mixed C_8 aromatics was the first of these separations. In 1945, the Oronite Chemical Co. produced 85 to 90% purity *o*-xylene by fractionation from crude xylenes (*1*). The *o*-xylene product is oxidized for the production of phthalic anhydride in a vapor phase reaction over a vanadium-base catalyst. By 1947 Oronite provided 5% of the United States production capacity for phthalic anhydride by this process (*2*).

The separation of *p*-xylene from mixed C_8 aromatics can be achieved commercially by crystallizing and centrifuging at temperatures in the range of −50° to −150° F.

In one patented process (*19*) a *m*-*p*-xylene fraction is produced from xylene mixtures by distillation, and is subsequently cooled to about −70° F. to produce *p*-xylene crystals, which are removed in high purity by filtering or centrifuging. The yield of *p*-xylene is limited by eutectic formation with *m*-xylene. As the mixture behaves as an ideal solution, the yield and temperature level can be calculated from the thermodynamic properties of xylenes, which were reported by Kravchenko (*12*).

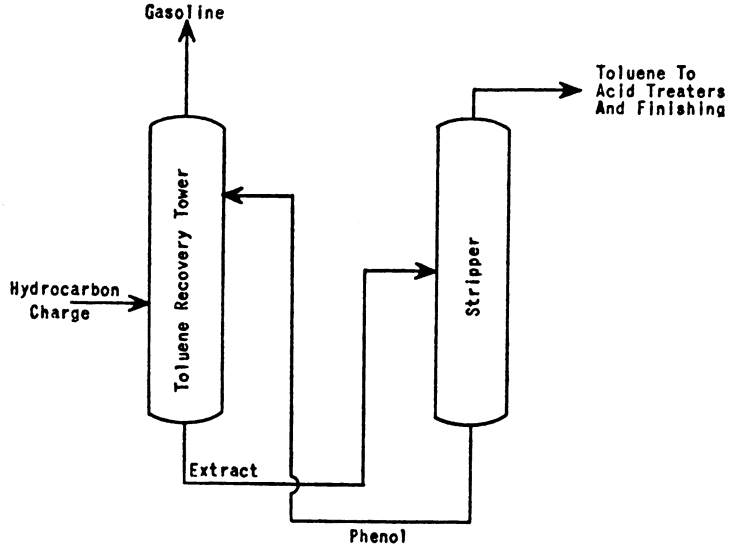

Figure 3. Extractive Distillation of Toluene

In another process (*14*) ethylbenzene is included with the crystallizer charge to inhibit eutectic formation, thereby increasing the yield of *p*-xylene.

The ultimate in xylene separation is claimed, however, by Hetzner (*10*), who first distills the mixture to remove *o*-xylene by taking *m*-*p*-xylene and ethylbenzene overhead in a column having about 35 to 60 theoretical plates. It is reported that concentrates containing up to 97% *o*-xylene have been produced by this process. The *m*-xylene, *p*-xylene, and ethylbenzene mixture is selectively sulfonated to remove *m*-xylene. In this operation, 2 moles of sulfuric acid (96 to 98%) are added per mole of *m*-xylene in the mixture to be treated. After separation, the aqueous layer is hydrolyzed at 250° to 300° F. to recover a concentrate containing 90% or more *m*-xylene. The hydrocarbon layer is cooled to produce *p*-xylene crystals, which are separated by filtration or centrifugation. The 85 to 90% *p*-xylene concentrate is reprocessed to recover a final product containing 96% *p*-xylene. The mother liquor from the *p*-xylene crystallization contains impure ethylbenzene and is rejected from the system.

At least one commercial installation for *p*-xylene separation is operating (*3*), and others are under consideration. *m*-Xylene, however, appears to sustain only a limited interest at the present time, and is available only in pilot unit quantities.

Ethylbenzene has not been separated commercially from C_8 aromatics because it cannot be obtained therefrom in high purity as readily as it can be synthesized from benzene and ethylene by alkylation to provide the necessary stock for styrene manufacture. The current shortage of benzene, however, re-establishes interest in separating ethylbenzene from hydroformed stocks.

Future Trends

The processes described for producing benzene by dehydrogenation of cyclohexane have contributed materially to relief of the acute benzene shortage. However, the charge

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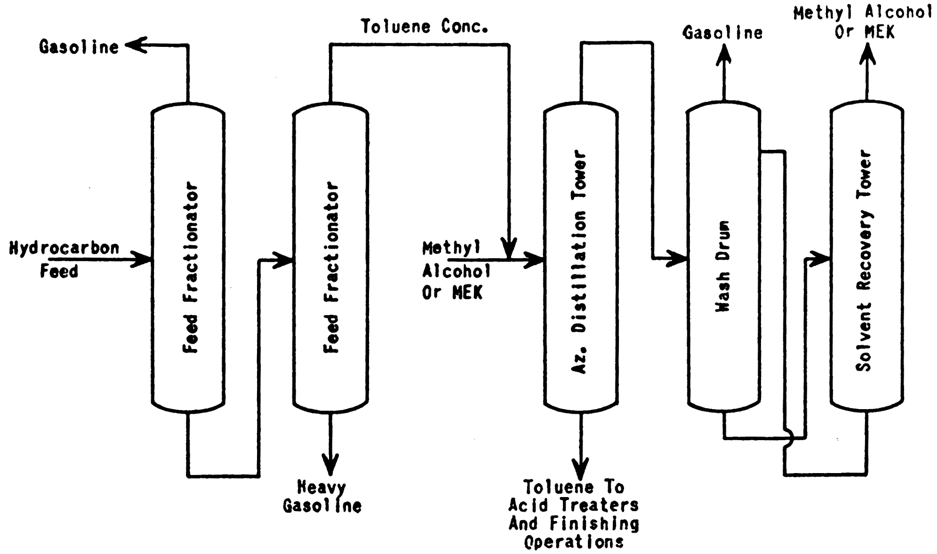

Figure 4. Azeotropic Separation of Toluene

stocks are expensive, as cyclohexane is a prime motor gasoline component having an unleaded blending Research octane number of 110, which is considerably in excess of the Research octane number of leaded premium grade motor fuels. Cyclohexane is in demand to replace benzene in the manufacture of nylon, which consumes about 12% of the benzene supply (*18*). Actually, benzene for nylon is hydrogenated to cyclohexane before oxidation to adipic acid. Therefore the cycle of dehydrogenation of cyclohexane to benzene and the subsequent hydrogenation of benzene back to cyclohexane is wasteful, because losses are suffered in both steps. The primary reason for this illogical cycle has been the existence of units for purification of benzene and the lack of proper facilities for the cyclohexane concentration.

In view of these considerations, a large amount of effort is reported in the scientific press on the development of a process to produce benzene from *n*-hexane by combined cyclization and dehydrogenation. *n*-Hexane has a low Research octane number of only 24.8 and can be separated in fair purities from virgin naphthas by simple distillation. Recently, an announcement was made of a process in the laboratory stage for aromatization of *n*-hexane (*16*). The process utilizes a chromia-alumina catalyst at 900° F., atmospheric pressure, and a liquid space velocity of about one volume of liquid per volume of catalyst per hour. The liquid product contains about 36% benzene with 64% of hexane plus olefin. The catalyst was shown to be regenerable with a mixture of air and nitrogen. The tests were made on a unit of the fixed-bed type, but it was indicated that the fluid technique probably could be used. If commercial application of this or similar processes can be achieved economically, it could be of immense help in relieving the benzene shortage.

In the field of aromatic separation, the trend of research is toward isolation of pure compounds for chemical purposes. Benzene, toluene, and some of the C_8 aromatics have been separated and used commercially. However, the physical properties of the C_9 and C_{10} aromatic hydrocarbons found in reformed stocks show that other aromatics could be separated from these mixtures by distillation, crystallization, or extraction processes. It is reasonably certain that if sufficient demand develops for the pure compounds, processes for their separation will become available. Present information indicates that perhaps methylethylbenzenes and trimethylbenzenes could be isolated in relatively high purity by distillation from aromatic stocks obtained by hydroforming, but no information is available as to their industrial uses. Similarly, durene (1,2,4,5-tetramethylbenzene) possibly could be isolated from its homologs by crystallization. Furthermore, large

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quantities of indan (2,3-dihydroindene), methylindan, isodurene, dimethylethylbenzene, and prehnitene are available in petroleum products, but no commercial separation of these materials has been disclosed.

The vast quantities of aromatics available or potentially available from petroleum provide a tremendous incentive to the petroleum technologists to develop new processes for the isolation of additional pure compounds, thereby extending the long list of materials available to the industry.

Acknowledgment

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Elastomers and Plastics

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The use of petroleum-derived chemical intermediates in the large scale manufacture of synthetic polymers began less than 25 years ago and within the last decade has developed into one of the principle outlets for petroleum chemicals. Ethylene, propylene, isobutylene, and butadiene are now used in large volumes for direct polymerization or as feed stocks for the synthesis of other polymerizable monomers such as vinyl chloride, styrene, acrylonitrile, and methyl methacrylate. Materials such as formaldehyde and acetic anhydride, produced in the oxidation of light hydrocarbons, are also employed in this field as well as a number of other intermediates such as glycerol, phthalic anhydride, cyclohexane, and ammonia that are now derived from petroleum. There is every indication that the present trends will continue, with further increasing outlets for petroleum products in polymerization processes. It is particularly significant that petroleum feed stocks are to be employed in increasing quantities in the production of large volume chemical intermediates such as acetylene and benzene that have been derived heretofore principally from other sources.

Paramount among the outlets for petroleum raw materials outside the field of fuels and lubricants are the elastomers and plastics. It is expected that synthetic rubber production in 1951 will exceed 800,000 long tons (1.8 billion pounds) while, during the same period, nearly two billion pounds of plastics also will be produced. It has been demonstrated to the American consumer that synthetic rubber is equal or superior to the natural product for many applications, and plastic products such as nylon fabrics, polyvinyl chloride upholstery, and polystyrene toys and gadgets are now considered a part of our way of life.

These sizable outlets for petroleum products are of relatively recent development. Only a decade ago synthetic rubber production was under 20,000,000 pounds per year. Twenty-five years ago synthetic rubber was virtually unknown in America, and total production of synthetic plastics, chiefly phenolics from coal tar, was only 12,000,000 pounds per year. Chemicals and chemical intermediates were produced from coal, minerals, and vegetable products, but the petroleum industry was devoting its interest almost exclusively to the production of fuels and lubricants.

The enormous increase in requirements for rubber and plastics has called for vast, new sources of organic raw materials, and an important part of it, particularly within the last 10 years, has been met by petroleum products. To the petroleum industry, accustomed to thinking in units of thousands of barrels per day, this is still a small volume outlet, accounting for less than 1% of the current production of petroleum products. Its

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importance cannot be appraised on the basis of the quantity of material involved, however, since it becomes of much greater significance when considered from the standpoint of the monetary value of the resulting products. Compared to most products of the petroleum industry, plastics and resins are high-priced materials which will allow relatively elaborate processing steps and large plant investments. Consequently, the petroleum companies, in searching for methods of expanding their activities with the supply of raw materials that will be available to them in years to come, have recognized the production of high polymers as a promising field of operation.

An over-all view of the reactions and processes that are involved in the use of petroleum raw materials in the various types of polymeric products presents a very complex picture. Some products require monomers such as mono- and diolefins that are recoverable by fairly straightforward processes from refinery operations. In other cases, these serve only as starting materials which must be converted by subsequent chemical reactions to a variety of more complex products. In this report an attempt is made to present the subject of elastomers and plastics from the view of the petroleum refiner who is interested principally in starting materials. Hence, the discussion is arranged according to the petroleum raw materials or petroleum processes from which the end products are produced, rather than according to the type of polymer involved as is usually done in reviews of elastomers and plastics.

Ethylene

The most versatile starting material presently derived from petroleum for the production of polymeric products is ethylene. This gaseous hydrocarbon is produced in large volumes in cracking processes and is recovered from refinery gases (*1*) for direct polymerization or for conversion to other polymerizable monomers. The production of ethylene for use in chemical processes has undergone a fourfold increase in the last 10 years; in 1950, production for this purpose was almost 1.5 billion pounds (*2*).

Figure 1 illustrates some of the commercial processes by which ethylene is converted to polymeric products.

Polyethylene. The most straightforward process for the production of polymers from ethylene is that of the direct polymerization of the olefin. The polymerization process usually requires pressures and temperatures of 15,000 to 30,000 pounds per square inch and 200° to 300° C., and may be effected in either gas or liquid phase reactions (*9*). The polymer of molecular weight above 20,000 is the white, translucent plastic, polyethylene, widely used in electrical insulation, packaging material for foods, cosmetics and pharmaceuticals, liners for paper bags, etc. Articles molded from polyethylene are semirigid or rigid, depending on their thickness, but in thin films the material has excellent flexibility, even at relatively low temperatures.

Pilot plant production of polyethylene was started in England in 1939, but it was not until 1942 that commercial production began in the United States. Production has been climbing steadily since that time. In 1950 it was estimated at 50,000,000 to 60,000,000 pounds, less than 4% of the commercial production of ethylene. Increased facilities are becoming available for processing polyethylene and new uses continue to be developed with additional expansion in production presently under way.

Vinyl Chloride. A second process by which petroleum-derived ethylene may be employed in the production of polymeric products is by conversion to vinyl chloride and subsequent polymerization or copolymerization with other vinyl monomers. The process involves the reaction of ethylene with chlorine followed by catalytic dehydrochlorination of ethylene dichloride.

$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2ClCH_2Cl \longrightarrow CH_2{=}CHCl + HCl$$

A competing process produces vinyl chloride from acetylene, which also can be derived from petroleum feed stocks but is usually made from calcium carbide. It has been estimated (*17*) that 45% of current production of vinyl chloride is from ethylene, the remainder from acetylene.

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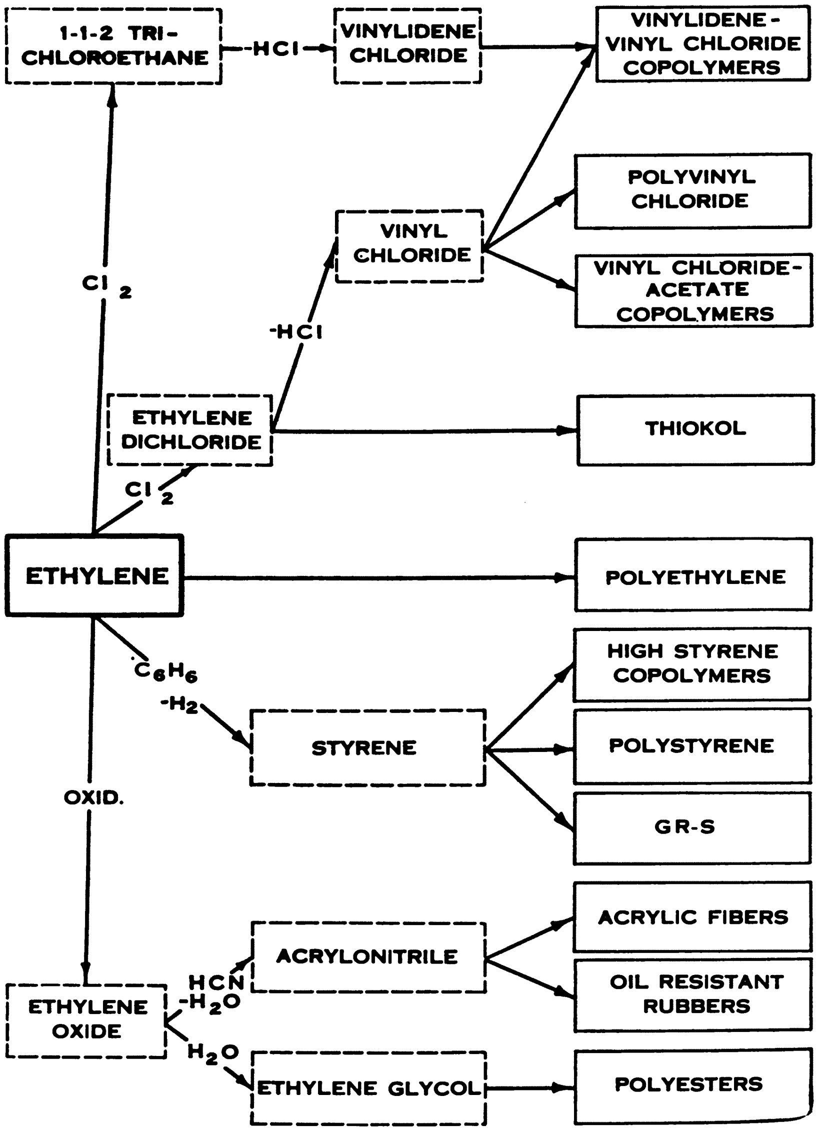

Figure 1. Polymers Derived from Ethylene

Vinyl chloride normally is a gaseous compound boiling at −14° C. Its principal use is for polymerization to vinyl resins. Polyvinyl chloride is a hard, brittle, nonflammable, thermoplastic resin; however, it is usually employed in highly plasticized formulations (frequently 50 parts or more plasticizer per 100 parts resin) in the form of flexible sheeting, film, and tubing. A number of leading concerns are engaged in the manufacture of plasticized polyvinyl chloride, and it is now widely used in applications such as furniture coverings, curtains, luggage, rainwear, wire covering, and gaskets.

In addition to the polymer, copolymers of vinyl chloride with other vinyl monomers are important commercial plastics. Copolymers with vinyl acetate, which is produced from acetylene and acetic acid, are widely used in sheeting, surface coating, and filaments, being less brittle and more readily soluble in organic solvents than is pure polyvinyl chloride. Copolymers with acrylonitrile are also of importance for the production of yarns and filaments, as discussed later. Still another type of copolymer is that of vinyl chloride with vinylidene chloride to give a well-known commercial product, saran, used in filaments and for the manufacture of pipes and tubing and linings for tanks, autoclaves, and other processing equipment. Vinylidene chloride, $CH_2{=}CCl_2$, is closely related to vinyl chloride and is produced from ethylene by an analogous process in which 1,1,2-trichloroethane is dehydrochlorinated to produce the monomer.

Large scale production of Vinylite resins, vinyl chloride–acetate copolymers, was started in 1933, at which time the material was marketed as molding compounds for the fabrication of phonograph records, dentures, rigid panels, and novelties (*21*). Several years elapsed before the introduction of highly plasticized polyvinyl chloride sheeting and the resultant widening market.

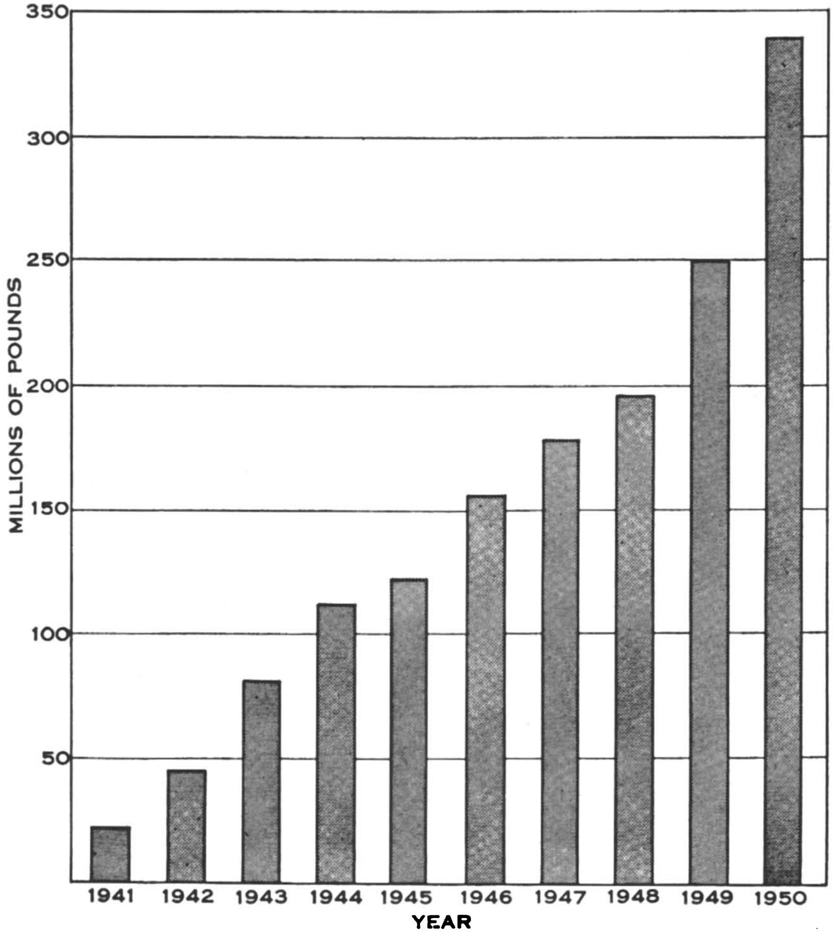

Figure 2. Production of Vinyl Resins

Production of all types of vinyl resins, exclusive of plasticizers and fillers, during 1941 to 1950 are presented in Figure 2. These totals are for production of all polymers customarily classified as vinyl resins, including polyvinyl chloride, copolymers of vinyl chloride with vinyl acetate or vinylidene chloride, or modified polymers derived from them. However, the principal monomeric raw material for this field of resins is vinyl chloride.

The spectacular increase in production of the vinyl resins can be attributed prin-

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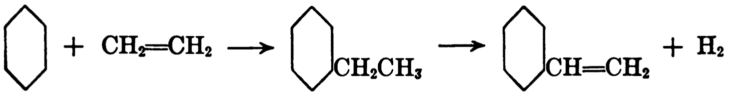
cipally to the development of new applications for these materials, and with additional new developments now under way, there is every prospect that the market for these products will continue to expand. The application of rubberlike coatings by the use of vinyl organosol or plastisol dispersions (*33*) and the use of new embossing and printing techniques to obtain novel surface effects in drapery and upholstery materials are examples of such developments.

Styrene. Still another process in which petroleum-derived ethylene serves as a raw material in the production of synthetic polymers is the reaction of ethylene with benzene to produce ethylbenzene, followed by dehydrogenation to styrene.

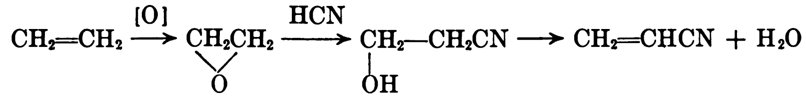


The first successful large scale production of polystyrene in the United States was started in 1937 with the introduction of Styron by the Dow Chemical Co. By 1942 production of the polymer had risen to 7,000,000 pounds per year, which sold in that year at an average wholesale price of 38 cents per pound. The rubber program of World War II led to the expansion of facilities for production of styrene for use as a comonomer with butadiene for GR-S synthetic rubber, and wartime capacity was 383,000,000 pounds per year in six plants operated by four different chemical concerns (*11*). As a result of the economical operation attendant with such large scale production, the price of polystyrene dropped to 25 cents per pound in the postwar period, thereby making it the lowest in price of the major synthetic thermoplastic molding resins. The decreasing styrene requirements for the government synthetic rubber program was offset by a steadily increasing demand for polystyrene, and styrene production was maintained at a high level throughout the postwar period and has increased sharply within the last year. Figure 3 shows styrene production for GR-S and other uses since 1941. In late 1950 production was at a rate of nearly 600,000,000 pounds per year, equivalent to 156,000,000 pounds per year of ethylene (11% of 1950 production).

Polystyrene is a thermoplastic resin sold under various trade names principally for use in injection molding of rigid articels such as toys, wall tile, and electrical insulation. It is available in transparent or colored grades and is usually molded without plasticizer or fillers. It has excellent electrical and water-resistant properties; however, it is chiefly because of the attractive appearance of molded articles, its low price, availability, and its adaptability to injection molding processes that the spectacular increase in the use of polystyrene can be attributed. The trend toward injection molding, and particularly the increase in size and capacity of injection molding presses, has resulted in large volume requirements for thermoplastic molding resins, and polystyrene has been the preferred material in this field.

GR-S employs styrene as the minor ingredient with butadiene, and it will be discussed under the heading of the latter compound. Copolymers in which styrene is the major component—i.e., about 70 to 85 parts of styrene with 30 to 15 parts of butadiene—are also produced (*23*), and they have found markets both as a solid in applications such as shoe soling and floor covering and in latex form as an emulsion paint for inside use. Latex paints (*19*) of this type have been introduced to the consumer market only within the last few years, but they are receiving widespread acceptance as a result of their excellent film properties, good covering power, and ease of application.

Acrylonitrile. Another monomeric raw material that is produced from ethylene is acrylonitrile. The present commercial process involves the oxidation of ethylene to ethylene oxide which reacts with hydrogen cyanide and dehydrates to acrylonitrile.



$$CH_2{=}CH_2 \xrightarrow{[O]} \underset{\diagdown O \diagup}{CH_2CH_2} \xrightarrow{HCN} \underset{\overset{|}{OH}}{CH_2{-}CH_2CN} \longrightarrow CH_2{=}CHCN + H_2O$$

The commercial production of acrylonitrile was initiated in 1939 by American

Cyanamid Co. at Walters, N. J., in a plant that now has a capacity of 28,000,000 pounds per year (*10*). The principal interest in the monomer at that time was for emulsion copolymerization with butadiene to produce oil-resistant synthetic rubbers such as Buna N, Hycar OR, Perbunan, and Chemigum. Manufacture of this type of copolymer started when the monomers became available, and output rose steadily during the war years to a peak of 37,000,000 pounds in 1944. Production dropped to approximately one half that figure after the war, but currently has risen again to about the former maximum level.

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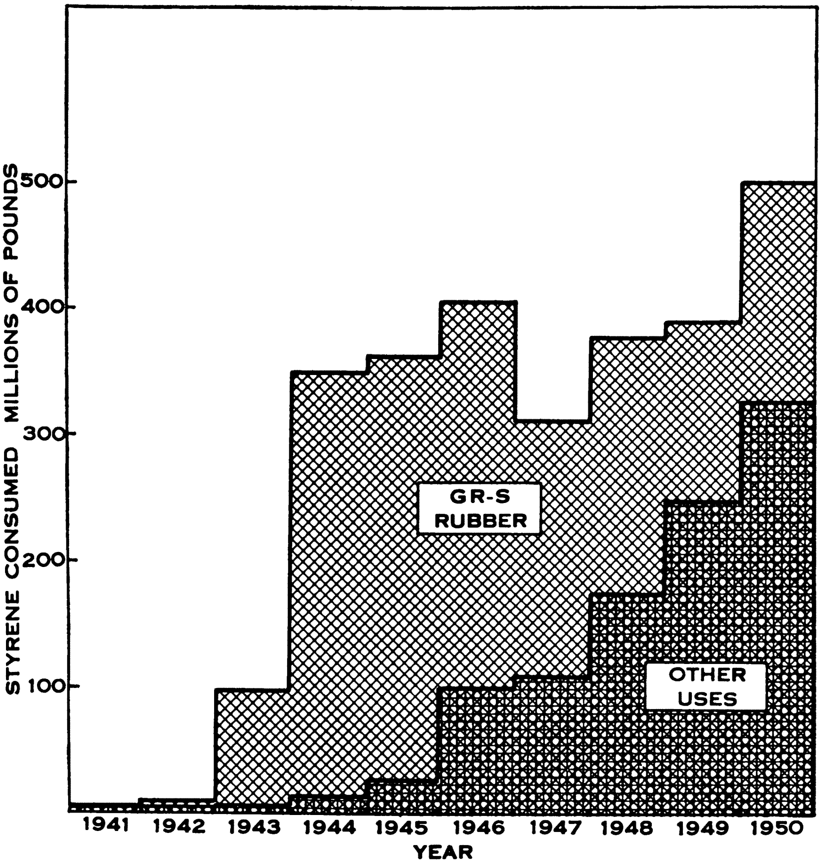


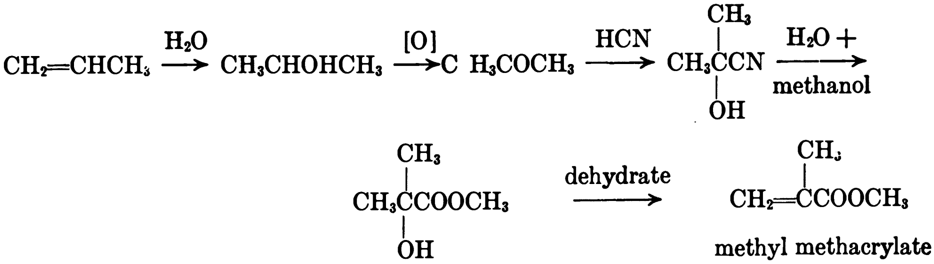
Figure 3. Consumption of Styrene

The interest in acrylonitrile for synthetic rubber has been overshadowed in recent years, however, by the development of new synthetic fibers. Examples of such products are Vinyon N (*5*, *14*), a copolymer of vinyl chloride and acrylonitrile produced by the Carbide and Carbon Chemicals Corp., and Orlon, a polyacrylonitrile fiber, output of which was recently begun (*15*) by Du Pont. The potential market for acrylonitrile in such products is expected to be a large one, and annual production of 100,000,000 pounds within 10 years with an ultimate market that may be as high as 300,000,000 pounds per year has been predicted (*10*). New plants are under construction for producing the monomer, and synthesis by the direct addition of hydrogen cyanide to acetylene will be employed in addition to the aforementioned process utilizing ethylene oxide. Of greater interest, however, is the report that acetylene for these plants is to be produced from light petroleum hydrocarbons, rather than from the conventional calcium carbide process.

Propylene

This second member of the olefin family is likewise the starting material for a versatile group of chemicals and was produced to the extent of 880,000,000 pounds for that purpose in 1950 (*2*). No commercial process has been disclosed for the direct polymerization of propylene to a high polymer; however, it plays an important role in the high polymer industry as a starting material for the production of other polymerizable derivatives.

Methyl Methacrylate. The principal chemical use for propylene is hydration to isopropyl alcohol. This in turn can be oxidized to acetone and thence by a series of reactions, requiring hydrogen cyanide and methanol which are likewise derivable from petroleum, converted to methyl methacrylate as outlined below.



$$CH_2{=}CHCH_3 \xrightarrow{H_2O} CH_3CHOHCH_3 \xrightarrow{[O]} C\,H_3COCH_3 \xrightarrow{HCN} CH_3\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}CN \xrightarrow[\text{methanol}]{H_2O\,+}$$

$$CH_3\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}COOCH_3 \xrightarrow{\text{dehydrate}} CH_2{=}\overset{\displaystyle CH_3}{C}COOCH_3$$

methyl methacrylate

Methyl methacrylate is only one of a family of monomers, including the various esters of acrylic, methacrylic, and ethacrylic acids, which are polymerized to produce the thermoplastic resins known as the acrylates. A wide variety of reactions and starting materials may be utilized for their production; however, the principal commercial product is polymethyl methacrylate, sold by Du Pont and Rohm & Haas under the trade names of Lucite and Plexiglas, respectively. These materials were introduced to the United States market in 1936 (*44*) and have received widespread acceptance due principally to their outstanding optical properties. Production in 1949 was reported as about 22,000,000 to 25,000,000 pounds and peak wartime capacity was above 30,000,000 pounds. While this can account for only about 2% of the current production of propylene for chemical purposes, the acrylate resins are of considerable commercial importance as they are sold at a relatively high price and are the only materials available that will meet the requirements for certain military and civilian products.

Glycerol. Another synthetic product that is derived from propylene for the production of resins is glycerol. Synthetic production of this material, which started in 1948 at the Houston, Tex., plant of Shell Development Co., culminated a long research program by E. C. Williams and coworkers (*45*) in which the process was developed through a complex series of reactions starting with the chlorination of propylene (*7*). The Houston plant has a reported capacity of 36,000,000 pounds per year, which is equivalent to 20% of the prewar production of glycerol (*8*).

The largest single outlet for glycerol is in the production of polyester or alkyd resins, in which it is esterified with polycarboxylic acids to give materials of drying or thermosetting properties. Numerous types of polyester resins are produced; glycols, glycerol, or pentaerythritol may be used as the polyhydroxy compound to be esterified with maleic or phthalic anhydrides or various polycarboxylic acids. Furthermore, the resins may be modified by various proportions of drying or nondrying fatty or rosin acids (*40*) or by the addition of a copolymerizable vinyl monomer such as styrene. Hence, not only glycerol but other petroleum-derived materials—i.e., phthalic anhydride, which is to be discussed in a later section, and ethylene glycol—are employed in the manufacture of the alkyds.

The bulk of polyester production in the United States has gone to the synthetic coatings field in the manufacture of glyptal resin coatings and varnishes, with production between 200,000,000 and 300,000,000 pounds in the postwar years. A recent development has been the use of polyester-styrene copolymers reinforced by Fiberglas for the manufacture of items such as low-pressure molded boats, corrugated structural sheet, and plastic pipe. The 1947 requirements for glycerol in the production of polyester resins and

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the related ester gums were estimated at 40,000,000 pounds, and while a relatively small share of glycerol production is presently derived via the synthetic route from propylene, the process provides an almost unlimited potential source and an effective price stabilizer for glycerol should it be required for future increase in production of polyester resins.

Isobutylene

Isobutylene, like the other olefins already discussed, is a by-product of petroleum cracking and could be produced by the petroleum industry in large amounts by dehydrogenation of the corresponding paraffin. Since 1944 the principal outlet for isobutylene, excluding use in the manufacture of fuels, has been for direct polymerization to polyisobutylene and Butyl rubber (GR-I).

The Butyl rubber process has been aptly described as a "unique American development" (*29*) resulting from a research program of the Standard Oil Co. of New Jersey. Construction of the first plant was initiated as a private venture in Baton Rouge, La., in 1941. Early in 1942 the plant was taken over by the Rubber Reserve Co. and was enlarged to a rated capacity of 38,000 long tons per year. A second Butyl plant was also constructed at Baytown, Tex., with a design capacity of 30,000 tons. Production rose rapidly during the war to 73,000 long tons in 1946 and has remained above 50,000 tons every year since that time.

Butyl rubber is produced by a process in which isobutylene is copolymerized with a small amount of isoprene using aluminum chloride catalyst at temperatures around −150° F. (*20*). The isoprene is used to provide some unsaturation, yielding a product that can be vulcanized (*43*). Vulcanized Butyl rubber is characterized by high tensile strength and excellent flex resistance; furthermore, as a result of its low residual unsaturation (only 1 to 2% of that of natural rubber) it has outstanding resistance to oxidative aging and low air permeability. These properties combine to make it an ideal material for automobile inner tubes (*3*), and Butyl rubber has continued to be preferred over natural rubber for this application, even when the latter has been available in adequate supply.

High polymers of isobutylene prepared in the absence of a diolefin are also produced commercially and are available in various molecular weight ranges under the name Vistanex (*42*). These materials are not vulcanizable by ordinary means as they are substantially free of residual olefinic unsaturation, and they have been used principally for compounding with other polymers or for special applications such as gaskets, tank liners, or calking compounds.

Butadiene

1,3-Butadiene has been known by chemists since 1773, and many of the early attempts to develop synthetic rubber centered around the preparation and polymerization of butadiene and its homologs. During the 20-year period preceding World War II, synthetic rubber processes were studied vigorously in both Germany and Russia, and products based on the polymerization of butadiene were developed in both countries. United States production of butadiene polymers cannot be attributed entirely to the war emergency, however, since commercial production of butadiene in this country began in 1938 and reached nearly 6,000,000 pounds in 1941, prior to the start of the government program. Production during this period was principally in oil-resistant butadiene-acrylonitrile copolymers as already discussed.

At the initiation of the government program in 1941, the product that was chosen for the general purpose synthetic rubber was a copolymer of butadiene and styrene, usually referred to as GR-S. It was prepared in an emulsion process from the following recipe (*22*):

	Parts
1,3-Butadiene	75
Styrene	25
Water	180
Potassium persulfate	0.3
Dodecyl mercaptan	0.5
Soap flakes	5.0

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The polymerization reaction was conducted in a stirred autoclave at 122° F., requiring about 12 hours for reaction to 78% conversion.

The selection of the above "mutual" recipe for the production of the general purpose rubber proved to be a fortunate choice, providing a dependable polymerization process and a product that has been the "workhorse" of the synthetic rubber industry. Considerable improvement has been made since 1946, however, with the development of the "cold rubber" process (*39*, *41*) in which more active polymerization recipes are employed at near freezing or lower temperatures. Polymer from this process, in combination with improved types of high abrasion furnace blacks (*36*), has resulted in the development of tire treads showing substantially longer wear than natural rubber. Consequently, synthetic rubber production has been gradually converted to the cold rubber process. As a result of the present national rearmament program, the production of GR-S–type rubber is being expanded rapidly to a rate of 760,000 long tons per year (*27*) of which over 40% will be cold rubber.

A question that frequently arises is: Why not make synthetic rubber from pure butadiene, omitting the styrene? Until recently, it was generally agreed that polybutadiene is unsatisfactory as a general purpose elastomer, processing with difficulty and having inferior stress-strain properties. However, recent work by Phillips Petroleum Co. in cooperation with the Office of Rubber Reserve has resulted in the development of a successful polybutadiene rubber process (*13*). By modifying to a lower Mooney viscosity and using the new high abrasion furnace black by the "black masterbatch" technique—i.e., mixing the black with the rubber in latex form—the difficulties of producing polybutadiene rubber have been largely overcome and very satisfactory tread stock polymers have been prepared.

The production of GR-S in the government rubber program involved the operation of fifteen polymerization plants having a total rated capacity of 705,000 long tons of rubber per year. In 1945 production reached 717,693 long tons (*37*), requiring approximately 513,000 long tons (1.15 billion pounds) of butadiene. The development of production for this vast quantity of butadiene in the short time available has been recognized as one of the major accomplishments of the war effort, requiring the construction and operation of 16 butadiene plants. Three of these plants produced butadiene from alcohol and the remaining 13, which are listed in Table I, employed petroleum feed stock.

Table I. Petroleum Butadiene Plants during World War II

Plant Location	Operator	Charge Stock	Rated Capacity, Short Tons/Year
Lake Charles, La.[a]	Cities Service Refining Co.	Butylene	55,000
Baytown, Tex.[a]	Humble Oil & Refining Co.	Butylene	40,000
Port Neches, Tex.[a]	Neches Butane Products Co.	Butylene	100,000
Borger, Tex.[a]	Phillips Petroleum Co.	Butane	56,200
Torrance, Calif.	Shell Union Oil Co.	Butylene	25,000
Los Angeles, Calif.	Southern California Gas Co.	Naphtha	30,000
Houston, Tex.	Sinclair Rubber Co.	Butylene	50,000
Baton Rouge, La.	Standard Oil Co. of N. J.	Butylene	15,000
	Standard Oil Co. of N. J.	Naphtha	10,000
Toledo, Ohio	Sun Oil Co.	Butane	15,000
Ingleside, Tex.	Humble Oil & Refining Co.	Naphtha	12,500
El Dorado, Ark.	Lion Oil Co.	Naphtha	3,500
Corpus Christi, Tex.	Taylor Refining Co.	Naphtha	2,600
El Segundo, Calif.	Standard Oil Co. of Calif.	Butane	18,000

[a] Continued production throughout postwar period.

In the postwar period, production was ultimately discontinued in all but four of these plants, but with the present increased requirements for synthetic rubber four of the closed plants have been reopened.

Petroleum butadiene is produced: (*a*) by the dehydrogenation of straight-chain butenes, (*b*) by the two-step dehydrogenation of normal butane, or (*c*) by cracking heavy petroleum stocks. The extent to which the various types of feed stock were used is illustrated in Table I. One of the principal difficulties has been that of separating the

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mixtures of butane, butenes, and butadiene obtained from the dehydrogenation processes and of recovering the latter in the high state of purity required. Among the processes used to effect that separation is the furfural extractive distillation process, which was developed by Phillips Petroleum Co. and has been employed in the butadiene plants at Borger, Houston, and Port Neches, Tex. These large plants have been among the lowest cost producers of butadiene.

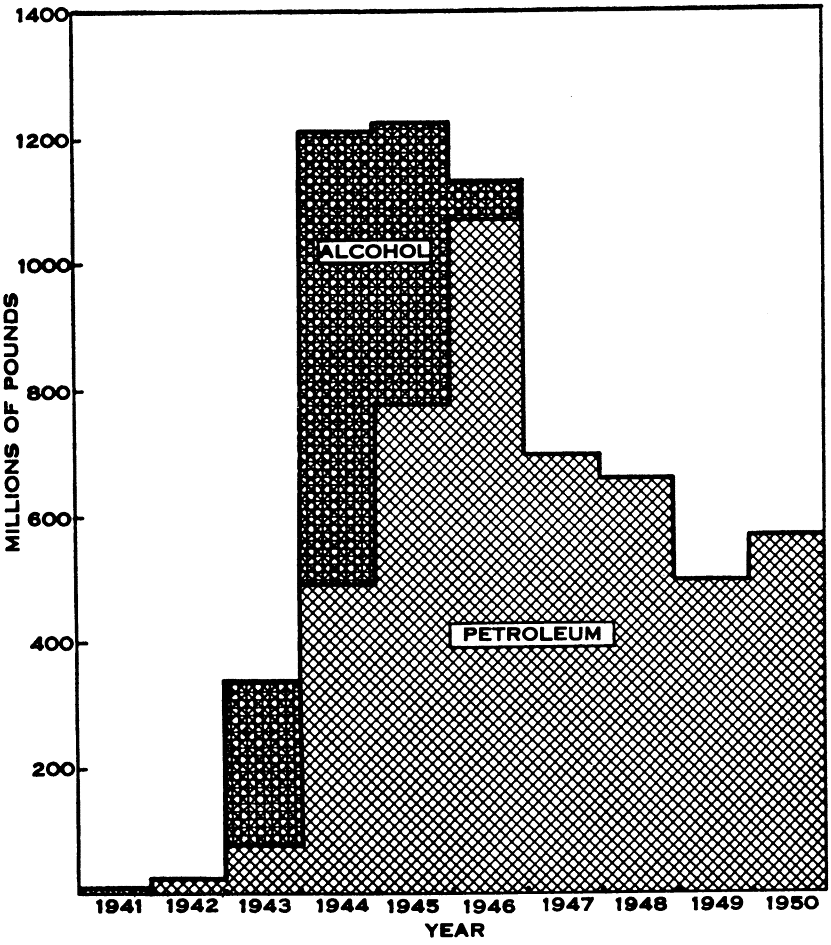

Figure 4. Butadiene Production

An alternate route for the production of butadiene involves the use of ethyl alcohol as the starting material. This process was also utilized for the production of butadiene in the early years of the program and was, in fact, the principal source of butadiene during 1943 and 1944 while the petroleum plants were coming on-stream, as illustrated in Figure 4. Owing to the high cost of butadiene from alcohol, production was discontinued in late 1945, but a part of the alcohol-butadiene capacity has been reactivated recently as a temporary expedient. Experience has indicated that butadiene produced from alcohol cannot compete economically with that produced from petroleum feed stocks. During the postwar period butylenes used as a starting material in a number of plants were diverted to other uses, but the two-step dehydrogenation of normal butane produces butadiene in good yield from a starting material that can be made available in large quantities by the petroleum industry.

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Oxygenated Derivatives of Petroleum

Numerous oxygen-containing chemicals are produced in commercial quantities from petroleum feed stocks, and a number of these materials find their principal market in the production of resins and plastics. An outstanding example is the chemcel plant of Celanese Corp. of America at Bishop, Tex., where a variety of basic chemicals, including formaldehyde, acetaldehyde, glacial acetic acid, methanol, and higher alcohols (*6*) are produced by the oxidation of propane and butanes. The utilization of these products is closely integrated (*28*) with this company's operations in plastics and textiles. In addition to this one, there are a number of other plants in operation in which petroleum feed stocks are converted by oxidation or hydration to oxygenated chemicals which are utilized in the plastics industry.

Formaldehyde. The two commercial processes for the production of formaldehyde are the oxidation of light hydrocarbons and the oxidation of methanol, which in turn may be derived from natural gas. The current production rate of formaldehyde is approximately 200,000,000 pounds per year (water-free basis), of which 80% is used in the plastics industry (*12*).

The process for condensing phenol with formaldehyde to produce phenolic resins was developed by Leo H. Baekeland prior to 1910, making it the first of the commercial synthetic plastics. Hence, Bakelite was known for many years prior to the introduction of the more recent types of polymers; nevertheless, the phenolic resins remain today among the principal plastics for molding processes and are produced in large volumes for use as adhesives and coatings. Various higher molecular weight aldehydes may be used in the process, but formaldehyde remains the principal one for the production of commercial resins.

In the early 1930's, a second type of resin prepared from formaldehyde was introduced to the market—namely, urea-formaldehyde resins. A few years later, melamine-formaldehyde resins also appeared. The same basic process is employed in polymerization of all these resins; it consists of the catalyzed reaction of formaldehyde with the second ingredient—phenol, urea, or melamine—to evolve water and produce three-dimensional, cross-linked thermosetting polymers.

These three resins constitute a large share of the entire production of molding plastics, and together they account for nearly all compression moldings being produced. These include large molded items such as radio and television cabinets, cases for clocks, adding machines or scales, plastic dishes, electrical insulators, and a multitude of others. Combined production of these three plastics in 1950 was 550,000,000 pounds (*31*).

Despite the fact that formaldehyde is the minor ingredient in the production of these resins and that only part of the formaldehyde is presently derived from petroleum sources, the production of formaldehyde from petroleum feed stocks is already an industrial process of considerable volume and one that promises to be of increasing future interest to the petroleum industry.

Acetic Anhydride. Other products recovered from the oxidation of light hydrocarbons (*6*) are acetic acid and acetic anhydride as well as acetaldehyde, acetone, and isopropyl alcohol, all of which may be converted to acetic acid or the anhydride. The direct oxidation process supplements the production of acetic anhydride from acetone derived from propylene, which has been the principal commercial source of the anhydride. The increasing production of cellulose acetate within recent years has been attributed to the low cost of acetic anhydride from the latter process (*44*).

The manufacture of cellulose acetate involves the acetylation of cellulose from cotton linters or wood pulp by acetic anhydride and acetic acid. Production started about 30 years ago, and early products that were developed include safety photographic films, airplane dopes, and "acetate" fabrics. It is now also produced in the form of sheeting, rods, and tubes and is widely used as a molding compound.

Other Petroleum Derivatives

In addition to the large volume intermediates already mentioned, there are numerous other miscellaneous petroleum-derived chemicals that are employed in the production of

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polymers. In the manufacture of nylon, for example, petroleum cyclohexane and ammonia are used as well as "coal, air, and water" as starting materials. Polytetrafluoroethylene (Teflon) (*35*), the chemically inert and heat-resistant polymer introduced by Du Pont in 1946, is made by the polymerization of tetrafluoroethylene which can be prepared in a process starting with chloroform. A closely related polymer is Kel-F (*30*), a polymer of trifluorochloroethylene.

An aromatic compound which is employed along with glycerol in the production of alkyd resins is phthalic anhydride. The conventional process for the manufacture of this chemical has been from the catalytic oxidation of coal tar naphthalene, and annual production of the anhydride in recent years has been around 150,000,000 pounds. In 1946 production was started (*4*) in a plant of the Oronite Chemical Co. at Richmond, Calif., to produce phthalic anhydride by the oxidation of *o*-xylene produced in a hydroformer unit of the adjacent Standard Oil Co. of California refinery. The Oronite plant was reported to have a design capacity of 7,000,000 to 8,000,000 pounds per year of 99.7% pure phthalic anhydride.

p-Xylene is also employed for oxidation in the presence of methanol to give dimethyl terephthalate which reacts with ethylene glycol to form a linear polyester resin, variously known as Fiber V (*18*), Dacron, and Terylene (*25*). It is to be produced by Du Pont in a new plant at Kingston, N. C., which has an estimated capacity of 10,000,000 pounds per year.

Various organic dihalides are employed in a reaction with sodium polysulfide to produce organic polysulfides (Thiokols). Ethylene dichloride, from the direct chlorination of ethylene, dichloroethyl formal, and β,β'-dichlorodiethyl ether are the principal dihalides that have been employed in the process (*44*). These elastomeric polymers have been commercially available for a number of years, and many applications have been developed for them. They have excellent oil resistance and one of their principal uses has been in hose and tank linings in which that property is required.

The coumarone-indene resins have been important commercial polymers produced in the sulfuric acid-catalyzed polymerization of mixed concentrates of these two compounds from coal tar naphthas. These and other unsaturated cyclics are also produced in the pyrolysis of petroleum oils for the production of manufactured gas, and the use of such petroleum-derived unsaturates is becoming of increasing significance in the production of this type of resin.

Future Prospects

There is every indication that the next several years will witness a continued rapid increase in the use of petroleum raw materials in the production of elastomers and plastics, and that the petroleum companies will become increasingly active, not only in providing the starting materials, but also in operating the chemical processes of converting them to the required monomers and polymers. The current increase in production of thermoplastic resins such as polystyrene, polyvinyl chloride, polyethylene, and acrylonitrile polymers is based on the development of widespread new applications at the consumer level, and the outlet for plastic materials in many of these uses is presently limited by the capacity to produce and process the resins rather than by consumer demand.

Of equal importance is the fact that synthetic rubber has been improved to such an extent that it is more than capable of meeting the competition of the natural product, and there is no longer any doubt that "synthetic rubber is here to stay." New types of synthetic rubber now in the development stage are expected to enhance the competitive position of synthetic rubber still further.

In addition to the established large volume products already mentioned, other plastic materials are known to be under study or have been introduced so recently that their markets have not been fully developed. It seems certain that products such as polyethylene terephthalate and polyacrylonitrile fibers will attain large volume production. A new type of resin that has appeared very recently is Shell Chemical Co.'s Epon series (*32*), a group of polymers of various molecular weight ranges which are produced from phenol, acetone, and epichlorohydrin.

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Another group of potentially large volume plastics that is under development are the polysulfone resins, made by the copolymerization of olefins such as 1-butene with sulfur dioxide (*24*). Both these feed stocks could be derived in abundant quantities and at relatively low costs from petroleum sources. The polysulfone resins are moldable thermoplastic polymers having physical properties that vary widely depending on the olefin from which they are prepared. They are considered to have excellent prospects for development to a large volume, low cost commercial plastic and may permit the entrance of plastic products into other fields in which they are now limited by the high cost and inadequate supply of present thermoplastic materials.

No doubt the most significant trend from the standpoint of future outlets for petroleum is that of the production from petroleum feed stocks of chemical intermediates such as acetylene, benzene, urea, and formaldehyde that have been produced heretofore from other sources. Acetylene is a starting material for the commercial production of chloroprene, vinyl chloride, vinyl acetate, acetic anhydride, and acrylonitrile, but it has been mentioned only briefly in this report since it is produced principally from calcium carbide. Several processes are known, however, for the production of acetylene from light petroleum hydrocarbons. Among these are the Schoch (*38*) process, in which natural gas or other light hydrocarbons are converted to acetylene by the silent electric discharge, and the Wulff process in which light hydrocarbons are cracked thermally in a regenerative furnace. A modification of the latter type process was being studied at the semiworks level by Tennessee Eastman Corp. prior to 1942 (*26*).

In view of the many studies that have been made to develop practical methods of producing acetylene from natural gas hydrocarbons, it is significant that several concerns are reported (*17*) to have plans actively under way or under study for initiating the large scale commercial production of acetylene from petroleum feed stocks, some of which is to be used directly for the production of acrylonitrile.

Another significant trend is the current program to increase the production of benzene from petroleum (*16*). Increasing requirements for the production of styrene, phenol, and other intermediates have made it essential that new sources be found to supplement current supplies of this aromatic hydrocarbon, and the only apparent source is from petroleum processes. To meet current needs of the military and civilian program the United States Petroleum Administration for Defense has been asked to increase petroleum benzene from the current rate of 12,000,000 gallons to 100,000,000 gallons per year (*34*). Present production from petroleum is small in comparison with that from other sources, but these proposed expansions may add materially to the output of petroleum-derived intermediates that will ultimately go to the manufacture of plastics and synthetic rubber.

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Synthetic Detergents from Petroleum

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The development over the past quarter century of both oil- and water-soluble detergent products derived from petroleum is reviewed. Beginning with the by-product mahogany soaps from specialty oil refining, the industry's progress is traced to the tailor-made synthetics of today. Methods of preparation of typical anionic, cationic, and nonionic detergents are described with particular emphasis on the alkyl aryl sulfonates. Product evaluation techniques illustrating the advantages for petroleum synthetics are discussed and a picture of many and varied uses for synthetic detergents is presented.

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A typical picture of the display of household cleaners that might be taken today in any supermarket or grocery would show that more than half of the packaged cleaners offered for sale are synthetic detergents. The majority of these contain materials that originated in petroleum. If a similar picture were available for 1932, the year that synthetic detergents began to appear in volume in the United States, it would not reveal a single recognized brand product containing synthetic detergents.

The story of this metamorphosis in consumer preference in cleaning materials is the history of synthetic detergent chemistry, which is typified by the development of these materials from petroleum.

The incentive to develop a synthetic detergent was a strong one. Although ordinary fatty acid soap has long been, and still is, recognized as a remarkable cleaning agent when used under ideal conditions, its practical use limitations have long been recognized by the consumer.

For instance, fatty acid soap is precipitated by the calcium and magnesium in hard water. If glasses or clothes are washed in such water even with normal rinsing, some of the insoluble soap formed usually remains on the glass or textile surfaces as a cloudy gray film. Synthetic detergents have been developed that are completely soluble not only in hard water but in sea water as well, and it is possible to carry out washing operations with these detergents without leaving a residual precipitate on the washed surface.

Fatty acid soaps are invariably alkaline, having a pH of 9 or higher in dilute solutions. This alkalinity is particularly undesirable in the washing of fine silks and woolens, where it can accentuate fabric shrinkage or color fading. Synthetic detergents have been developed that are neutral and have no more effect than plain water on fine fabrics.

At pH values below 6, fatty acid soaps are completely hydrolyzed to insoluble fatty acids which have no detergent action. But some cleaning operations, specifically in the dairy industry, are best carried out with acid baths. Synthetic detergents have been developed which are stable under these conditions (*22*).

In the synthesis of chemical compounds designed to overcome the disadvantages of soap, but maintaining all of soap's good qualities, one of the biggest problems has been the development of reliable laboratory evaluation methods for measuring detergency and lathering. These laboratory methods lean more to the practical than to the scientific side of the problem.

In measuring the detergency of a material with respect to textiles, a typical laboratory evaluation method includes: soiling a standardized textile swatch with a soil comprising fatty and mineral oils and carbon black; agitating this swatch in the detergent solution under test in a miniature washing machine called a launderometer; then measuring by means of light reflectance the amount of carbon black removed during the operation (*10*, *11*, *14*). A typical detergency pattern can then be obtained by plotting the per cent of detergency against the detergent concentration and comparing the slope of the curve with that of a detergent of proved performance such as tallow soap (Figure 1).

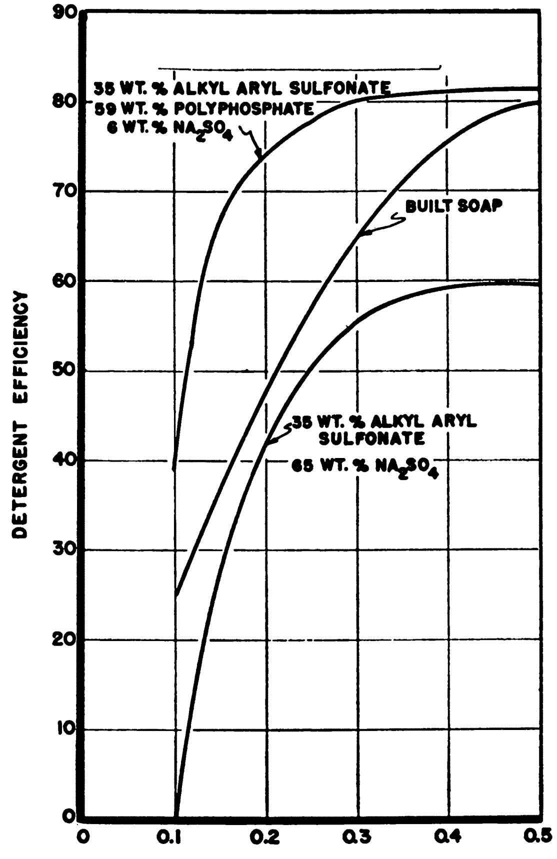


Figure 1. Colton Detergency

For measuring lather and lather stability, a simple means for recording the foam height resulting from agitation of the detergent solution under controlled conditions—shaking in a graduated cylinder or dropping through a standardized column—has been used (*2*, *20*). More faith, however, is put in practical tests, such as one in which dishes are soiled with a mixture of egg and bacon grease and then washed in a given volume of detergent solution. The number of dishes that can be washed before all the lather disappears from the dishpan is a measure of lather stability.

To the skilled physical chemist these evaluation procedures may appear crude, but a rather good correlation has been obtained between laboratory evaluations and performance as measured by the consumer under use conditions. No serious marketer of detergents, however, offers new products for sale until he has first laboratory tested them and then obtained favorable consumer reaction in a blind market survey. In this the test material and a product of known value are compared by a cross section of the consumer public.

This expensive and rather cumbersome method of proving the value of cleaning compounds has probably retarded the progress of synthetic detergents more than any other single factor, including the quality of the products offered and the desire of the public to accept them.

As far back as 1932, the general structure of a good detergent was recognized and the intervening years have served primarily to contribute to the quality improvement of basic materials. Color, odor, wetting, and washing efficiency have been continually bettered but the theoretical concepts of a good detergent have not changed.

The most effective detergents are characterized by a molecular structure which is bifunctional—one portion consisting of a hydrophobic hydrocarbon radical and the other portion consisting of either an inorganic ionizable group or a polar group which is hydrophylic (*23*). Such chemical structures, illustrated in the formulas of Table I, are common with the broader class of products termed surface-active agents; for, by virtue of their structures, solute molecules concentrate at interfaces altering surface effects as evidenced by changes in surface tension, wetting speed, detergency, and foaming characteristics. Detergents constitute a relatively limited molecular weight group in this class of products, as requisite properties are obtained only when a precise balance between the two portions of the molecule exists. Such a balance usually results in borderline solubility in both aqueous and organic media.

Numerous materials of varying chemical structure meeting these requirements can be made from petroleum.

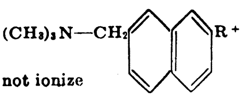
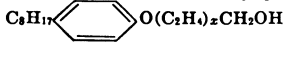
Alkyl Aryl Sulfonates

The alkyl aryl sulfonates, specifically those having a molecular weight and structure approaching dodecyl benzene sulfonate, were among the first and have grown to be the major detergent products produced from petroleum today (*6*). The development of the better detergent products of this approximate composition has followed the expedient course of synthesizing and testing those homologous and isomeric mixtures of compounds which may be prepared from available low-cost raw materials by practical reaction techniques. The preparation and sifting of individual isomeric products as a means to finding optimum structures have received but limited attention—and, indeed, would be an impractical approach, as there are 38,636 possible isomeric $C_{18}H_{30}$ alkyl benzenes, 355 of which are monoalkyl benzene isomers (*7*). As the more expedient syntheses have evolved, however, and improved analytical methods have developed, increased attention has been given to correlations between molecular weight and structure of process reactants and final product performance characteristics.

Green Acid Sulfonates

The first alkyl aryl sulfonates produced in this country were those which resulted from the sulfuric acid refinement of kerosene, gas oil, and lubricating oils and were initially

Table I. Ionic Classification of Detergents

	Anion	Cation
Tallow soap or sodium stearate	$C_{17}H_{35}COO^-$	Na^+
Sodium dodecyl benzene sulfonate		Na^+
Alkyl naphthal trimethyl ammonium chloride	Cl^-	
Poly ethenoxy ether of iso-octyl pheno 	Does not ionize	

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noted for their nuisance value alone (*5*). As their occurrence and refinement became better understood, in several cases they have evolved to useful by-products and finally to primary products.

The water-soluble sulfonic acids resulting from the acid treatment of oils boiling under 550° F.—known as "green acids" in the trade—upon extraction from the spent sulfonation acid sludge with a suitable solvent, gave water-soluble salts of limited commercial utility. A choice oil for producing high yields of a green acid type product would be a refractory cracked gas oil from a relatively aromatic crude such as Lea-Ward, and would have the inspections shown in Table II.

Table II. Inspections on Cracked Gas Oils from Lea-Ward Crude

	%	° F.
ASTM distillation	0	248
	10	403
	50	466
	90	526
	95	564
	E.p.	590
API gravity	26.2	
Components	20 to 22% polyalkyl aromatics, some polynuclear	
Olefins, %	20 to 25	
Naphthenes, etc., %	52 to 60	

Aromatics in this oil can be converted almost quantitatively to sulfonates by controlled sulfonation with 98% sulfuric acid at about 150° F. The sulfonic acids are soluble in the spent acid and must be extracted with a nonreactive solvent.

Similar treating procedures can be used on more concentrated aromatic materials such as the polyalkylated benzenes which are formed as heavy by-products in the manufacture of cumene from propylene and benzene (*18*).

Principal use of these products as detergents occurred during World War II when they were used with fatty acid soaps in formulating army all-purpose detergent bars (*25*). Their low molecular weight and high water solubility limited their value for use alone in efficient detergent formulations.

Oil-Soluble Sulfonates

The oil-soluble sulfonates resulting from the acid treatment of oil boiling above 550° F. are typified by the mahogany or white oil sulfonates which for many years were the unwanted by-products of white oil manufacture, but which in view of recent industrial applications have reversed positions with the former primary product.

Mahogany sulfonic acids are most readily formed by the action of fuming sulfuric acid on a naphthenic-type petroleum distillate, preferably one having a Saybolt Universal viscosity at 100° F. of about 800 to 900 seconds and an API gravity of about 22. Following acid treatment of such a distillate with approximately 40 volume % of acid, the acid or sour oil is simultaneously neutralized and extracted with alcoholic caustic. The mahogany sulfonates which are soluble in the alcohol extract are then freed of excess sodium sulfate and caustic by drying and redissolving in a low boiling hydrocarbon (*5*).

These products find their main applications as emulsifiers, rust preventives, and detergents for use in motor oil. For the latter application, salts other than sodium are preferred and the conversion can be made either by double decomposition or by neutralization of the original sulfonic acids with the desired base (*9*).

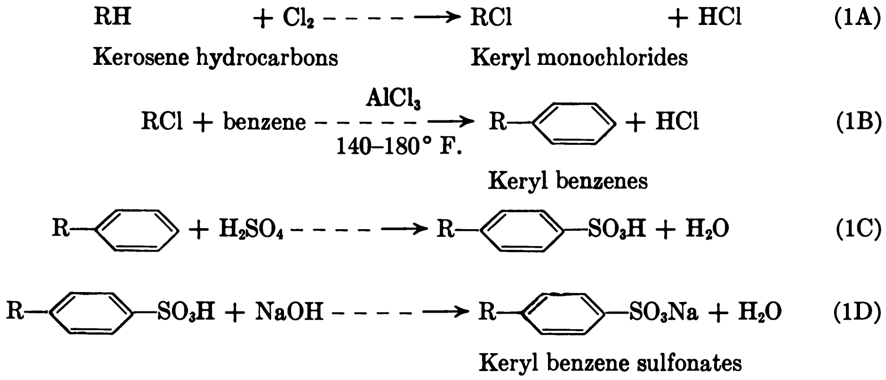
The detergent effect of barium and calcium sulfonates in heavy-duty lubricating oils, particularly those used in Diesel equipment, is evidenced by the striking decrease in engine deposits and ring fouling resulting from their use (*8*).

While synthetic oil-soluble sulfonates have also been made by reacting high molecular weight olefins or chlorinated wax with selected aromatics and sulfonating the resulting compound, the oil detergent properties of these materials have been reported to be inferior to those made by conventional acid-treating procedures on petroleum distillates.

Keryl Benzene Sulfonates

In the early thirties, at about the same time that sulfonated petroleum hydrocarbons were being rigorously explored for utility in the surface-active field the first keryl benzene sulfonates were produced.

These products, prepared from highly paraffinic fractions averaging about fourteen carbon atoms per molecule, are synthesized according to the reactions:

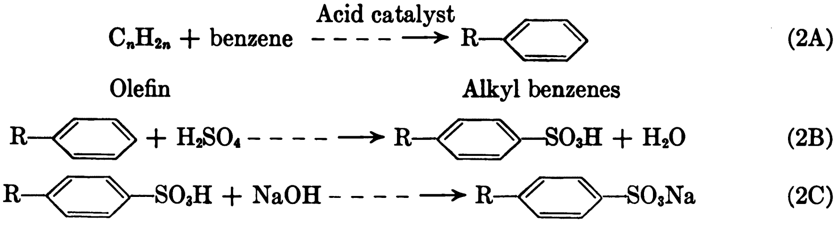


In practice, the kerosene is usually a close-cut highly acid-treated or solvent-refined material boiling in the range 425° to 475° F. It is chlorinated at about 140° F. until 1.1 to 1.2 atoms of chlorine are added to each molecule of hydrocarbon, after which the keryl chloride is reacted with an excess of benzene in the presence of aluminum chloride to give a keryl benzene which can be further purified by distillation prior to sulfonation (*6*).

The product structures available in this process are primarily determined by components in the paraffinic distillates used. The heterogeneity of virgin distillates has been illustrated by API sponsored work on distillate components (*21*). The preferred predominance of relatively straight-chain alkyl groups may be effected by combinations of selection of paraffin distillate source, and use of acid or solvent refining to effect enrichment of paraffinic components. With the advent of the urea precipitation technique of isolating the *n*-paraffins (*26*), particularly those in the decyl to hexadecyl range, it is now possible to produce products which are limited principally to the isomeric secondary phenyl alkanes: a dodecyl benzene mixture prepared by this process from a 95+% *n*-dodecane would consist essentially of the 2-, 3-, 4-, 5-, and 6-phenyl-substituted dodecanes.

In general the detergent properties of the keryl benzene sulfonates are good. From their very inception they were favorably received for light detergent jobs such as the washing of wool and dishes, and with the advent of alkali building of detergent formulas their efficiency was carried over into the cotton washing field. Their chief drawback has been the strong kerosene odor which persists in the sulfonate after sulfonation and drying, but recent improvements in keryl benzene have improved this characteristic.

Supplementing the keryl benzene sulfonates prepared according to Reaction I, above, are those products derived from olefins according to the equations:



The olefin should have from 10 to 15 carbon atoms and the unsaturation should be

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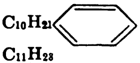
near the end of the molecule. Such materials can be obtained from cracking processes, from dehydrohalogenation of halogenated paraffins and from polymerized lower olefins. The most economical source is probably the latter, with propylene being the preferred starting material (*12*, *15*).

Using a typical C_3 refinery gas stream resulting from catalytic cracking and containing approximately 12% ethane, 6% ethylene, 37% propylene, 43% propane, and 2% C_4 hydrocarbons, a liquid polymer representing better than 90% of the olefin present can be obtained by catalytic polymerization in the presence of phosphoric acid at about 500° F. and 500 pounds per square inch of pressure. Of this polymer approximately 25% is the tetramer which is the desired olefin for detergent production. If the lower polymers resulting from this operation are recycled through the catalyst bed with fresh feed, additional conversion to the tetramer can be achieved.

In carrying out the alkylation of benzene the propylene tetramer is reacted with an excess of benzene in the presence of a Friedel-Crafts catalyst such as aluminum chloride, boron trifluoride, or hydrofluoric acid. With careful control of this reaction, yields of alkylate boiling from 500° to 650° F. are of the order of 80% of theory with the losses due to slight olefin degradation and dialkylation. Inspection of commercial aromatic products, believed to be typical of this process, indicates the composition to be that shown in Table III.

Table III. Molecular Weight Distribution in Typical Commercial Dodecyl Benzene—Boiling Range 500° to 650° F.

	Weight %
 $C_{10}H_{21}$	0-2.0
$C_{11}H_{23}$	12-28
$C_{12}H_{25}$	40-55
$C_{13}H_{27}$	15-20
Other	3.5-4.5

The analogous alkyl derivatives of toluene, xylene, and lower alkyl naphthalenes are included in the vast number of alkyl aromatics which are also described in the literature as sulfonation stocks (*16*). While several sulfonates derived from such products have enjoyed partial success, they have limitations with respect to yield, sudsing, and handling characteristics which place them at a disadvantage with respect to the alkyl benzenes described above.

Sulfonation of Alkyl Aromatics

The sulfonation of alkyl aromatic hydrocarbons as typified by dodecyl benzene is a relatively simple chemical operation which can be successfully carried out with 98% sulfuric acid, fuming sulfuric acid, or any combination of the two.

For example, a typical dodecyl benzene can be sulfonated with a 95% sulfonation yield with either 50 volume % of 20% fuming sulfuric acid at 90° F. or 90 volume % of 98% sulfuric acid at 150° F.

Neutralization of Alkyl Benzene Sulfonic Acids

Direct sodium hydroxide neutralization of the sulfonation mixture resulting from the fuming acid sulfonation of dodecyl benzene gives a product which, upon drying, contains approximately 50% active detergent and 50% sodium sulfate. If a higher active content is desired, the unreacted sulfuric acid can be partially removed from the sulfonation mixture by the addition of about 10 volume % of water at the end of sulfonation. By this means the active content of the dried detergent can be increased to about 85%, but unless the heat of dilution is carefully controlled, the hydrolysis of undesirable by-products in the spent acid may lead to unpleasant odors in the dried product.

The active content of the finished detergent can also be raised by solvent extraction of either the sulfonic acids or the neutral sulfonates.

Ordinarily sodium hydroxide is used to neutralize the sulfonic acids although other bases including lime, magnesia, potash, and organic amines have been used.

Alkyl Sulfonates

The direct reaction of paraffinic petroleum fractions to alkyl sulfonates by the Reed process has been extensively investigated in this country. In this process paraffin-rich stocks are reacted with sulfur dioxide and chlorine (*16*) and processed to sulfonates as indicated by the equations:

$$\underset{\text{Paraffin preferred}}{C_nH_{2n+2}} + SO_2 + Cl_2 \xrightarrow{\text{Actinic light}} RSO_2Cl + HCl \qquad (3A)$$

$$RSO_2Cl + 2NaOH \longrightarrow RSO_3Na + NaCl \qquad (3B)$$

For the paraffin, a highly acid-treated oil having a Saybolt Universal viscosity of 40 to 50 seconds at 100° F. is preferred. Reaction is rapid at 200° F. using about 1.7 parts by weight of sulfur dioxide and 0.9 part by weight of chlorine for each part of paraffin. The resulting sulfonyl chloride is neutralized with sodium hydroxide and separated from unreacted oil prior to drying.

The detergent properties of the alkyl sulfonates approach those of the alkyl aryl sulfonates, but the commercial processing problems have placed these materials at an economic disadvantage.

Somewhat analogous to the Reed process is a recent development in which an olefin is reacted with nitrosyl chloride to form a nitrosyl halide, which in turn is converted to a mixture of complex sulfonates by reaction with sodium sulfite (*4*). These materials are reported to be excellent metal cleaning detergents.

Alkyl Sulfates

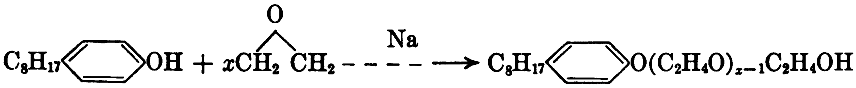
Another class of detergents that merits attention is represented by the alkyl sulfates. These materials have been prepared by the direct sulfation of high boiling olefins resulting from the cracking of paraffin wax or the sulfation of alcohols derived from petroleum.

The direct sulfation of wax olefins has been perfected in Europe but has not been commercialized to any extent in the United States. More work has been done in this country on alcohols that have been prepared by Fischer-Tropsch syntheses, oxo process reactions, and reduction of the fatty acid mixtures obtained by paraffin wax oxidation. In most instances these alcohols as well as the olefins have been branched chain or secondary products, both of which have been reported to give inferior detergent and sudsing properties (*13*, *24*).

Nonionics

There is a whole class of synthetic detergents, originating partly or wholly from petroleum, characterized by the fact that the detergents do not ionize in water. These compounds are high molecular weight polyglycol ethers and esters which usually are prepared by reacting ethylene or propylene oxide with a polar organic compound having a replaceable hydrogen as in an OH, SH, or NH group (*12*).

By way of example, iso-octyl phenol from diisobutylene and phenol reacts quantitatively with ethylene oxide in the presence of an alkaline catalyst to add any desired number of (C_2H_4O) groups as follows:



(4)

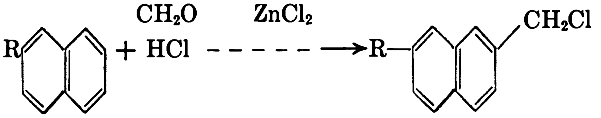
For good detergency the length of the ethenoxy chain should carefully balance the hydrophobic part of the molecule. In the above example, from eight to ten such groups appear to be optimum. The ethylene oxide for these products comes from petroleum ethylene, either by direct oxidation or decomposition of ethylene chlorohydrin (*17*).

In addition to the alkylated phenol mentioned, the hydrophobic part of the molecule may be derived from the fatty acids resulting from wax oxidation, and mercaptans from the reaction of high molecular weight olefins with hydrogen sulfide or Oxo process alcohols (*12*, *19*).

Nonionic detergents are usually viscous liquids with excellent solubility in all kinds of water. They are particularly good detergents for wool and have found their widest acceptance in this branch of the textile industry.

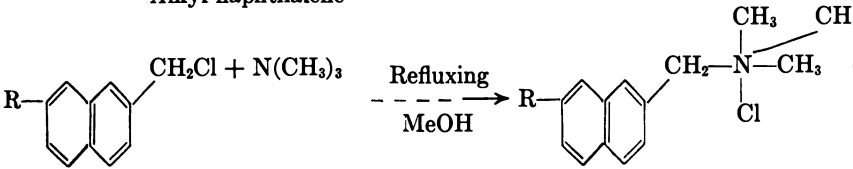
Cationics

The final class of water-soluble synthetic detergents derived from petroleum are the cationics. These products, when ionized, have the hydrophobic portion of the molecule in the cation. They are of interest principally because of the bactericidal properties they exhibit. Their performance as detergents is poor. The principal products marketed to date have been derived from normal long-chain amines, but procedures for their preparation from petroleum hydrocarbons (*1*) have been described as follows:



(5A)

Alkyl naphthalene



(5B)

Alkyl napthal trimethyl ammonium chloride

Detergent Forms

Synthetic detergents are marketed as liquids, slurries, drum-dried flakes and spray-dried beads, the latter being the form most frequently appearing in consumer packages.

Liquid detergents are used primarily for dishwashing or shampoos and usually are composed of highly water-soluble materials such as the nonionics, the lower molecular weight alkyl aryl sulfonates, the organic amine sulfonates, or mixtures of the same. Active product concentrations in water or an alcohol solvent will vary from 5 to 95%.

Drum dried flakes find their biggest outlet in industrial detergent mixtures where the original 30 to 90% active flakes are frequently dry-mixed with alkali builders for specific cleaning applications.

The spray-dried beads are formed in a spray tower by blending a host of additives or builders with highly active detergent slurries and drying to homogeneous beads.

From the consumer viewpoint there are two important and distinct products which are referred to as light- and heavy-duty detergents. The light-duty products, recommended for use on dishes and fine fabrics, usually have the composition shown in Table IV.

Table IV. Light Duty Synthetic Detergent

	%
Active detergent	20–35
Tripolyphosphate	5–10
Fluorescent dye	0–0.5
Sodium sulfate	75–55

Heavy-duty products, designed specifically for the cleaning of cottons, are illustrated in Table V.

Production Trends

The production trends (*3*) shown in Figure 2 are for all synthetic detergents. No split-up is available for petroleum-based materials alone, but the indications are that better than 50% of the products fall into this category. As can be seen from the curve, the

Table V. Heavy Duty Synthetic Detergent

	%
Active detergent	25–40
Tripolyphosphate	25–50
Fluorescent dye	0.5–1.0
Carboxymethylcellulose	1.0–4.0
Sodium sulfate	49–5.0

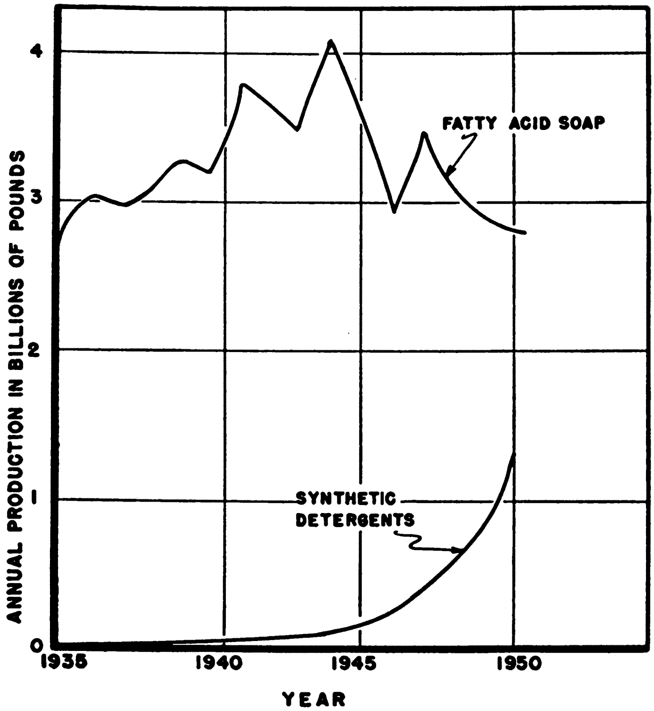


Figure 2. Production Pattern for Detergents

industry is still growing and can be expected to continue, up to perhaps 3 billion pounds per year.

Petroleum-based products should get a lion's share of this market, provided that the raw materials—particularly benzene and olefins of the right molecular weight and structure—can be made available at prices that will permit competition with synthetics and improved soaps based on products from agricultural sources.

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Composition of Petroleum

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This paper presents a survey of our present knowledge of the composition of petroleum. Included in the presentation is a brief discussion of the nonhydrocarbon constituents of petroleum, covering sulfur, nitrogen, oxygen, and metallic constituents, together with more detailed information regarding the hydrocarbon constituents which comprise the bulk of crude petroleum. In addition to a discussion of the hydrocarbon compounds and types of hydrocarbon compounds occurring in one representative petroleum, the problem is considered of how different crude petroleums differ in their composition with respect to the hydrocarbon components.

Petroleum is recognized today not only as one of the most important natural resources of the world, but also as one of nature's most interesting and intriguing ones. Until about 1920, investigations on the nature of petroleum and its components were usually of a sporadic and casual nature. About that time, however, the petroleum industry began to be very seriously concerned about the composition of its raw material. Whereas in the early days petroleum was commercially separated roughly according to molecular size by the process of simple distillation, the industry desired to produce special products that could better satisfy the more exacting requirements of modern commerce and industry. This could be done, of course, only with reliable information concerning the composition and properties of petroleum and its components.

Prior to 1900, the results of work on the composition of petroleum had been published by the following investigators: de La Rue and Miller (*28*) in 1856; Schorlemmer (*53*) in 1832; Silliman (*55*) in 1871; Engler (*12, 13*) in 1879 and 1885; Mabery and coworkers (*32–35*) in 1895 to 1902; Markownikoff (*37–40*) in 1895 to 1900; Young (*62–64*) in 1897 to 1899; Fortey (*18, 19*) in 1898 and 1899; and Aschan (*2*) in 1898. Very few significant new investigations were reported between 1900 and 1920. Following 1920, active work was started in a number of laboratories to begin unraveling the secrets of nature regarding the components of petroleum.

In 1927, the petroleum industry, through the American Petroleum Institute, established API Research Project 6 to investigate the composition of petroleum with respect to its hydrocarbon components. This project operated continuously at the National Bureau of Standards in Washington, D. C., until June 1950, when it was moved to the Carnegie Institute of Technology in Pittsburgh, Pa. Concurrently, important related work was carried on at the Petroleum Refining Laboratory of the Pennsylvania State College, and in the laboratories of the U. S. Bureau of Mines. In the period 1935 to 1940, spectrometric methods of analysis were taken up and developed by the petroleum industry to assist in the analysis of the complex mixtures being encountered in petroleum processing. Within the past ten years, the cooperative work of a number of the American Petroleum Institute Research Projects has provided standard samples for spectrometer calibration and catalogs of spectral data for guidance in analytical work. As a result of these developments, the laboratories of the petroleum industry were in a position themselves to engage in fruitful examination of various portions of crude petroleum with respect to individual components or types of components.

The acquisition during the past quarter century of an enormous amount of basic fundamental information on the composition and properties of petroleum and its components has placed the petroleum industry in a highly competitive and favorable position with regard to the most economical use of its raw material, including the tailor-making of the highly specialized products required by modern industry.

Investigations on Nonhydrocarbon Constituents

Sulfur Compounds. A statistical analysis of the sulfur content of crude petroleums of the United States, according to their geographical location, has recently been given by Smith (*57*). For the United States as a whole, nearly 40% of the petroleum currently being produced has a sulfur content of less than 0.25% by weight, while approximately 7% has a sulfur content of more than 2% by weight. Substantially all the petroleum production from the Appalachian and Gulf Coast areas of the United States contains less than 0.25% by weight of sulfur, whereas 35% of the production from the Mississippi area contains more than 2% by weight of sulfur.

A summary of the work on the identification of sulfur compounds in crude oils has been given recently by Ball, Rall, Waddington, and Smith (*31*), who list the sulfur compounds isolated from petroleum by earlier investigators and, in addition, give several new compounds which have recently been isolated from a Wasson, Tex., crude petroleum by the API Research Project 48. Birch and Norris (*5*) isolated a substantial number of the thiol (mercaptan) type of sulfur compounds from an Iranian crude petroleum.

The sulfur compounds present in crude petroleum include thiols (mercaptans), open-chain sulfides, and cyclic sulfides. Both straight and branched-chain thiols and sulfides have been identified. Among the cyclic sulfides, the presence of both thiacyclopentanes and thiacyclohexanes has been established. In its investigation of the sulfur compounds in the naphtha fraction of a Wasson, Tex., crude petroleum, API Research Project 48 found present in significant amount all but three of the possible sulfur compounds normally boiling in the range 6° to 86° C. The sulfur compounds so identified include six of the thiol type and three of the sulfide type: methanethiol (methyl mercaptan), ethanethiol (ethyl mercaptan), 1-propanethiol (*n*-propyl mercaptan), 2-propanethiol (isopropyl mercaptan), 2-butanethiol (*sec*-butyl mercaptan), 2-methyl-2-propanethiol (*tert*-butyl mercaptan), 2-thiapropane (dimethyl sulfide), 2-thiabutane (methylethyl sulfide), and 3-methyl-2-thiabutane (methylisopropyl sulfide).

In addition to the sulfur compounds listed above, hydrogen sulfide has been found in many crude petroleums. Elemental sulfur has been definitely found in several crude petroleums by API Research Project 48 (*23*). Although Birch and Norris (*5*) isolated several disulfides from the spent caustic used in treating gasoline from Iranian petroleum, these compounds may have resulted from the oxidation of the thiols and their presence in the original petroleum is regarded as doubtful. Other types of sulfur compounds, such as thiophenes and aromatic thiols, have been identified in cracked petroleum products, but the presence of such compounds in naturally occurring petroleums has not yet been established.

Nitrogen Compounds. Smith (*57*) has recently given a survey of the nitrogen content of crude petroleum from about 150 fields throughout the United States. The amount of nitrogen in these petroleums varies from less than 0.05 to more than 0.5% by weight, with the California petroleums usually having the higher values. Bailey (*43*) found that certain California petroleums had a nitrogen content as high as 0.8% by weight.

Our knowledge of the composition of nitrogen compounds in petroleum is due largely to the investigations at the University of Texas, including the work of Bailey and coworkers from 1928 to 1941, and the more recent work of Lochte and coworkers. These and other pertinent data have been summarized recently by Lochte (*30*). Approximately half of the nitrogen in California petroleum is present in the form of nitrogen bases, and

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there have been isolated at the University of Texas a substantial number of quinolines and pyridines with alkyl substituents, as well as a few pyridines in which the substituent was a cyclopentyl or cyclohexyl group. In this latter category are included 3-cyclopentylpyridine, 4-cyclopentylpyridine, and 2,4-dimethyl-6-(2,2,6-trimethylcyclohexyl)pyridine. Recently, a constituent belonging to a different type of base—namely, 2-methylpyridine—was isolated at the University of Texas (*30*). Hackman, Wibaut, and Gitsels (*25*) have isolated isoquinoline and 1- and 3-methylisoquinoline, as well as other quinolines, from the bases from a California cracked petroleum stock. It is not known, however, whether these compounds were present in the original crude petroleum or resulted from thermal decomposition.

The other nitrogen compounds which are nonbasic, and are not extracted from hydrocarbons by dilute acid, have not been investigated in detail, though there are indications that they contain pyrroles. In addition, it is possible that some part of the nitrogen in this material is present in the form of amides, derived from primary or secondary amines and petroleum acids.

Oxygen Compounds. According to Gruse and Stevens (*24*), the total content of oxygen in petroleum is generally low, but in some cases may be as high as 2% by weight. Some of the oxygen is present in the form of carboxylic acids and some in the form of phenols. Lochte (*31*) has established the presence of acid anhydrides. Esters, alcohols, and ketones may also be present, though the evidence regarding them is not conclusive. Resins and asphaltic materials from petroleum frequently contain considerable amounts of oxygen, although the manner in which oxygen is combined in these substances is not known.

As a result of the investigations of Lochte (*31*), von Braun (*7, 8*), and Nenitzescu (*42*), and their coworkers, fairly complete information is now available concerning the composition of the carboxylic acids from the lower boiling fractions of petroleum. A summary of this information by Lochte (*31*) includes references. A substantial number of acids have now been separated and identified, including straight-chain and branched-chain acids as well as acids with cyclopentane or cyclohexane rings in the molecule. In the case of the cyclic acids, the carboxyl group may be attached directly to the ring, or through one, two, or possibly three CH_2 groups. Very small amounts of aromatic acids have been detected in the acid mixtures from California petroleum.

The aliphatic acids isolated from a California crude petroleum by Lochte and coworkers (*31*) include: 2-methylpentanoic acid, 3-methylpentanoic acid, *n*-hexanoic acid, 2-methylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 5-methylhexanoic acid, *n*-heptanoic acid, *n*-octanoic acid, and *n*-nonanoic acid.

These investigators found that the normal acids occurred in much greater abundance than the branched acids. The cyclic acids isolated by Lochte and coworkers (*31*) include: cyclopentanecarboxylic acid, 2-methylcyclopentanecarboxylic acid, 3-methylcyclopentanecarboxylic acid, cyclopentaneacetic acid, 3-methylcyclopentaneacetic acid, 2,3-dimethylcyclopentaneacetic acid, 1,2,2-trimethylcyclopentanecarboxylic acid, cyclohexanecarboxylic acid, *p*-methylcyclohexanecarboxylic acid, and the cis and trans forms of 2,2,6-trimethylcyclohexanecarboxylic acid. In addition, Lochte and coworkers (*31*) isolated dimethylmaleic anhydride, which has also been isolated by Nenitzescu and coworkers (*42*).

Not much is known concerning the structure of acids with more than one ring per molecule, though von Braun (*7, 8*) has separated acids with two rings per molecule and has obtained indications that in some instances these are substituted acetic acids. Goheen (*22*) separated a mixture of acids from a Gulf Coast petroleum, converted them to the corresponding hydrocarbons, and, by the methods for hydrocarbon ring analysis, found that they contained on the average 2.6 rings per molecule.

Little information is available concerning the composition of phenols from distillates of petroleum, though in certain instances they may be present in the acid mixtures in fairly high concentrations. However, phenol, various alkyl phenols, and cresols have been separated from cracked distillates.

Metallic Constituents. The total ash content of crude petroleum is stated by Gruse and Stevens (*24*) to be of the order of 0.01 to 0.05%. Some of the mineral constit-

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uents in crude petroleum are contained in solution in water globules which are finely dispersed in the oil. Others are, however, soluble in the oil and may be concentrated into certain fractions by extraction with hydrocarbon and other organic solvents.

In an investigation on a California petroleum, Skinner (*56*) showed that a reduction in the amount of the metallic constituents was effected by dehydrating the wet crude in a high tension alternating electric field. A further reduction was obtained by washing the relatively dry crude produced in this manner with fresh water and again dehydrating. These two operations removed 85% of the chlorides from the crude petroleum and reduced mineral content by about one third. Boron, magnesium, silicon, iron, copper, nickel, and vanadium were detected spectrographically in the dry crude petroleum produced by these operations, while the original wet crude petroleum contained, in addition, sodium and strontium.

Skinner (*56*) precipitated an asphaltic portion from the dry Santa Maria Valley crude with propane and then extracted the asphaltic portion with a succession of solvents in the following order: *n*-pentane, *n*-hexane, *n*-heptane, 2,2,4-trimethylpentane, cyclohexane, benzene, and pyridine.

Some of the metallic constituents were somewhat soluble in the propane-oil portion, but all tended to be concentrated in the asphaltic portion. Although vanadium (0.02% by weight in the original crude petroleum) was present in all fractions, the greater part was found in the cyclohexane and benzene fractions. From the similarity of the absorption spectra of the vanadium concentrates from petroleum and those of synthetic vanadium porphyrin complexes, Skinner arrived at the conclusion that vanadium compounds from the petroleum of the Santa Maria Valley Field in California exist as porphyrin complexes. Additional metallic constituents were detected by Skinner as these became concentrated in the various solvent fractions, including aluminum, titanium, calcium, and molybdenum.

Gruse and Stevens (*24*) list still other metallic constituents which may be present in recognizable amounts in the ash from various petroleums, including tellurium, barium, lead, manganese, chromium, and silver. According to these authors, oil-soluble salts of petroleum acids probably account for the small portions of most metallic constituents present in crude oil.

Investigations on Hydrocarbon Constituents

In the period since 1920, the important investigations dealing with the hydrocarbon components of petroleum have included the following, in addition to the work of API Research Project 6 begun in 1927:

Francis, Watkins, and Wallington (*20, 21*) in 1922, relating to normal paraffins (in Scottish shale oil)

Chavanne (*11*) in 1922, relating to various hydrocarbons present in the gasoline fraction of a Borneo petroleum

Anderson and Erskine (*1*) in 1924, relating to propane, *n*-butane, isobutane, *n*-pentane, isopentane, *n*-hexane, *n*-heptane, *n*-octane, and C_6 and C_7 branched paraffins in a natural gasoline

Birch and Norris (*6*) in 1926, relating to toluene, *m*-xylene, 1-methyl-4-ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, naphthalene, and two C_{10} alkylbenzenes in a Persian petroleum

Ferris, Cowles, and Henderson (*15, 16*) in 1929 and 1931, relating to the waxes in the lubricant fraction of a mid-continent petroleum

Shepard, Henne, and Midgley (*54*) in 1931, relating to the *n*-paraffins, C_5 to C_{12}, in a Michigan petroleum

Fenske, Tongberg, and Quiggle (*14, 58*) in 1932 and 1936, relating to 2-methylpentane, *n*-heptane, *n*-octane, methylcyclohexane, and many other compounds of the paraffin, cycloparaffin, and alkyl benzene types, in Pennsylvania petroleum

Müller and Pilat (*41*) in 1935, relating to the types of hydrocarbons in the lubricant fraction

Kalvoort, Moser, and Verver (*27*) in 1937, relating to petroleum waxes

Hicks-Bruun, Bruun, and Faulconer (*26*) in 1939, relating to 2,2-dimethylbutane

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Watson and Spinks (*61*) in 1940, relating to the composition of the gasoline fraction of a Canadian petroleum

Fischer and Welty (*17*) in 1944, relating to toluene and methylcyclohexane in 15 different petroleums

Gooding, Adams, and Rall (*23*) in 1946, relating to the compounds in ten different light naphthas

Ward, Gooding, and Eccleston (*59*) in 1947, relating to the compounds in the light gasoline fraction of Oklahoma petroleum

Bell (*4*) in 1950, relating to the hydrocarbons in the light gasoline fraction of East Texas petroleum

Zimmerschied, Dinerstein, Weitkamp, and Marschner (*65*) in 1950, relating to the normal paraffins, C_{12} to C_{18}

Cady, Marschner, and Cropper (*9*) in 1951, relating to the composition of the light naphtha fraction of mid-continent petroleum

Charlet, Lanneau, and Johnson (*10*) in 1951, relating to the types of aromatic compounds in the gas oil fraction of petroleum

Lillard, Jones, and Anderson (*29*) in 1951, relating to the types of hydrocarbons in the lubricating oil fraction of a mid-continent and a Gulf Coast petroleum

The work of API Research Project 6 has been summarized at various stages in its progress (*36*, *44–52*, *60*) and the current status of the work of this project is summarized in the following section of the present paper.

Results Obtained by API Research Project 6 on One Representative Petroleum

Problem and General Method of Operation. The goal set before API Research Project 6 was essentially one of ascertaining the major hydrocarbon constituents of one representative petroleum and then learning how the amounts of the major components vary in different petroleums. Substantially all of the hydrocarbons in petroleum are composed of paraffin groups, cycloparaffin or naphthene groups, aromatic groups, mixed aromatic-naphthene nuclei, or combinations of these. No olefin or acetylene hydrocarbons appear to be in naturally occurring petroleum in any significant amount. The problem is that of separating, without altering the constituents, the complex mixture of hydrocarbons that constitute petroleum, and to obtain the major components in a substantially pure state. The general method of operation is to utilize the various processes of fractionation in such combinations as will produce a "sifting" of the molecules with respect to size on the one hand and to type on the other. To be successful in separating a given mixture of hydrocarbons, any process of fractionation must involve a physical property that has significantly different values for the several components of the mixture to be separated. Furthermore, the procedure must be one for which a workable apparatus is available, or for which one can be developed.

The standard processes of fractionation used in this work are distillation, extraction, adsorption, and crystallization, which involve the properties of vapor pressure (or boiling point), solubility, adsorbability, and freezing point (and cryoscopic constant). These processes of fractionation may be used in several variations:

Distillation. At different pressures; with an added volatile azeotrope-forming substance (for azeotropic distillation); with an added relatively nonvolatile selective solvent (for extractive distillation).

Extraction. At different temperatures; with different single solvents; with different multiple solvents.

Adsorption. At different temperatures; with different adsorbents; with the hydrocarbons in the gas phase; with the hydrocarbons in the liquid phase; with eluting and diluting liquids; with desorbing liquids.

Crystallization. From the mixture of hydrocarbons alone; from a solution of the hydrocarbons in an appropriate solvent; with centrifuging.

In addition, it is occasionally possible to use special methods, such as that of separating large *n*-paraffins through the formation of adducts with urea (*65*).

With regard to the nature of the separation obtained, the foregoing processes of fractionation, excluding crystallization, may be classified according to whether they fractionate primarily with respect to size of molecule or to type of molecule. Separation primarily according to size of molecule (or boiling point or molecular weight) is produced by distillation at one fixed pressure. Separation primarily according to type of molecule is produced by distillation alternately at two fixed pressures, by azeotropic distillation, by extractive distillation, by extraction, and by adsorption. In connection with separations by type it is important to note that, except in certain special cases, alternate distillation at two fixed pressures, distillation with an azeotrope-forming substance, and extractive distillation require a charging stock that is homogeneous with respect to boiling point (or size of molecules)—that is, a relatively narrow boiling charge. On the other hand, the process of extraction may be used successfully on rather wide boiling charges, and the process of adsorption may be used on extremely wide boiling material.

In connection with separation by crystallization, two general statements may be made regarding hydrocarbons: For a given degree of symmetry of the molecule the freezing point usually is higher the greater the size of the molecule; for a given number of carbon atoms in the molecule, the freezing point usually is higher the greater the symmetry of the molecule.

Except for those few hydrocarbons in the volatile range that have boiling points relatively far from their neighbors, and for certain other hydrocarbons present in relatively large amount (as *n*-paraffins in a Pennsylvania or a Michigan petroleum), regular distillation alone will not separate pure hydrocarbons from petroleum, and one or more of the other methods (including the variations of distillation) must also be used.

The order in which the several methods are used is determined by the effectiveness of a given process in increasing the separation attained by the preceding method. Thus, although a given process may be ineffective when used alone, its systematic use in appropriate combination with other processes can often lead to the complete separation of an otherwise unseparable constituent.

Identification and Purity of Single Substances. Before attempting to identify a material separated from petroleum as a given compound by comparison of its properties with those of known pure compounds, it is necessary to prove that the material is substantially a single substance and not a mixture. If a logical sequence of fractionating processes, including distillation at high efficiency, has been followed, the given material will consist of molecules of the same size and type—that is, a mixture of isomers. In some cases, one of the isomers will constitute the bulk of the material, which may then be considered substantially one compound.

In deciding upon the property which is to be used in establishing the fact that the material is or is not substantially one compound, consideration must be given to the following facts:

> The material is substantially constant-boiling as a result of its having been produced by a sequence of fractionating processes involving high-efficiency distillation. Therefore, examination of the boiling point as a function of the percentage of the sample vaporized or condensed will be of little or no value in this connection.
>
> The minor components present with the major component will normally be isomers of the latter, as a result of the material's having been well fractionated by type of molecule. The isomers will have values of the density, refractive index, and similar properties, very nearly the same as those of the major component, so that these properties will be of little or no value in this connection. Furthermore, such isomeric minor components will constitute the very compounds which will be most likely to form with the major component a substantially ideal solution.
>
> One of the most effective methods for evaluating the purity of chemical substances is that involving determination of the freezing point, with appropriate observation of the temperature of the liquid-solid equilibrium as a function of the fraction of sample frozen or melted.

In the absence of information as to the identity of the impurities or minor components associated with the parent substance, or of the identity of parent substance as well as the impurities, it appears that the freezing point is the only property which may be utilized to give a quantitative estimate of the purity.

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Whenever the identities of the major component and of its impurities are known, the amounts of the major and minor components can be satisfactorily determined by means of spectrometric measurements (infrared, ultraviolet, Raman, or mass, as appropriate), provided pure standard samples of the major component and each of the minor components are available for calibration of the given spectrometer.

In the problem of identifying and determining the purity of individual hydrocarbons separated from petroleum, the following cases occur, in order, as knowledge of the material being investigated increases.

At first, no information is available as to the chemical·constitution of the material except a knowledge of the elements which compose it. In this case, the investigation may proceed as follows:

The fact that the material separated is substantially a single substance and not a mixture is established. This may be done, as described before, by suitable observations of the temperature of the liquid-solid equilibrium as a function of the fraction of the sample frozen or melted. Such observations also serve to determine, within appropriate limits, the amount of impurity in the given sample.

By measurements of elemental composition and molecular weight, the molecular formula of the substance is determined.

Measurements are made of the simple physical properties of the freezing point (this property will usually already have been measured in the determination of purity), boiling point, density, and refractive index. The foregoing properties are necessary. The following properties may also be determined if equipment is available: viscosity, solubility in a proper solvent, and critical solution temperature in a proper solvent.

The simple physical properties of the given substance are compared with the same properties of known pure compounds of the same molecular formula. If adequate matching can be made of the freezing point, refractive index, and density of the given substance with a known pure compound of the same molecular formula, the identification may be considered substantially complete.

If, however, the identification just outlined cannot be made, it will appear that the given substance is not identical with any known compound of the same molecular formula and, to complete the identification, further steps must be taken:

Measurement is made of the spectrographic properties, including infrared absorption and ultraviolet absorption. The Raman spectra and mass spectrometer pattern may also be determined.

By analysis and comparison of the physical and spectrographic properties of the unknown substance with those of known compounds of the same molecular formula, it will be possible to establish the identity of the group of isomeric compounds to which the unknown substance belongs. It should be possible also to establish the several most probable compounds with which the unknown may possibly be identified.

Arrangements are made for the synthesis of the most probable compounds in turn until one is prepared, the properties of which match those of the substance separated from petroleum sufficiently well to establish the identity.

After sufficient information has been obtained as to the types of components which constitute a given fraction or boiling range of petroleum, subsequent examination of such material can be greatly simplified by the elimination of certain steps. In most cases, for example, it becomes unnecessary to make an elemental analysis or determine the molecular weight.

Whenever all the possible components present in significant amount in any given fraction of petroleum are known, and when reliable values are available for the simple physical properties of pure samples of the possible components, the identification of a substance separated from the given fraction becomes a relatively simple matter. In such case, the procedure would be to establish the fact that the material separated is substantially a single substance, measure its simple physical properties, and match these physical properties with those of one of the possible components. In many cases, spectrographic identification can be made more readily than identification by measurement of the simple physical properties.

Characterization of Homogeneous Mixtures of Hydrocarbons. In the higher boiling fractions of petroleum, such as the gas oil and lubricant portions, the isolation

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Table I. Hydrocarbons Isolated from One Representative Petroleum from the Ponca, Okla., Field

Formula	Compound	Type[a]	Boiling Point at 1 Atm., ° C.	Purity of Best Sample Isolated[b]— Mole %	Estimated Amount in Crude Petroleum[c]— Vol. %	Research Papers on This Work[d]
CH_4	Methane	*n*-Paraffin	−161.49	[e]	[e]	
C_2H_6	Ethane	*n*-Paraffin	−88.63	[e]	[e]	
C_3H_8	Propane	*n*-Paraffin	−42.07	[e]	[e]	
C_4H_{10}	Isobutane	Branched paraffin	−11.73	[e]	[e]	
C_4H_{10}	*n*-Butane	*n*-Paraffin	−0.50	[e]	[e]	
C_5H_{12}	2-Methylbutane	Branched paraffin	27.85	[e]	[e]	
C_5H_{12}	*n*-Pentane	*n*-Paraffin	36.07	[e]	[e]	
C_5H_{10}	Cyclopentane	Cyclopentane	49.26	[e]	0.05	84
C_6H_{14}	2,2-Dimethylbutane	Branched paraffin	49.74	[e]	0.04	84
C_6H_{14}	2,3-Dimethylbutane	Branched paraffin	57.99	97	0.08	8, 84
C_6H_{14}	2-Methylpentane	Branched paraffin	60.27	99.97	0.4	8, 84, 97
C_6H_{14}	3-Methylpentane	Branched paraffin	63.28	99.9	0.3	8, 84, 97
C_6H_{14}	*n*-Hexane	*n*-Paraffin	68.74	99.9	1.8	12, 84, 97
C_6H_{12}	Methylcyclopentane	Cyclopentane	71.81	98.7	0.9	14, 84
C_7H_{16}	2,2-Dimethylpentane	Branched paraffin	79.20	97	0.02	21, 84
C_6H_6	Benzene	Benzene	80.10	99.6	0.2	12, 84
C_7H_{16}	2,4-Dimethylpentane	Branched paraffin	80.50		0.08	84
C_6H_{12}	Cyclohexane	Cyclohexane	80.74	99.9	0.7	13, 84
C_7H_{14}	1,1-Dimethylcyclopentane	Cyclopentane	87.85	98	0.2	26, 84
C_7H_{16}	2,3-Dimethylpentane	Branched paraffin	89.78	58[f]	0.1[g]	84, 127
C_7H_{16}	2-Methylhexane	Branched paraffin	90.05	97	0.7[g]	26, 84, 127
C_7H_{14}	1,*trans*-3-Dimethylcyclopentane	Cyclopentane	90.77	85	0.9	75, 84, 127
C_7H_{14}	1,*cis*-3-Dimethylcyclopentane	Cyclopentane	91.72	51[f]	0.2[g]	127
C_7H_{16}	3-Methylhexane	Branched paraffin	91.85	93	0.5	75, 84, 127
C_7H_{14}	1,*trans*-2-Dimethylcyclopentane	Cyclopentane	91.87	93	0.5[g]	75, 84, 127
C_7H_{16}	3-Ethylpentane	Branched paraffin	93.47	98.7[f]	0.05	127
C_7H_{16}	*n*-Heptane	*n*-Paraffin	98.43	99.9	2.3	18, 84
C_7H_{14}	Methylcyclohexane	Cyclohexane	100.93	99.8	1.6	18, 84
C_7H_{14}	Ethylcyclopentane	Cyclopentane	103.47	98	0.2	105
C_8H_{16}	1,1,3-Trimethylcyclopentane	Cyclopentane	104.89	98.1	0.3	105
C_8H_{18}	2,2-Dimethylhexane	Branched paraffin	106.84	50[f]	0.01	105
C_8H_{18}	2,5-Dimethylhexane	Branched paraffin	109.10	55[f]	0.06[f]	125
C_8H_{16}	1,*trans*-2,*cis*-4-Trimethylcyclopentane	Cyclopentane	109.29	84[f]	0.2	125
C_8H_{18}	2,4-Dimethylhexane	Branched paraffin	109.43	41[f]	0.06[f]	125
C_8H_{18}	2,2,3-Trimethylpentane	Branched paraffin	109.84	1.0[f]	0.004[f]	125
C_8H_{16}	1,*trans*-2,*cis*-3-Trimethylcyclopentane	Cyclopentane	110.2	98.6	0.3	125
C_7H_8	Toluene	Benzene	110.62	98	0.5	10, 84
C_8H_{18}	3,3-Dimethylhexane	Branched paraffin	111.97	86[f]	0.03	125
C_8H_{18}	2,3,4-Trimethylpentane	Branched paraffin	113.47	17[f]	0.005[f]	125
C_8H_{16}	1,1,2-Trimethylcyclopentane	Cyclopentane	113.73	98	0.06	125
C_8H_{18}	2,3,3-Trimethylpentane	Branched paraffin	114.76	10[f]	0.006[f]	125
C_8H_{18}	2,3-Dimethylhexane	Branched paraffin	115.61	65[f]	0.07[f]	125
C_8H_{18}	2-Methyl-3-ethylpentane	Branched paraffin	115.65	51[g]	0.06[f]	125
C_8H_{16}	1,*cis*-2,*trans*-4-Trimethylcyclopentane	Cyclopentane	116.73	84[g]	0.01[g]	[h]
C_8H_{16}	1,*cis*-2,*trans*-3-Trimethylcyclopentane	Cyclopentane	117.5	90[g]	0.07[g]	[h]
C_8H_{18}	2-Methylheptane	Branched paraffin	117.65	90	0.90[g]	27,[h]
C_7H_{14}	Cycloheptane	Cycloheptane	117.7	90	0.01[g]	[h]
C_8H_{18}	4-Methylheptane	Branched paraffin	117.71	34[g]	0.02[g]	[h]
C_8H_{18}	3,4-Dimethylhexane	Branched paraffin	117.72	40[g]	0.13[g]	[h]
C_8H_{18}	3-Methyl-3-ethylpentane	Branched paraffin	118.26	6[g]	0.20[g]	[h]
C_8H_{18}	3-Ethylhexane	Branched paraffin	118.53	43[g]	0.09[g]	[h]
C_8H_{18}	3-Methylheptane	Branched paraffin	118.92	98[g]	0.30[g]	[h]
C_8H_{16}	1,*trans*-4-Dimethylcyclohexane	Cyclohexane	119.35	75[g]	0.25[g]	[h]
C_8H_{16}	1,1-Dimethylcyclohexane	Cyclohexane	119.54	84[g]	0.06[g]	[h]
C_8H_{16}	1,*cis*-3-Dimethylcyclohexane	Cyclohexane	120.09	84[g]	0.63[g]	42,[h]
C_8H_{16}	1-Methyl-*trans*-3-ethylcyclopentane	Cyclopentane	120.8	57[g]	0.12[g]	[h]
C_8H_{16}	1-Methyl-*cis*-3-ethylcyclopentane	Cyclopentane	121.0			
C_8H_{16}	1-Methyl-*trans*-2-ethylcyclopentane	Cyclopentane	121.2	74[g]	0.14[g]	[h]
C_8H_{16}	1-Methyl-1-ethylcyclopentane	Cyclopentane	121.52	65[g]	0.03[g]	[h]
C_9H_{18}	1,1,*cis*-3,*trans*-4-Tetramethylcyclopentane	Cyclopentane	121.6	83[g]	0.04[g]	[h]
C_8H_{16}	1,*trans*-2-Dimethylcyclohexane	Cyclohexane	123.42	98[g]	0.31[g]	48,[h]
C_9H_{20}	2,2,5-Trimethylhexane	Branched paraffin	124.09	11[g]	0.002[g]	[h]
C_8H_{16}	1,*cis*-4-Dimethylcyclohexane	Cyclohexane	124.32	76[g]	0.09[g]	[h]

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Table I. Hydrocarbons Isolated from One Representative Petroleum from the Ponca, Okla., Field *(Continued)*

Formula	Compound	Type[a]	Boiling Point at 1 Atm., ° C.	Purity of Best Sample Isolated[b]—Mole %	Estimated Amount in Crude Petroleum[c]—Vol. %	Research Papers on This Work[d]
C_8H_{16}	1,*trans*-3-Dimethylcyclohexane	Cyclohexane	124.45	49[g]	0.07[g]	[h]
C_8H_{18}	*n*-Octane	*n*-Paraffin	125.66	99.2	1.9	11, [h]
C_9H_{18}	Tetramethylcyclopentane[i]	Cyclopentane	127.4	[e]	[e]	[h]
C_8H_{16}	*n*-Propylcyclopentane	Cyclopentane	130.95	73	[e]	[h]
C_8H_{16}	Ethylcyclohexane	Cyclohexane	131.78	94	0.2	44
C_9H_{20}	2,6-Dimethylheptane	Branched paraffin	135.21	98.6	0.05	52, 70
C_8H_{10}	Ethylbenzene	Benzene	136.19	96	0.2	28, 84
C_9H_{18}	1,1,3-Trimethylcyclohexane	Cyclohexane	136.63	99.9	0.2	37
C_8H_{10}	*p*-Xylene	Benzene	138.35	99.8	0.1	24, 84
C_8H_{10}	*m*-Xylene	Benzene	139.10	99.9	0.5	24, 84
C_9H_{20}	2,3-Dimethylheptane	Branched paraffin	140.5	60	0.05	68
C_9H_{18}	Trimethylcyclohexane[i]	Cyclohexane	141.2	95	0.2	68
C_9H_{20}	4-Methyloctane	Branched paraffin	142.48	80	0.1	56
C_9H_{20}	2-Methyloctane	Branched paraffin	143.26	99.9	0.4	56
C_9H_{20}	3-Methyloctane	Branched paraffin	144.18	95	0.1	56
C_8H_{10}	*o*-Xylene	Benzene	144.41	99.7	0.3	24, 84
C_9H_{18}	Monocycloparaffin[i]	Monocycloparaffin	145.6	99	[e]	[h]
C_9H_{16}	Dicycloparaffin[i]	Dicycloparaffin	146.7	99	[e]	[h]
C_9H_{20}	*n*-Nonane	*n*-Paraffin	150.80	99.94	1.8	17, 103, [h]
C_9H_{12}	Isopropylbenzene	Benzene	152.39	99.8	0.07[j]	61, 84, 111
C_9H_{12}	*n*-Propylbenzene	Benzene	159.22	98	0.09[j]	84, 111, [h]
C_9H_{12}	1-Methyl-3-ethylbenzene	Benzene	161.30	99[f]	0.2[j]	111, [h]
C_9H_{12}	1-Methyl-4-ethylbenzene	Benzene	161.99	94[f]	0.06[j]	111, [h]
C_9H_{12}	1,3,5-Trimethylbenzene	Benzene	164.72	99.9	0.1[j]	33, 111
C_9H_{12}	1-Methyl-2-ethylbenzene	Benzene	165.15	89[f]	0.09[j]	111, [h]
$C_{10}H_{22}$	4-Methylnonane	Branched paraffin	165.7	96	[e]	[h]
$C_{10}H_{22}$	2-Methylnonane	Branched paraffin	166.8	99.9	[e]	[h]
$C_{10}H_{22}$	3-Methylnonane	Branched paraffin	167.8	98	[e]	[h]
$C_{10}H_{14}$	*tert*-Butylbenzene	Benzene	169.12	[e]	0.01[j]	111
C_9H_{12}	1,2,4-Trimethylbenzene	Benzene	169.35	99.7	0.5[j]	33, 97
$C_{10}H_{22}$	*n*-Decane	*n*-Paraffin	174.12	99.9	1.8	19, [h]
C_9H_{12}	1,2,3-Trimethylbenzene	Benzene	176.08	99.8	0.1	33, 97
$C_{10}H_{14}$	1-Methyl-3-propylbenzene	Benzene	181.8	[e]	0.1	[h]
$C_{10}H_{14}$	1,2-Diethylbenzene	Benzene	183.48	[e]	[e]	[h]
$C_{10}H_{14}$	1-Methyl-2-propylbenzene	Benzene	184.75	[e]	0.3	[h]
$C_{10}H_{14}$	1,4-Dimethyl-2-ethylbenzene	Benzene	186.91	[e]	0.1	[h]
$C_{10}H_{18}$	*trans*-Decahydronaphthalene	Dicycloparaffin	187.25	[e]	[e]	[h]
$C_{11}H_{24}$	*n*-Undecane	Normal paraffin	195.88	99.97	1.7	116, [h]
$C_{10}H_{14}$	1,2,4,5-Tetramethylbenzene	Benzene	196.8	[e]	[e]	[h]
$C_{10}H_{14}$	1,2,3,5-Tetramethylbenzene	Benzene	197.93	[e]	[e]	[h]
$C_{11}H_{16}$	Alkyl benzene[i]	Benzene	204.1	98	0.06	[h]
$C_{10}H_{14}$	1,2,3,4-Tetramethylbenzene	Benzene	205.04	99.9	0.2	79
$C_{11}H_{16}$	Alkyl benzene[i]	Benzene	206.6	96	0.03	[h]
$C_{10}H_{12}$	1,2,3,4-Tetrahydronaphthalene	Tetrahydronaphthalene	207.57	98.5	0.03	79
$C_{11}H_{16}$	Alkyl benzene[i]	Benzene	208.5	99	0.03	[h]
$C_{11}H_{16}$	Alkyl benzene[i]	Benzene	212.3	97	0.04	[h]
$C_{12}H_{26}$	*n*-Dodecane	*n*-Paraffin	216.28	99.9	1.7	74
$C_{10}H_8$	Naphthalene	Naphthalene	217.96	99.9	0.06	74
$C_{11}H_{14}$	Phenylcyclopentane[k]	Benzene-cyclopentane	220.7	97	0.04	[h]
$C_{11}H_{14}$	6-Methyl-[1,2,3,4-tetrahydronaphthalene]	Tetrahydronaphthalene	229.03	99.5	0.09	79
$C_{11}H_{14}$	5-Methyl-[1,2,3,4-tetrahydronaphthalene]	Tetrahydronaphthalene	234.35	99.7	0.08	79
$C_{13}H_{28}$	*n*-Tridecane	*n*-Paraffin	235.5	98	1.6	[h]
$C_{11}H_{10}$	2-Methylnaphthalene	Naphthalene	241.14	99.9	0.2	74
$C_{11}H_{10}$	1-Methylnaphthalene	Naphthalene	244.78	99.7	0.1	74
$C_{14}H_{30}$	*n*-Tetradecane	*n*-Paraffin	253.6	98.5[l]	1.4	[h]
$C_{12}H_{12}$	2,6-Dimethylnaphthalene	Naphthalene	262.0	[e]	[e]	[h]
$C_{15}H_{32}$	*n*-Pentadecane	*n*-Paraffin	270.7	98.5[l]	1.2	[h]
$C_{16}H_{34}$	*n*-Hexadecane	*n*-Paraffin	287.1	98[l]	1.0	[h]
$C_{17}H_{36}$	*n*-Heptadecane	*n*-Paraffin	302.6	97[l]	0.9	[h]

[a] Compounds classified according to types: *n*-paraffin; branched paraffin; cyclopentane (cyclopentane and its alkyl derivatives); cyclohexane (cyclohexane and its alkyl derivatives); benzene (benzene and its alkyl derivatives); naphthalene (naphthalene and its alkyl derivatives); tetrahydronaphthalene (tetrahydronaphthalene and its alkyl derivatives); benzene-cyclopentane (mixed type); dicycloparaffin. "Monocycloparaffin" indicates either "cyclopentane" or "cyclohexane" type.

(Footnotes concluded on facing page)

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of individual compounds (except for the *n*-paraffins) will be extremely difficult. In such cases, the fractionation will usually be halted at the stage where homogeneous fractions of molecules of substantially the same size and type are produced. In order to characterize such materials, the following procedure may be followed:

Measurements are made of the properties of boiling point (at an appropriate pressure), density, refractive index, refractive dispersion (for appropriate wave lengths), viscosity, critical solution temperature in one or more appropriate solvents, infrared absorption (normally in the range 2 to 15 microns), ultraviolet absorption (normally in the range 0.2 to 0.4 micron or 2000 to 4000 A.), elemental composition, and average molecular weight.

With the above data, it is possible to establish the molecular formula, and, by proper analysis, combination, and correlation of these data with values for known pure compounds, to determine the type of hydrocarbons constituting the homogeneous mixture, as paraffin, cycloparaffin, dicycloparaffin, benzene derivative, naphthalene derivative, tetrahydronaphthalene derivative, etc.

Description of the Petroleum. The large quantity of one representative crude petroleum which has been under investigation by API Research Project 6 was obtained (*51*) in 1928 from Brett No. 6 well in the Ponca City field, in Oklahoma, through the courtesy of the Marland Oil Co. (now part of the Continental Oil Co.). The exact location of this well is in the center of the northeast $^1/_4$ southeast $^1/_4$ of section 8, Township 25 North, Range 2 East, Kay County, Okla. This well, located near the crest of the Ponca anticlinal structure, produced oil from the uppermost part of the Wilcox sand formation of the Simpson group, Middle Ordovician in age. The top of the producing horizon was encountered at a depth of 3865 feet, the total depth of the hole being 3872 feet. The Brett No. 6 well, brought in as a producer under its own gas pressure on July 14, 1919, was placed on the pump on January 21, 1926, and produced under vacuum until October 26, 1936, when the well was plugged and abandoned because of saltwater encroachment.

The above crude petroleum which was selected for the systematic exhaustive investigation was classed as "intermediate" in composition. The Engler distillation of the original crude was given by the Marland Oil Co. as: naphtha, 38.9%; kerosene, 15.4%; gas oil, 16.0%; wax distillate, 18.1%; bottoms, 10.2%. A report of the standard U. S. Bureau of Mines Hempel distillation (*51*), gave the following results: light gasoline, 12.4%; naphtha, 30.0%; kerosene, 12.7%; gas oil, 16.6%; lubricating distillate, 14.3%; residuum, 12.5%. A 600-gallon lot of this petroleum was first carefully distilled for API Research Project 6 in a semicommercial column by the Sun Oil Co., the material being handled so as to avoid any chemical action or decomposition and to minimize loss by evaporation.

Hydrocarbons Isolated from Gas, Gasoline, Kerosene, and Gas-Oil Fractions. Utilizing in appropriate combination and sequence the methods discussed above,

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[b] Where amount of best sample isolated was sufficient, and sample was crystallizable, purity has been calculated from value of freezing point previously reported and present best values of freezing point for zero impurity and cryoscopic constants from API Research Projects 44 and 6. Where not evaluated cryoscopically, purity has been evaluated from physical properties or spectrographic measurements or both.

[c] Values for amount in the crude petroleum are rounded estimates subject to revision as data become available.

[d] Numerals in this column refer to published papers of API Research Project 6. List obtainable from the project, Carnegie Institute of Technology, Pittsburgh 13, Pa.

[e] Not determined.

[f] Determined spectrographically from measurements made in Socony-Vacuum Laboratories, Paulsboro, N. J.

[g] Determined spectrographically from measurements made in laboratories of Humble Oil and Refining Co., Houston, Tex.

[h] Unpublished.

[i] Identity not yet established.

[j] Determined spectrographically from measurements made in these laboratories: Humble Oil and Refining Co., Baytown, Tex.; Socony-Vacuum Laboratories, Paulsboro, N. J.; Standard Oil Development Co., Elizabeth, N. J.; Sun Oil Co., Norwood, Pa.

[k] Tentative; identification not complete.

[l] Purification of samples not completed because much purer samples were available from other sources.

API Research Project 6 has, by exhaustive fractionation from the gas, gasoline, kerosene, and gas-oil fractions of the large lot of the foregoing representative petroleum, separated 122 different hydrocarbon compounds, as of June 30, 1951. These compounds are listed in Table I, which gives the molecular formula, name, and type of the compound; its normal boiling point; the purity of the best sample of the given compound actually isolated in the work of the project; and the estimated amount of the given compound in the crude petroleum.

Table II gives the distribution of the 122 isolated compounds, by type of compound and boiling range.

Fractionation and Analysis of the Lubricant Fraction. Because of the greater complexity of the lubricant fraction and the lack of sufficient quantity of material, the resolution of the lubricant fraction of the Ponca, Okla., petroleum under investigation was carried to the stage of homogeneous fractions, each containing molecules of the same size and type.

The lubricant fraction was separated into four broad portions having quite different properties. The material was dewaxed at −18° C. with ethylene chloride to produce a "wax" portion containing, in addition to the true wax, a considerable portion of clear oil. The remaining material was then subjected to extraction at about 40° C. with liquid sulfur dioxide to produce a sulfur dioxide extract. The material insoluble in the sulfur dioxide was treated by adsorption with silica gel to produce a "water-white" oil and a portion representing the silica-gel holdup. The sulfur dioxide extract was brought into solution in liquid sulfur dioxide at −55° C., and extracted with petroleum ether at the same temperature to produce a petroleum ether–soluble portion and an "asphaltic" portion, the latter from the material remaining in the sulfur dioxide layer. The petroleum ether–soluble material was combined with the silica gel holdup to make what may be called the "extract oil" portion of the lubricant fraction. In this manner the original lubricant fraction was separated into the following four broad fractions: wax, 35%; asphaltic, 8%; extract oil, 22%; water-white oil, 35%.

A part of the wax portion, which contained a considerable amount of oil in addition to the true wax, was further processed by fractionation by adsorption and by treatment with urea to form adducts of the latter with the *n*-paraffins. The wax portion was found to contain about 8% of aromatic hydrocarbons, which had been imperfectly separated from the main bulk of the aromatic hydrocarbons occurring in the extract oil portion. Of the remaining 92% of the wax portion, about 39% was determined to be *n*-paraffins and 53% cycloparaffins, with possibly a relatively small amount of branched paraffins.

The asphaltic portion, the greater part of which was solid at room temperature and which contains all the black tarlike constituents, was placed in storage and was not further separated. The extract oil portion and the water-white oil portion were each subjected to an exhaustive separation with respect to molecular size and type.

Figure 1 illustrates the manner in which the water-white oil portion was fractionated exhaustively by distillation and extraction.

This oil was first subjected to a systematic distillation in high vacuum, through about eight stages, to produce a large number of substantially constant-boiling fractions. An indication of the properties of these fractions, which are mixtures of different types of molecules, is given in the two blocks, one at the low-boiling and one at the high-boiling end. These substantially constant-boiling fractions were then subjected to extraction with reflux in 46-foot columns, with acetone (plus some water for the more soluble fractions) as the solvent, to produce the final fractions shown in the lower part of the figure. The nature of these final fractions is indicated by the properties given in the blocks for the most soluble and the least soluble fractions of both the low-boiling and the high-boiling ends, together with one fraction in the center of the "spread" formation.

Figure 2 illustrates the exhaustive separation of the extract oil portion, by distillation and extraction. This material was processed in the same manner as the water-white oil, except that the extraction occurred in 55-foot columns with methyl cyanide (plus some acetone for the less soluble fractions) as the solvent. The nature of the final fractions is indicated by the properties in the blocks.

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The quantity of each of the final "homogeneous" fractions of both in water-white oil and extract oil portions was about 15 grams, representing $^{1}/_{40,000}$th part of the original crude petroleum from which it came, and consisted of compounds of substantially similar sizes and types. These fractions, although far from being pure compounds, appear to be nearer to pure compounds than any material (except *n*-paraffin hydrocarbons) hitherto separated from the lubricant fraction of any crude petroleum.

Both the wax and water-white oil portions of this lubricant fraction were substantially pure hydrocarbon material. The extract oil portion contained some sulfur, nitrogen, and oxygen compounds, but the bulk of the nonhydrocarbon material remained in the asphaltic portion. Analyses of the extract oil portion showed that the fractions of the distillate contained on the average about 0.9% sulfur, 0.1% nitrogen, and 0.5% oxygen. The final process of extraction distributed this nonhydrocarbon material among the various final homogeneous fractions as shown in the blocks in the lower part of Figure 2.

Types of Hydrocarbons in Lubricant Fraction. The following properties were determined for all the important final fractions from both the water-white oil and extract oil portions: molecular weight; content of carbon and hydrogen; content of sulfur, nitrogen, and oxygen; boiling point at a pressure of 1 mm. of mercury; density; refractive index, n_D; refractive dispersion, $n_F - n_C$; kinematic viscosity at 100° and 210° F.; and aniline point. The aromatic content of selected fractions of the extract oil portion was determined by hydrogenation. The foregoing properties were also determined for the hydrogenated material.

These data on the properties of the fractions of the water-white oil and extract portions were compared with those of known hydrocarbons of high molecular weight in order to deduce the kinds of molecules constituting the various fractions.

From all the data obtained, the following conclusions were drawn with respect to the types of hydrocarbons, and their corresponding amounts, occurring in the middle portion (near C_{30}) of the lubricant fraction of the large lot of the representative petroleum of the project:

n-Paraffins, about 14%
Branched paraffins, not measurable
Monocycloparaffins, with one ring plus appropriate paraffin side or connecting groups, about 10%
Dicycloparaffins, with two rings plus appropriate paraffin side or connecting groups, about 27%
Tricycloparaffins, with three rings plus appropriate paraffin side or connecting groups, about 15%
Mononuclear aromatics, containing one aromatic ring, plus one, two, or three cycloparaffin rings, plus appropriate paraffin side or connecting groups, about 10%
Dinuclear aromatics, containing two aromatic rings (probably condensed), plus one or two cycloparaffin rings, plus appropriate paraffin side or connecting groups, about 9%
Trinuclear aromatics, containing three aromatic rings (probably condensed), plus one (or possibly two) cycloparaffin ring, plus appropriate paraffin side or connecting groups, about 7%
Residue, about 8%

Table II. Distribution of Hydrocarbons Isolated from One Representative Petroleum[a]

Type of Compound	Fraction				Total
	Gas	Gasoline	Kerosene	Gas-oil	
n-Paraffins	4	6	2	5	17
Branched paraffins	1	35	..	..	36
Alkyl cyclopentanes	..	20	..	..	20
Alkyl cyclohexanes[b]	..	12	..	..	12
Alkylbenzenes	..	15	11	..	26
Alkyl cycloheptanes	..	1	..	..	1
Dicycloparaffins	..	1	1	..	2
Alkylnaphthalenes	..	..	3	1	4
Dicyclo-aromatic-cycloparaffins	..	..	4	..	4
Total	5	90	21	6	122

[a] By API Research Project 6 as of June 30, 1951.
[b] One may be an alkyl cyclopentane.

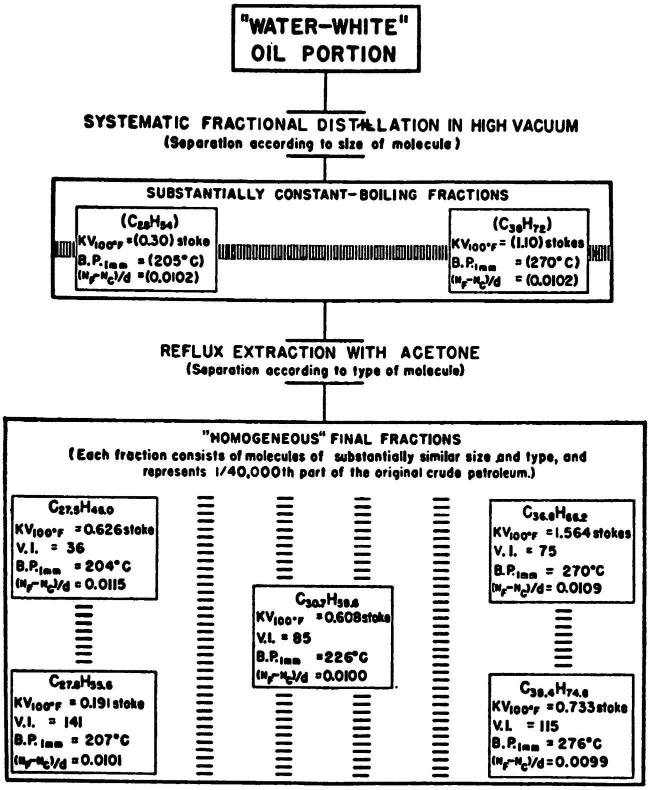

Figure 1. Exhaustive Separation of Water-White Oil Portion of Lubricant Fraction

Discussion. In connection with the hydrocarbons isolated from the gas, gasoline, kerosene, and gas-oil fractions of the project's one representative petroleum, the following points are of interest:

All of the normal paraffins, C_1 to C_{17}, have been isolated.

Of the branched paraffins, all of the four branched hexanes, all but two of the eight branched heptanes, and all but two of the seventeen branched octanes are included.

Of the alkyl cyclopentanes, cyclopentane, methylcyclopentane, all but one of the six C_7 isomers, and all but four of the fifteen C_8 isomers are included.

Of the alkyl cyclohexanes, cyclohexane, methylcyclohexane, and all but one of the eight C_8 isomers are included.

Of the alkyl benzenes, benzene, toluene, all of the four C_8 isomers, and all of the eight C_9 isomers are included.

The relation between the number of substituents on the main nucleus of the molecule and the relative amount of the sum of the isomers having given numbers of substituents is:

Among the isomeric branched octanes, the approximate relative amounts of the singly, doubly, and triply branched isomers are: sum of the four singly branched isomers, 100; sum of the eight doubly branched isomers, 30; sum of the four triply branched isomers, 1.

Among the isomeric C_7 alkyl cyclopentanes, the approximate relative amounts of the monoalkyl and the sum of the dialkyl isomers are: ethyl isomer, 1; sum of the five dimethyl isomers, 10.

Among the isomeric C_8 alkyl cyclopentanes, the approximate relative amounts of the monoalkyl, dialkyl, and trialkyl isomers are: *n*-propyl plus isopropyl, 1; sum of the five methylethyl isomers, 10; sum of the eight trimethyl isomers, 30.

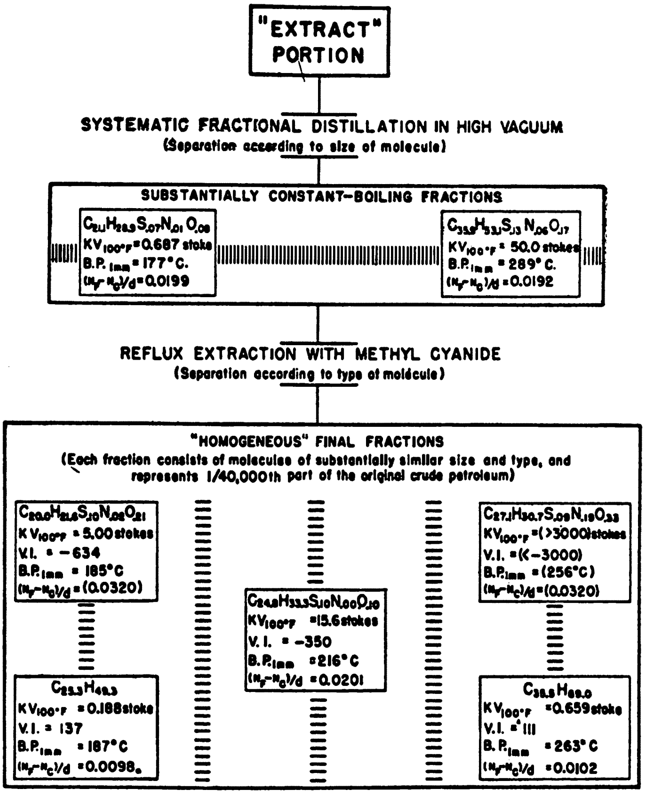

Figure 2. Exhaustive Separation of Extract Oil Portion of Lubricant Fraction

Among the isomeric C_8 alkyl cyclohexanes, the approximate relative amounts of the mono and dialkyl isomers are: ethyl isomer, 1; sum of the seven dimethyl isomers, 7.

Among the isomeric C_8 alkyl benzenes, the approximate relative amounts of the monoalkyl and dialkyl isomers are: ethyl isomer, 1; sum of the three dimethyl isomers, 5.

Among the isomeric C_9 alkyl benzenes, the approximate relative amounts of the monoalkyl, dialkyl, and trialkyl isomers are: *n*-propyl plus isopropyl, 1; sum of the three methylethyl isomers, 3; sum of the three trimethyl isomers, 5.

Figure 3 gives a plot of the percentage of the gasoline fraction, 40° to 180° C., constituted by any given number of components, with the components taken in the order of their abundance—the most abundant being counted first, the next most abundant being counted second, and so on. From this plot, one sees that a relatively large portion of the gasoline fraction is constituted by a relatively small number of components, although the total number of different hydrocarbons present in the gasoline fraction in any amount is of the order of 500. For this petroleum, Figure 3 gives the relation between the number of components and the percentage of the gasoline fraction, 40° to 180° C., constituted by them as: 18%, 3 components; 36%, 7 components; 54%, 16 components; 72%, 40 components; 80%, 73 components; 81%, 88 components.

In connection with the analysis of the lubricant fraction of the project's representative petroleum, the striking part is that branched paraffins are not present in any measurable amount and that, except in the residue portion, purely aromatic hydrocarbons (containing aromatic rings plus appropriate paraffin side or connecting groups) are not present in any measurable amount.

Figure 4 shows the relative amounts of the different types of hydrocarbons present in the several broad fractions of the petroleum, including the gasoline, kerosene, gas-oil, and lubricant fractions for the project's one representative petroleum. The scale above the chart gives the normal boiling point in degrees Fahrenheit. The scales below the chart show the normal boiling point in degrees centigrade (Celsius), and the location, in terms of this true normal boiling point, of the various members of the series of *n*-paraffins, the series of alkyl cyclopentanes, the series of alkyl cyclohexanes, the series of alkyl benzenes, the series of condensed polycycloparaffins, and the series of condensed polynuclear aromatics. This chart is based upon the data so far obtained by the project and is subject to change as new data become available. The values given for the material normally boiling in the range 300° to 400° C. or C_{17} to C_{25} *n*-paraffins have been entirely interpolated from the values for the neighboring regions. Small quantities of tetracycloparaffins and tetranuclear aromatics are included in the types of compounds occurring in the lubricant fraction. Also, a very small amount of branched paraffins is shown in the lubricant fraction, although the amount present is so small as not to be measurable as yet. The range ordinarily covered by the gasoline, kerosene, gas-oil, and lubricant fractions is shown approximately at the top of Figure 4, though the exact lines of demarcation of such fractions are arbitrary.

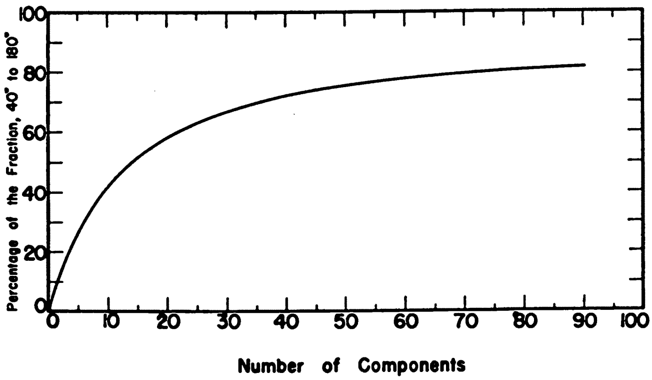

Figure 3. Relation between Number of Components and Amount of Gasoline Fraction They Constitute

The values given in Figure 4 for the relative amounts of the different types of hydrocarbons in the several broad fractions are more reliable for some of the fractions than for others. The data for the gasoline fraction, 40° to 180° C., are very reliable; the data for the kerosene fraction, 180° to 230° C., are fairly reliable; in the light gas-oil fraction, 230° to 300° C., the data for the *n*-paraffins and mononuclear and dinuclear aromatics are reliable, while the values for the branched paraffins and cycloparaffins are less reliable; for the heavy gas-oil and light lubricant fraction, 300° to 400° C., the values are all interpolated from the values for the light gas-oil and the lubricant fraction; for the lubricant fraction, all the values are reliable.

Hydrocarbons in Different Petroleums

The results obtained by API Research Project 6 from the exhaustive fractionation of the gasoline fraction of one representative petroleum serve to indicate what hydrocarbon compounds are in the gasoline fraction of petroleum and the amounts which may be expected to be present in a petroleum of intermediate type. In order to obtain information as to how the amounts of the hydrocarbon components vary in petroleums of appreciably different type, an investigation has been made of the hydrocarbons in the gasoline fraction of seven representative petroleums. The present status of the work of API Research Project 6 is summarized here, including the results of earlier investigations plus some unpublished results (*45*).

The seven naphthas investigated are listed in Table III, which gives the field from which the petroleum was produced, the general type of the naphtha, the content of sulfur, and the content of aromatic hydrocarbons. The intermediate naphtha labeled Ponca, Okla., is from the same petroleum used in American Petroleum Institute Research Project 6.

In this work it was found that while the relative amounts of the main classes of hydrocarbons in the gasoline fraction varied from petroleum to petroleum, the relative amounts of the individual compounds within a given class were of the same magnitude for the different petroleums.

Table III. Gasoline Fraction of Seven Representative Petroleums

Source	Supplier	Type	Sulfur Content, % by Weight	Aromatic Hydrocarbon Content, % by Volume
Ponca, Okla.	Continental Oil Co.	Intermediate	0.017	9.8 ± 0.2
East Texas	Standard Oil Development Co.	Intermediate	0.033	10.4 ± 0.2
Bradford, Pa.	Quaker State Oil Refining Co.	High in paraffins	0.012	8.3 ± 0.3
Greendale-Kawkawlin, Mich.	Pure Oil Co.	High in *n*-paraffins	0.014	7.2 ± 0.2
Winkler, Tex.	Standard Oil Co. (Indiana)	High in isoparaffins	0.159	4.9 ± 0.2
Midway, Calif.	Standard Oil Co. of California	High in cycloparaffins	0.045	9.0 ± 0.2
Conroe, Tex.	Humble Oil & Refining Co.	High in aromatics	0.002	27.6 ± 0.5

This is illustrated by the following data:

The relative amounts of the four *n*-paraffins were: C_6, 23 ± 3; C_7, 27 ± 4; C_8, 24 ± 2; C_9, 26 ± 3. The total amounts of the four *n*-paraffins varied from 5% in one sample to 43% in another.

The relative amounts of the two dimethylbutanes and the two methylpentanes were: the two dimethylbutanes, 14 ± 2; the two methylpentanes, 86 ± 2. The total amounts of these components varied from 2.6% in one sample to 6.6% in another.

The relative amounts of the C_5, C_6, and C_7 alkylcyclopentanes were: C_5, 4 ± 1; C_6, 35 ± 8; C_7, 61 ± 9. The total amounts of these components varied from 3.4% in one sample to 13.8% in another.

The relative amounts of the C_6 and C_7 cyclohexanes were: C_6, 28 ± 4; C_7, 72 ± 4. The total amounts of these components varied from 2.1% in one sample to 13.7% in another.

The relative amounts of the C_6, C_7, and C_8 alkylbenzenes were: C_6, 7 ± 2; C_7, 31 ± 4; C_8, 62 ± 5. The total amounts of these components varied from 1.3% in one sample to 19.5% in another.

Similar relative magnitudes were found among the individual C_8 alkylbenzenes, the individual C_9 alkylbenzenes, and the C_6 and C_7 branched paraffins.

On the basis of the results obtained, the following conclusions are made with regard to the composition of the gasoline fraction of different petroleums:

The gasoline fraction of different crudes may be characterized by specifying the relative amounts of the following five main classes of hydrocarbons: *n*-paraffins, branched paraffins, alkyl cyclopentanes, alkyl cyclohexanes, and alkyl benzenes.

The gasoline fractions of different crudes are composed of the same hydrocarbons, the differences from one crude to another being essentially in the relative amounts of the foregoing five classes of hydrocarbons.

Within each of these five classes, the individual hydrocarbons in the gasoline fraction occur in proportions which are of the same order of magnitude for different petroleums.

With adequate data on one representative petroleum, it appears possible to predict the order of magnitude of the amounts of the individual hydrocarbons in an appropriate fraction of a given naphtha when the relative amounts of the foregoing five classes of hydrocarbons are known, or alternatively for each class, the amount of one of the main components of that class is known.

In line with the findings of API Research Project 6 regarding the hydrocarbons in different petroleums, it is interesting and important to note that the results obtained in the investigations of other workers on different petroleums are in substantial accord with the conclusions drawn above. In particular, attention may be called to the following investigations in this regard:

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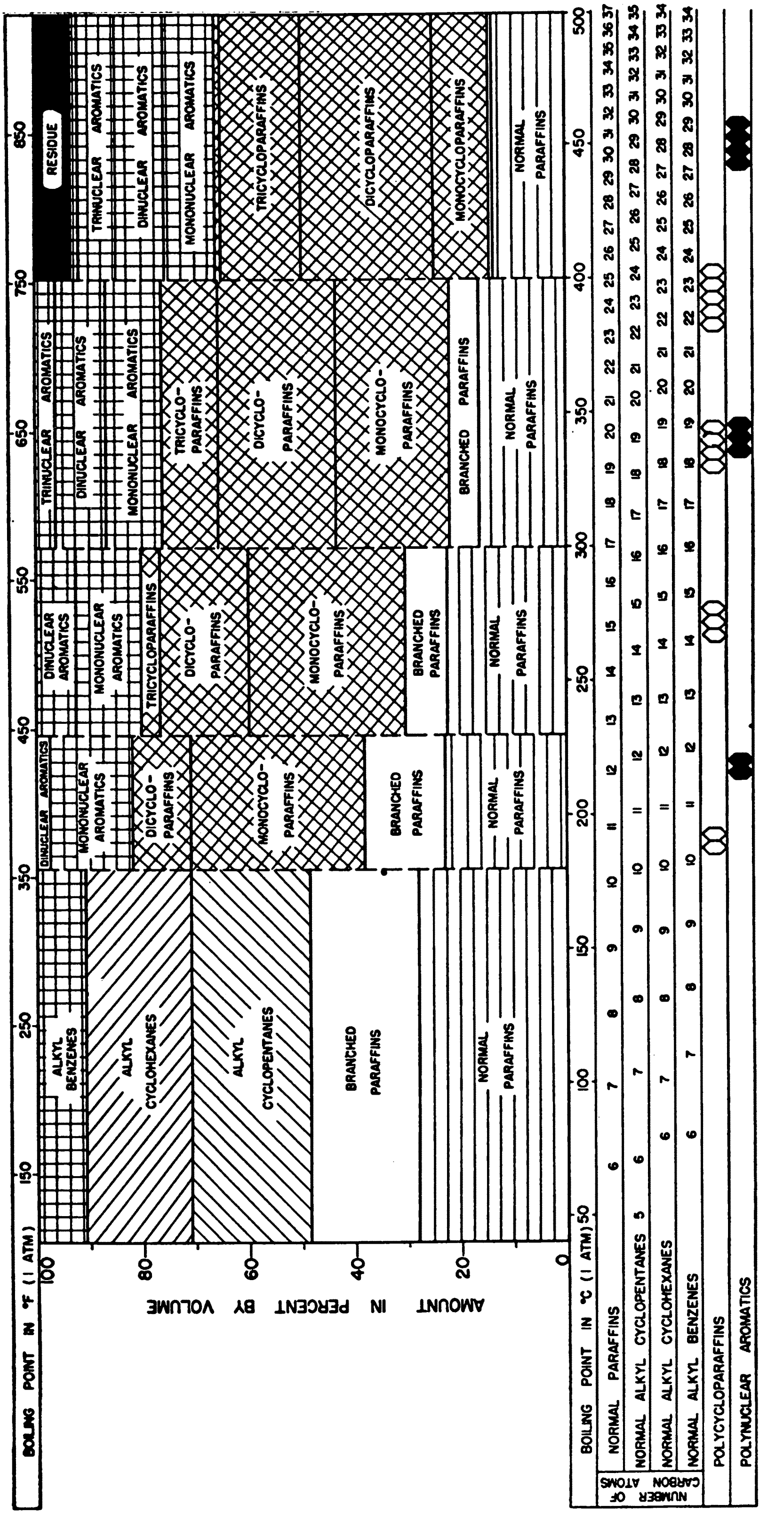

Figure 4. Relative Amounts of Different Types of Hydrocarbons in Several Broad Fractions of One Representative Petroleum

On the gasoline fraction: Fenske, Tongberg, and Quiggle (*14*, *58*); Gooding, Adams, and Rall (*23*); Ward, Gooding, and Eccleston (*59*); Bell (*4*); and Cady, Marschner, and Cropper (*9*).

On the kerosene or gas-oil fractions: Smith (*57*) and Charlet, Lanneau, and Johnson (*10*).

On the lubricant fraction: Lillard, Jones, and Anderson (*29*).

Conclusion

From the present state of our knowledge of the composition of petroleum, the following general conclusions may be drawn:

Small but frequently very significant amounts of sulfur, nitrogen, oxygen, and metallic components must be considered in the processing of petroleum.

Different crude petroleums may vary greatly with regard to the abundance of the hydrocarbon components as a function of the number of carbon atoms per molecule or in boiling range—that is, some petroleums may have a preponderance of the more volatile fractions while others may have a large amount of the less volatile lubricant fractions.

Considering equivalent amounts of the same broad fractions, it will be expected that different petroleums will contain the same hydrocarbons but in varying amounts.

Different petroleums will vary because of differences in the relative amounts of the main classes of hydrocarbons.

Within a given class of hydrocarbons, it will be expected, as a first approximation, that the individual compounds will be present in relative amounts which are of the same magnitude for the different petroleums.

It is planned that the work of API Research Project 6 on the exhaustive examination of one representative crude petroleum will be continued into those portions not yet fully investigated. With firm and reliable data on the components in a given portion of one representative petroleum, short-cut methods may then be developed with confidence for the rapid examination of similar portions of other petroleums.

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Relation of Properties to Molecular Structure for Petroleum Hydrocarbons

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Two methods of approach are used in considering the relationship of properties to molecular structure for hydrocarbons: to observe the changes produced as one moves from point to point (1) along the subseries curve in the direction of increasing chain length, and (2) along a cross-sectional line at any given carbon atom level. The actually measured values of the property under investigation or the magnitude of the deviation from corresponding point on the curve for the normal isomer may be observed. Chain length, chain branching, methyl groups, double bonds, and aromatic nuclei play a dominant role in determining the properties of a hydrocarbon. A careful analysis of the changes brought about by varying these elements of molecular structure leads to the conclusion that the properties, both physical and chemical, are a function of the electron distribution within the hydrocarbon molecule. Much has been accomplished in the synthesis, separation, purification, and careful determination of both physical properties and engine characteristics. Much still remains to be done, but the work is progressing. There still lie ahead a more careful correlation of chemical properties with structure, and a study of the relative rates of reactivity for the hydrogen atoms on the different parts of the hydrocarbon molecule and the effects which these differences impose upon the velocity of combustion.

Relation of Physical Properties and Chemical Constitution" was the title of a book published in 1920 by Kauffmann (*20*). It lists the freezing and boiling points of the normal paraffins and records the increments of rise with the addition of each methylene group. The same year Thomas Midgley (*26*) observed wide differences in the combustion of fuels in internal combustion engines. The differences were found not only in different classes of hydrocarbons but also between isomeric hydrocarbons of the same class.

The following year Ricardo (*27*) published the results of investigations on the highest useful compression ratio of a number of hydrocarbons and found a wide variation among different fuels in this respect. Since that time the relations between physical properties of hydrocarbons and their molecular structure on the one hand, and the knocking characteristics of the same hydrocarbons and their molecular structure on the other, have received more intensive study.

Graham Edgar (*12*) in 1927 proposed the use of mixtures of *n*-heptane and 2,2,4-trimethylpentane, commonly known as isooctane, as standards for rating fuels for knock. Two years later the same investigator, together with Calingaert and Marker (*13*), made a

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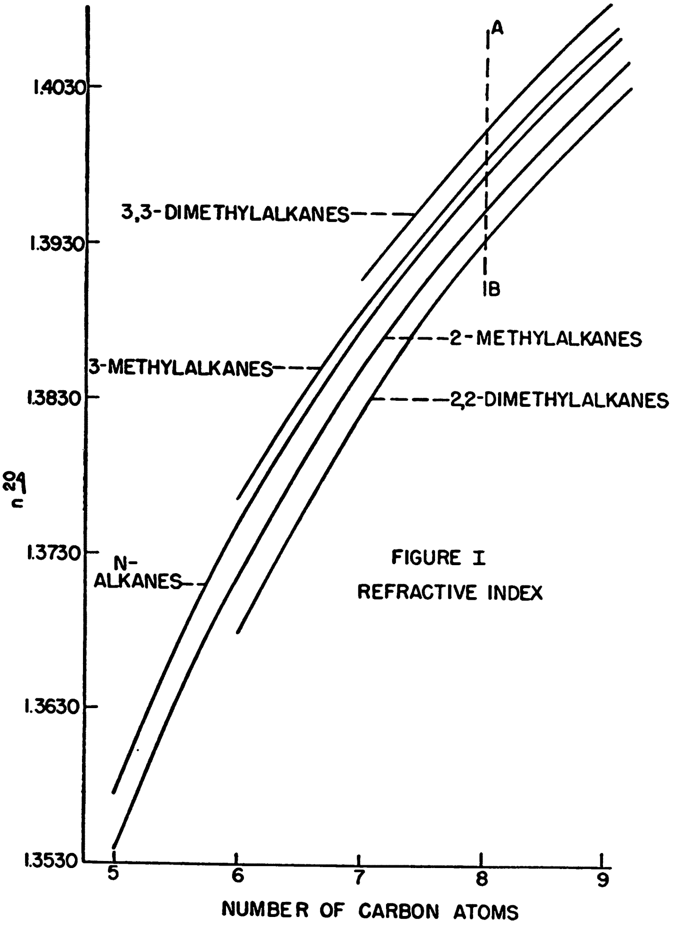

FIGURE I
REFRACTIVE INDEX

comprehensive study of the synthesis and characterization of the isomeric heptanes. By 1931 Shepard, Midgley, and Henne (*31*) had isolated, from a paraffinic gasoline, the normal paraffins from pentane to dodecane, inclusive, in quantity and high purity; and they had carefully determined the physical properties.

The petroleum refiners were not idle. Around the turn of the century C. F. Mabery (*25*) had amply demonstrated the fundamental hydrocarbon nature of petroleum oil. In 1927 the American Petroleum Institute established at the National Bureau of Standards a research project for the purpose of separating and identifying the component parts of a typical mid-continent crude (*29*). This project, commonly known as A.P.I.–R.P. 6—first under the leadership of E. W. Washburn and, after his death, under the direction of F. D. Rossini—had by the end of 1948 separated and identified 91 hydrocarbons from the selected crude. The work in the low boiling range has been completed and is continuing on the hydrocarbons of the high boiling range. The separation and identification of the components of a typical crude are not the sole accomplishments of Dr. Rossini and his associates. The development and perfection of methods for the separation and purification of hydrocarbons and the establishment of criteria of purity have been of equal value (*28*).

The automotive engineers were also busy. In 1931 Lovell, Campbell, and Boyd (*23*) published data on an extended series of pure paraffin and olefin hydrocarbons in fairly dilute solution in gasoline. These data showed a number of definite relations between the molecular structure of the pure hydrocarbon and the tendency of the fuel to knock. The

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following year Garner and his associates (*16*), a group of British investigators, published similar data on blends of olefins and on naphthene and aromatic hydrocarbons. In 1934 Lovell, Campbell, and Boyd (*24*) published extensive information on about 100 hydrocarbons in the pure state.

The petroleum refiner, by the mid-thirties, was faced with two problems: (*a*) What hydrocarbon constituents did his gasolines and low boiling naphthas contain? and (*b*) What were the knocking characteristics of each of these constituents?

It was in this atmosphere that the American Petroleum Institute Hydrocarbon Research Project, later to be known as A.P.I.–R.P. 45, was established in 1938 (*2*). Now after 13 years of operation, 298 pure hydrocarbons, as well as other products, have been tested, some under as many as 29 sets of engine conditions. Two hundred forty-six of these products were synthetically produced and/or purified in the project's Hydrocarbon Laboratory at the Ohio State University.

So acute was the need for accurate data on freezing point, boiling point, refractive index, density, and the spectrographic fingerprints of pure hydrocarbons that two new projects were set up. These included A.P.I.–R.P. 44, a project for the collection, evaluation, and distribution of physical, chemical, and thermodynamic data (*1*), and A.P.I.–R.P. 46, a project for the preparation and distribution of standard spectrometric samples (*3*). A.P.I.–R.P. 45 made substantial contribution to these new ventures.

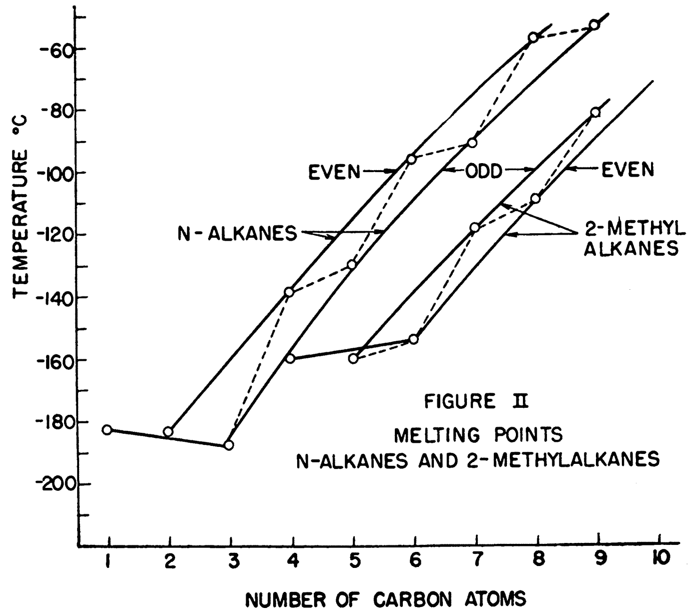


FIGURE II
MELTING POINTS
N-ALKANES AND 2-METHYLALKANES

Just as the improvements in our knowledge of the physical properties and performance of the hydrocarbon constituents of gasoline enable us to make better gasolines, so would an extension of our knowledge of the properties and performance of lubricating oils enable us to make better lubricating oils. To provide such data A.P.I.–R.P. 42 was established at Pennsylvania State College in 1944 (*4*), first under the leadership of the late F. C. Whitmore and more recently under the direction of Robert Schiessler.

These cooperative programs, with the generous support and contributions from the research laboratories of the petroleum and automotive industries, are filling in a scientific background against which these industries can view their technical advances. Petroleum refiners can now evaluate their refining, cracking, and reforming processes scientifically upon the basis of the quality of the products these processes produce. And if they are sufficiently ingenious they can devise semisynthetic and total-synthesis methods for the production of specialty products. These refiners no longer operate by rule of thumb.

Table I. Deviation of Physical Constants

Hydrocarbons	Normal Value	Series Deviation	2-Me	3-Me	4-Me
Melting point deviation, ° C.					
Butanes	−138.33	(−)	−21.27	...	...
Pentanes	−129.72	+8.61	−30.17	...	...
Hexanes	−95.32	+34.2	−58.36	(−)	(−)
Heptanes	−90.60	+4.72	−27.68	(−)	(−)
Octanes	−56.80	+33.8	−52.24	−63.70	−64.16
Nonanes	−53.60	+3.2	−26.8	−53.9	−59.6
Boiling point deviation, ° C.					
Butanes	−0.50	(−)	−11.23	...	...
Pentanes	36.07	+36.57	−8.22	...	...
Hexanes	68.74	+32.67	−8.47	−5.46	...
Heptanes	98.43	+29.69	−8.38	−6.48	...
Octanes	125.67	+27.24	−8.02	−6.69	−7.95
Nonanes	150.80	+25.13	−7.66	−6.62	−8.32
Refractive index deviation, n_D^{20}					
Pentanes	1.35748	(−)	−0.00405	...	...
Hexanes	1.37486	+0.01738	−0.00341	+0.00166	...
Heptanes	1.38764	+0.01278	−0.00274	+0.00101	...
Octanes	1.39745	+0.00981	−0.00250	+0.00057	+0.00047
Nonanes	1.40549	+0.00804	−0.00239	+0.00007	+0.0006
Density deviations, d_4^{20}					
Butanes	0.5788	(−)	−0.02160	...	...
Pentanes	0.62624	+0.04744	−0.00657	...	...
Hexanes	0.65937	+0.03313	−0.00622	+0.00496	...
Heptanes	0.68368	+0.02431	−0.00503	+0.00432	...
Octanes	0.70260	+0.01892	−0.00470	+0.00322	+0.00203
Nonanes	0.71770	+0.01510	−0.00430	+0.00300	+0.00220

Molecular structure in organic chemistry is based upon the two fundamental principles of homology and isomerism. The hydrocarbons, the simplest of organic derivatives, are divided into two great groups, cyclic and noncyclic in structure. The paraffins form the basis of the noncyclic group, inasmuch as the monoolefins, diolefins, and acetylenes may be regarded as derivatives of the parent hydrocarbon having the same arrangement of carbon atoms.

In like manner the cycloparaffins form the structural basis of the cyclic group. Cycloolefins, -diolefins, and -triolefins may be regarded as derivatives of the cycloparaffins having the same carbon skeleton. The aromatic series forms a particular case among the cyclohexatrienes, in which the three double bonds are spaced symmetrically around a six-atom carbon ring.

The term homologous series is used both generically and specifically. When one speaks of the paraffin series the term is being used generically. Such a concept does not express the whole truth. The normal paraffins form a simpler and more logical series, whereas the 2-methylalkanes, 3-methylalkanes, and 2,2-dimethylalkanes each form analogous series having a characteristic structural group. The paraffins are therefore to be regarded as a collection of many subseries, the collection growing more numerous and the structure more complex as the number of carbon atoms is increased.

When the refractive indices of the paraffins are plotted against carbon content, a compact family of curves may be drawn, each representing a characteristic type of structure. Figure 1 shows the simpler paraffins plotted in this manner. When one follows any one of these subseries curves from point to point, in the direction of increasing carbon content, there is an intensification of physical properties. The structural changes are those characteristic of homology and involve an increase in both chain length and molecular weight.

When one moves from point to point along the indicated cross section *A-B* in Figure 1, the structural changes are those of isomerization. The isomerization may involve either a change in the position of the side chain along the principal chain or an increase in the number of side chains. In isomerization there is no change in the carbon content or molecular weight, but an increase in the number of side chains is accompanied by a diminution in the principal chain length.

Any study of the relation of physical constants or engine characteristics of a hydrocarbon to its molecular structure will, therefore, be made by observing the changes produced either by moving from point along the subseries curve, increasing or decreasing the

of Normal, Methyl, and Dimethyl Alkanes

Isomer Deviation					
2,2-Me$_2$	2,3-Me$_2$	2,4-Me$_2$	2,5-Me$_2$	3,3-Me$_2$	3,4-Me$_2$
(−)	...	...	...	...	...
−113.12	...	...	...	...	...
−4.41	−33.19	...	...	...	...
−33.20	(−)	−28.63	(−)	−43.86	...
−64.38	(−)	(−)	−34.40	−69.20	(−)
(−)	(−)	(−)	(−)	(−)	(−)
...	...	...	...	...	...
−26.57	...	...	...	...	...
−19.00	−33.19	...	...	...	...
−19.22	(−)	−17.86	...	· 12.36	...
−18.82	−10.06	−16.24	−16.56	-13.70	−7.94
(−)	(−)	(−)	(−)	(−)	(−)
...	...	...	...	...	...
−0.00610	+0.00009	...	...	...	...
−0.00547	+0.00436	−0.00614	...	+0.00326	...
−0.00396	+0.00383	−0.00454	−0.00499	+0.00264	+0.00673
(−)	(−)	(−)	(−)	(−)	(−)
...	...	...	...	...	...
(−)	...	...	...	...	...
−0.01020	+0.00227	...	...	...	...
−0.00982	+0.01126	−0.01088	...	+0.00956	...
−0.00732	+0.00964	−0.00224	−0.00905	+0.00740	+0.01670
(−)	(−)	(−)	(−)	(−)	(−)

principal chain length, or from point to point along a cross-sectional line, *A-B*. Such a cross-sectional perspective may be had at any given carbon content and will become more and more complex as the number of carbon atoms is increased.

The observations will be made in the first case by comparing the measured experimental values, or the increments of change as one moves from point to point along the subseries curve. The observations will be made in the case of isomerization either by arranging the measured values in an ascending or descending series or by comparing the increments of deviation from the normal or parent hydrocarbon. Sometimes one and sometimes the other method of comparison seems to be the more revealing. Since data of highest accuracy are available for only a relatively small number of hydrocarbons, all of low molecular weight, one is not able to plot the subseries curves over an extended range. After the structural group characteristic of any subseries has been fully developed it is usually true that the order of intersection along any cross-sectional line remains the same. The relative orders for boiling points, densities, and refractive indices are the same although the position of the group with respect to the normal or parent hydrocarbon may be changed. These cross-sectional relations are useful since they may be shown by tabulation as well as by curves and are not invalidated by missing data.

Tables I to IV show the melting points, boiling points, refractive indices, and densities of the simpler paraffins and monoolefins tabulated in this manner. The comparisons are made on the basis of deviations at each cross-sectional level. Tables V to VII show the same physical constants for the aromatic hydrocarbons and a group of cis-trans isomers. In the latter cases the comparisons are made between the actually measured values.

Melting Points

It has long been known that the melting points of the normal paraffins do not fall on a smooth curve (*10, 20*). When the melting points are plotted against carbon content, alternately large and small increases in the values are revealed. Two smooth curves may be drawn, one connecting the melting points of the normal paraffins having even numbers of carbon atoms and the other connecting those having odd numbers. In other words, the normal paraffins are separated into two series on the basis of their melting points, as shown in Figure 2. Alternation is also characteristic of the melting points of the 2-methylalkanes (Figure 2 and Table I), and the butylbenzenes (Table V). It has frequently been observed that the properties of the first member of an homologous series are anomalous. This is true for the melting points of the first members of both the odd and even series of *n*-paraffins.

Closer examination of Figure 2 shows that the phenomenon of alternation is more a function of chain length than of carbon content, since in the 2-methylalkane series the relative positions of the odd and even series are reversed from that characteristic of the normal series.

The study of Tables I and II has revealed the fact that isomerization of a normal paraffin to an isoparaffin produces certain specific and characteristic changes in the physical constants as the methyl group is moved from point to point along the chain. In a paper presented before the Refining Division of the American Petroleum Institute in November 1942, attention was called by this author to alternation in the melting points of the *n*-octenes and *n*-octynes as the point of unsaturation is moved from position 1 to 2 to 3 to 4 (*5*). Now that the cis-trans pairs have been separated and more highly purified, the alternation remains characteristic of both forms, although the data on the cis forms are not fully verified.

MELTING POINTS OF *n*-OCTENES AND *n*-OCTYNES, ° C.

	cis	trans		
1-Octene	102.4		1-Octyne	−79.5
2-Octene	−100.3	−87.4	2-Octyne	−62.0
3-Octene	−126	−110.0	3-Octyne	−105.0
4-Octene	−118.7	−93.7	4-Octyne	−109.9

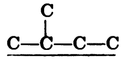
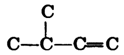
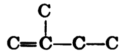
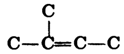
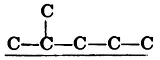
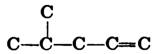
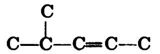
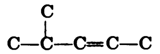
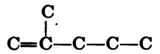
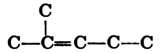
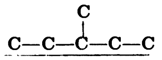
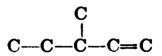
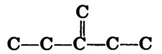
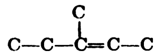
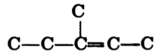
Boiling Points

The boiling points of the noncyclic hydrocarbons show the usual series relations. The increment of rise of the boiling point with increasing carbon content, for the lower members, is nearly constant, as illustrated by the 2-methyl-, 3-methyl-, and 2,2-dimethylalkanes (columns 4, 5, and 7, respectively, of Table I). As the carbon content is further increased, the increment becomes smaller, the subseries curves converging on the curve for the normal hydrocarbons. Every isoparaffin boils at a lower temperature than does the corresponding normal paraffin of the same carbon content; this again shows the influence of chain length. The increment of deviation from the normal isomer becomes less as the methyl group side chain is moved toward the middle of the principal chain, as is illustrated by the 2-methyl-, 3-methyl-, and 4-methylheptanes or the 2,2-dimethyl- and 2,5-dimethyl- *vs.* the 3,4-dimethylhexanes (columns 4, 5, 6, and 7, 10, 12, respectively, Table I).

Table II. Deviation of Physical Constants of Normal Mono-olefins

Parent Hydrocarbons	Normal Value	Series Deviation from Paraffin	Isomer Deviation					
			2 (=)		3 (=)		4 (=)	
			cis	trans	cis	trans	cis	trans
Melting point, ° C.								
Butane	−138.33	−47.02	+46.44	+79.80	...	...	...	...
Pentane	−129.72	−35.50	+13.85	+24.98	...	...	...	...
Hexane	−95.32	−44.58	−1.32	+5.64	+1.5	+26.30	...	...
Heptane	−90.60	−28.60	...	...	...	...	...	...
Octane	−56.80	−45.6	+2.4	+14.7	...	+7.6	+17.6	+8.9
Boiling point, ° C.								
Butane	−0.50	−5.76	+2.54	+5.38	...	...	...	...
Pentane	36.07	−6.10	+7.13	+6.39	...	...	...	...
Hexane	68.74	−5.28	+5.14	+4.44	+4.14	+4.64	...	...
Heptane	98.43	−5.13	+5.2	+4.7	...	...	...	...
Octane	125.67	−4.40	+4.3	+3.7	+1.6	+2.0	+1.5	+1.1
Refractive index, n_D^{20}								
Butane	(−)	(−)	(−)	(−)	...	...	...	...
Pentane	1.3575	+0.0139	+0.0116	+0.0079	...	...	...	...
Hexane	1.3749	+0.0127	+0.0078	+0.0058	...	...	...	...
Heptane	1.3876	+0.0118	+0.0066	+0.0066	...	...	...	...
Octane	1.3975	+0.0112	+0.0062	+0.0044	+0.0047	+0.0038	+0.0056	+0.0030
Density, d_4^{20}								
Butane	0.5788	+0.0163	+0.0262	+0.0091	...	...	...	...
Pentane	0.6262	+0.0148	+0.0150	+0.0072	...	...	...	...
Hexane	0.6595	+0.0140	+0.0111	+0.0046	+0.0062	+0.0045	...	...
Heptane	0.6896	+0.0073	+0.0112	+0.0072	(+0.0032)		...	...
Octane	0.7026	+0.0134	+0.0083	+0.0039	+0.0049	+0.0008	+0.0065	+0.0019

Table III. Physical Constant Deviation of Branched Olefins

Structure	Olefin Type	Melting Point, ° C.	Boiling Point, ° C.	Refractive Index, n_D^{20}	Density d_4^{20}
2-Methylbutane derivatives					
 $C-\overset{C}{\overset{\vert}{C}}-C-C$	....	159.89	27.85	1.3537	0.6197
 $C-\overset{C}{\overset{\vert}{C}}-C{=}C$	I	−8.61	−7.78	+0.0106	+0.0075
 $C{=}\overset{C}{\overset{\vert}{C}}-C-C$	III	+22.33	+3.25	+0.0241	+0.0307
 $C-\overset{C}{\overset{\vert}{C}}{=}C-C$	IV	+26.11	+10.68	+0.0337	+0.0426
2-Methylpentane derivatives					
 $C-\overset{C}{\overset{\vert}{C}}-C-C-C$	....	−153.68	60.27	1.3715	0.6532
 $C-\overset{C}{\overset{\vert}{C}}-C-C{=}C$	I	−0.16	−6.32	+0.0113	+0.0107
 $C-\overset{C}{\overset{\vert}{C}}-C{=}C-C$	II trans	....	−5.27	+0.0165	+0.0168
 $C-\overset{C}{\overset{\vert}{C}}-C{=}C-C$	II cis	....	−1.87	+0.0175	+0.0188
 $C{=}\overset{C}{\overset{\vert}{C}}-C-C-C$	III	+17.52	+0.31	+0.0210	+0.0288
 $C-\overset{C}{\overset{\vert}{C}}{=}C-C-C$	IV	+18.64	+6.99	+0.0289	+0.0331
3-Methylpentane derivatives					
 $C-C-\overset{C}{\overset{\vert}{C}}-C-C$	....	(−)	63.28	1.3765	0.6643
 $C-C-\overset{C}{\overset{\vert}{C}}-C{=}C$	I	(−153.0)	+9.48	+0.0075	+0.0032
 $C-C-\overset{C}{\overset{\Vert}{C}}-C-C$	III	(−131.96)	+1.67	+0.0129	+0.0251
 $C-C-\overset{C}{\overset{\vert}{C}}{=}C-C$	IV trans	(−135.3)	+4.52	+0.0176	+0.0299
 $C-C-\overset{C}{\overset{\vert}{C}}{=}C-C$	IV cis	(−138.4)	+7.24	+0.0205	+0.0343

The same type of phenomenon is found in the boiling point relations of the normal olefins, as is evidenced by the diminishing increments of deviation as the double bond is moved from position 1 to 2 to 3 to 4 along the normal octene chain (Table II).

The alternation so characteristic of the melting points does not appear, and each subseries of hydrocarbons shows a smooth curve when the boiling points are plotted against carbon content. As was pointed out in the previous paper (*5*), alternation is again revealed when one considers the increment of rise in the boiling point brought about by replacing each hydrogen atom of a parent hydrocarbon in turn by a methyl group. Let us consider, for example, *n*-heptane. If one substitutes a methyl group for hydrogen successively upon carbon atoms 1, 2, 3, and 4 the isomers *n*-octane, 2-methylheptane, 3-methylheptane, and 4-methylheptane will be produced. The increments of boiling point rise produced by these substitutions form an alternating series. A more extensive examination of such data shows that when a heptane is converted into the corresponding octane, the increment of rise in the boiling point is a function of the length of the uninterrupted chain fragment produced. The point is illustrated by the following tabulation:

Change in Length of Chain Fragment	No. of Cases	Av. Increment, ° C.
CH_3 to $CH_3{-}CH_2$	6	31.3
$CH_3{-}CH_2$ to $CH_3{-}CH_2{-}CH_2$	4	25.7
$CH_3{-}CH_2{-}CH_2$[a] to $CH_3{-}CH_2{-}CH_2{-}CH_2$[a]	4	27.4

[a] Or longer.

Refractive Index and Density

The refractive indices and the densities of the alkanes vary in an analogous manner. As one moves from point to point along any subseries curve, the refractive indices and densities increase with each added carbon atom. The increments of deviation become smaller with increasing molecular weight so that the subseries curves converge upon those of the normal alkanes. It has been shown repeatedly that methyl groups in position 2 tend to lower the density and refractive index. Two methyl groups in the 2,2- or the 2,2′- are still more effective. A methyl group in position 3 sharply increases the density or refractive index (*13*) and two methyl groups in this position are more effective than one. These effects are revealed by the positive and negative increments in the isomerization portion of Table I.

When a point of unsaturation is introduced into the 1 position of a normal alkane the refractive index and density are increased. The increase is greatest for the hydro-

Table IV. Additivity of Physical Constants

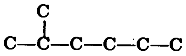
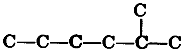
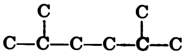
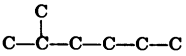
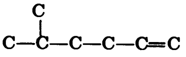
Structure	Melting Point, ° C.	Boiling Point, ° C.	Refractive Index, n_D^{20}	Density, d_4^{20}
Normal hexane derivatives				
C—C—C—C—C—C	−95.32	68.74	1.3749	0.6594
2,5-Dimethylhexane				
 $C-\overset{C}{\overset{\vert}{C}}-C-C-C-C$	−22.95	+21.31	+0.0100	+0.0193
 $C-C-C-C-\overset{C}{\overset{\vert}{C}}-C$	−22.95	+21.31	+0.0100	+0.0193
Summation	−45.90	+42.62	+0.0200	+0.0386
 $C-\overset{C}{\overset{\vert}{C}}-C-C-\overset{C}{\overset{\vert}{C}}-C$	+4.12	+40.37	+0.0176	+0.0342
1,5-Hexadiene				
C—C—C—C—C═C	−43.68	−5.19	+0.0127	+0.0140
C═C—C—C—C—C	−43.68	−5.19	+0.0127	+0.0140
Summation	−87.36	−10.38	+0.0254	+0.0280
C═C—C—C—C═C	−45.68	−9.14	+0.0293	+0.0320
5-Methyl-1-hexene				
 $C-\overset{C}{\overset{\vert}{C}}-C-C-C-C$	−22.95	+21.31	+0.0100	+0.0193
C—C—C—C—C═C	−43.68	−5.19	+0.0127	+0.0140
Summation	−66.63	+16.12	+0.0227	+0.0333
 $C-\overset{C}{\overset{\vert}{C}}-C-C-C{=}C$	....	+16.91	+0.0221	+0.0330

Table V. Physical Constants of Monoalkylbenzenes

Hydrocarbon	M.P., ° C.	B.P., ° C.	Refractive Index, n_D^{20}	Density, d_4^{20}
Benzene	−5.53	80.10	1.5011	0.8790
Toluene	−94.99	110.62	1.4969	0.8669
Ethylbenzene	−94.98	136.19	1.4959	0.8670
n-Propylbenzene	−99.50	159.22	1.4920	0.8620
n-Butylbenzene	−87.97	183.27	1.4898	0.8601
n-Propylbenzene	−99.50	159.22	1.4920	0.8620
Isopropylbenzene	−96.03	152.39	1.4915	1.8618
n-Butylbenzene	−87.97	183.27	1.4898	0.8601
Isobutylbenzene	−51.48	172.76	1.4895	0.8532
sec-Butylbenzene	−75.47	173.30	1.4902	0.8621
tert-Butylbenzene	−57.85	169.11	1.4926	0.8665

carbons of low carbon content, the increments again indicating that the subseries curves converge upon those of the normal alkanes with increasing molecular weight (Table II).

As the double bond is moved from 1 to the 2 position, there is a further increase in both the density and the refractive index, the increments becoming smaller as the double bond is buried more deeply in the normal olefin chain (normal octenes, Table II).

Table VI. Methylbenzenes

Hydrocarbon	Position Isomers: Vicinal		Unsymmetrical			Symmetrical	
Melting point, ° C.							
C_6H_6				−5.53			
$C_6H_5—CH_3$				−100.32			
$C_6H_4(CH_3)_2$	(1, 2)	−25.18	(1, 3)		−47.87	(1, 4)	+13.26
$C_6H_3(CH_3)_3$	(1, 2, 3)	−25.38	(1, 2, 4)		−43.80	(1, 3, 5)	−44.72
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	−6.25	(1, 2, 3, 5)		−23.85	(1, 2, 4, 5)	+79.3
Boiling point, ° C.							
C_6H_6				80.10			
$C_6H_5—CH_3$				110.62			
$C_6H_4(CH_3)_2$	(1, 2)	144.41	(1, 3)		139.10	(1, 4)	138.35
$C_6H_3(CH_3)_3$	(1, 2, 3)	176.08	(1, 2, 4)		169.35	(1, 3, 5)	164.71
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	205.04	(1, 2, 3, 5)		197.93	(1, 2, 4, 5)	196
Refractive index, n_D^{20}							
C_6H_6				1.5011			
$C_6H_5—CH_3$				1.4969			
$C_6H_4(CH_3)_2$	(1, 2)	1.5054	(1, 3)		1.4972	(1, 4)	1.4958
$C_6H_3(CH_3)_3$	(1, 2, 3)	1.5139	(1, 2, 4)		1.5049	(1, 3, 5)	1.4994
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	1.5201	(1, 2, 3, 5)		1.5125	(1, 2, 4, 5)	1.512
Density, d_4^{20}							
C_6H_6				0.8790			
$C_6H_5—CH_3$				0.8669			
$C_6H_4(CH_3)_2$	(1, 2)	0.8802	(1, 3)	0.8642		(1, 4)	0.8611
$C_6H_3(CH_3)_3$	(1, 2, 3)	0.8944	(1, 2, 4)	0.8758		(1, 3, 5)	0.8652
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	0.9053	(1, 2, 3, 5)	0.8899		(1, 2, 4, 5)	0.889

Variation with Olefin Type

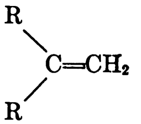
It now becomes of interest to know what the effects will be if both methylation and unsaturation are present in the same molecule. In a previous paper, it was pointed out that the ethylene olefins may be classified into five types (*6*):

$R—CH{=}CH_2$

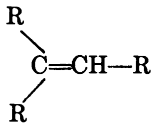
I

$R—CH{=}CH—R$

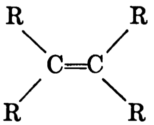
II



III



IV



V

Table III illustrates the point, using the olefin derivatives of the isoparaffins of the hexene family. The isohexenes are shown in comparison with the corresponding isohexanes and have been arranged in the order of increasing olefin type. The numerical values of the deviation for the melting points, boiling points, refractive indices, and densities all stand in the same order as the olefin types. The melting points and boiling points of the olefins of types I and III are generally lower than those of the corresponding paraffins. The refractive indices and densities are in all cases higher. The melting points of the olefin derivatives of 3-methylpentane are shown as true values in parentheses, since the melting point of 3-methylpentane is still unknown.

The first member of an homologous series quite commonly shows anomaly in its physical constants; this sets it off from the remaining members of the series. This characteristic was observed in the melting points of both the odd and even series of the normal paraffins. Benzene, the first member of the aromatic series, melts at −5.53° C., nearly 90 degrees higher than the members of the series immediately following. It seems remarkable that the following three monoalkylbenzenes (Table V) melt so nearly at the

Table VII. Geometric Isomers

Cis-Trans Pairs	Melting Point, ° C.	Boiling Point, ° C.	Refractive Index, n_D^{20}	Density, d_4^{20}
cis-2-Pentene	−151.37	37.1	1.3830	0.656
trans-2-Pentene	−140.24	36.36	1.3793	0.6482
cis-2-Hexene	−141.80	68.86	1.3954	0.6845
trans-2-Hexene	−133.16	67.91	1.3935	0.6780
cis-3-Hexene	−138.30	66.51	1.3934	0.6796
trans-3-Hexene	−113.50	68.1	1.3938	0.6779
cis-3-Methyl-2-pentene	−138.4	70.52	1.4045	0.6986
trans-3-Methyl-2-pentene	−135.3	67.8	1.4016	0.6942
cis-4-Methyl-2-pentene	−134.48	56.37	1.3878	0.6671
trans-4-Methyl-2-pentene	−140.82	58.59	1.3888	0.6691
cis-4,4-Dimethyl-2-pentene	−135.74	80.43	1.4025	0.6995
trans-4,4-Dimethyl-2-pentene	−115.31	76.74	1.3980	0.6889
cis-1,2-Dimethylcyclopropane	−140.93	37.03	1.3830	0.6941
trans-1,2-Dimethylcyclopropane	−149.82	28.20	1.3710	0.6698
cis-1-Methyl-2-ethylcyclopropane	glass	67.01	1.3953	0.7146
trans-1-Methyl-2-ethylcyclopropane	glass	58.66	1.3846	0.6935
cis-1-Methyl-2-propylcyclopropane	glass	96.6	1.4051	0.7295
trans-1-Methyl-2-propylcyclopropane	glass	88.9	1.3976	0.7155
cis-1,2-Diethylcyclopropane	glass	94.5	1.4047	0.7303
trans-1,2-Diethylcyclopropane	glass	87.5	1.3958	0.7131
cis-1,3-Dimethylcyclopentane	−133.98	91.73	1.4107	0.7488
trans-1,3-Dimethylcyclopentane	−133.70	90.77	1.4089	0.7448
cis-1,2-Dimethylcyclohexane	−50.02	129.73	1.4360	0.7963
trans-1,2-Dimethylcyclohexane	−88.19	123.42	1.4270	0.7760
cis-1,3-Dimethylcyclohexane	−75.57	120.09	1.4229	0.7660
trans-1,3-Dimethylcyclohexane	−90.11	124.45	1.4309	0.7847
cis-1,4-Dimethylcyclohexane	−87.44	124.32	1.4297	0.7829
trans-1,4-Dimethylcyclohexane	−36.96	119.35	1.4208	0.7626

same temperature. The melting points of the four monobutylbenzenes show alternation as the side chain is telescoped upon the aromatic nucleus. In all other respects the monoalkylbenzenes show the usual subseries relations.

The polymethylbenzenes (Table VI) present an interesting picture. The melting points show no obvious regularity, but the remaining physical constants fall into a definite pattern. The vicinal compounds such as *o*-xylene, hemimellitene, and prehnitene have the highest boiling points, highest refractive indices, and highest densities, each within its own group. The symmetrical derivatives such as *p*-xylene, mesitylene, and durene, on the other hand, have the lowest values in each group. The unsymmetrical derivatives have intermediate values. The effect of symmetry is noteworthy, involving as it does both para- and meta-substituted derivatives, such as *p*-xylene and mesitylene. One comes logically to the conclusion that a balanced arrangement of the methyl groups is responsible for the low values of the physical constants in the one case, and the unbalanced arrangement, in the vicinal derivatives, the cause of the high values in the other.

In all cases the polymethyl derivatives of benzene have higher boiling points, refractive indices, and densities than do the monoalkyl derivatives containing the same number of carbon atoms. This fact seems to indicate a dominant influence resident in the methyl groups. It is possible that the electron release characteristic of the methyl groups, when counterbalanced across the benzene ring, augments but restrains the electron pattern of the nucleus. In the vicinal type of polymethyl derivative, it not only augments but distorts this pattern. The result of these changes seems to be an intensification of the physical properties in the manner indicated.

Cis-Trans Isomerism

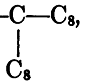
Application of the very excellent methods of purification devised by A.P.I.–R.P. 6 (*28*) has made it possible to separate and bring to high purity a considerable number of the cis-trans pairs of geometric isomers. Fourteen such pairs are listed in Table VII. Since the work of Kistiakowsky *et al.* (*21*) and of Sherrill and Matlock (*32*) it has become customary to assign the cis configuration to the higher boiling isomer. The higher boiling forms also have the higher densities and higher refractive indices.

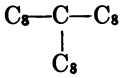
More recently Hall and Mikos (*19*) have found by infrared spectrographic analysis that the high boiling form of 4-methyl-2-pentene has the characteristic peak at 10.3 microns, which represents a trans-II configuration, while the low boiling form has its peak in the cis-II region at 13.9 microns. Greenlee and Shepherd (*18*) have confirmed this assignment by the synthesis of the high boiling isomer from 4-methyl-2-pentyne, by reduction using sodium in liquid ammonia, a method known to be a unique synthesis of the trans configuration (*17*).

A similar situation has been observed by Rossini and Pitzer. After a careful study of 1,3-dimethylcyclohexanes (b. 120.09° and 124.45° C.) they found the cis configuration to be less strained and accordingly assigned to the low boiling isomer.

J. M. Derfer (*11*) of the A.P.I.-R.P. 45 staff has pointed out that the molecular refractivities of nine mono- and polyalkylcyclopropanes show an average exaltation of 0.69 and that the average exaltation of the trans forms of four cis-trans pairs is 0.71, while the average for the corresponding cis forms is 0.57.

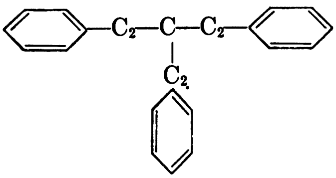
Additivity

It has been frequently observed that a characteristic structural grouping of any subseries may extend its influence for several carbon atoms down the normal paraffin chain. Some authors believe this influence for some groupings may extend far down the chain. In so far as this is true, structural relations may not become strictly additive until compounds of high molecular weight are reached. Robert Schiessler and his associates in A.P.I.-R.P. 42, working with high molecular weight hydrocarbons, have found a number of cases in which strict additivity does seem to occur (*30*). Using the typical basis structure,  $C_8—\underset{\displaystyle C_8}{\underset{|}{C}}—C_8$, and varying the structural design of each C_8 grouping, the following typical structures have been synthetically produced:

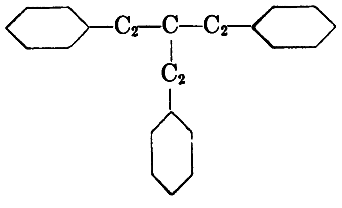


$C_8—\underset{\displaystyle C_8}{\underset{|}{C}}—C_8$

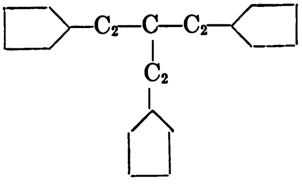
PSC 25



PSC 89

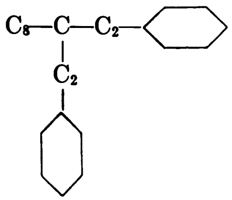


PSC 90

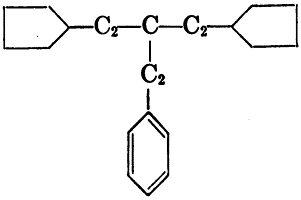


PSC 113

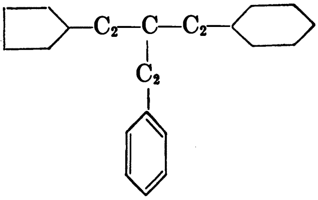
A large number of hydrocarbons also synthetically produced have the same over-all typical basis structures and composition but contain various combinations of the eight carbon atom groupings, as shown by the following examples:



PSC 19



PSC 128



PSC 130

The physical properties of pure hydrocarbons or "chemical mixtures" were then compared with the same property measured on a physical mixture of the typical structures 25, 89, 90, and 113, which would match in structure and composition. The following conclusions were drawn:

1. The densities of the naphthenic paraffins binary mixtures at all temperatures are in amazingly good agreement with the densities of the corresponding pure hydrocarbon.
2. The viscosity data for the naphthenic binary mixtures and their corresponding pure hydrocarbons again indicate an amazing agreement.

Excellent agreement was also found for viscosity index, refractive index, and aniline point.

The agreement between the physical properties of the pure hydrocarbons and the binary physical mixture is much poorer for these hydrocarbons which contain the aromatic phenyl group than it is for the naphthenic-paraffinic mixtures. The derivatives for the aromatic mixtures are from four to nine times those of the physical mixtures of the pure hydrocarbons where no aromatic rings are present.

It would be interesting to know what the effect would be of increasing the length of the interconnecting chain of methylene groups.

Refractivity Intercept and Refractivity Quotient

Kurtz and Ward (*22*) have described a composite function of the refractive index and density which they call the refractivity intercept. The equation is $R.\ \mathrm{Int} = n - d/2$. The value of the refractivity intercept lies in the fact that for hydrocarbon isomers it is more constant than most other functions. Its chief uses are the rapid checking of physical property data found in the literature and distinguishing between naphthenes, paraffins, and aromatics.

Smittenberg has described a composite function of the refractive index and density which he calls the refractivity quotient (*33*). When the refractivity quotient is plotted against the reciprocal of the number of carbon atoms the *n*-alkylbenzenes, *n*-alkylcyclohexanes, and *n*-alkylcyclopentanes, all show alternation for the first several members of the series.

It becomes evident, therefore, that alternation is characteristic not only of melting points but also of boiling points, refractive indices, and/or density. It is also frequently apparent in the curves plotted from engine data. Two conclusions seem to be indicated:

1. Both the physical properties and the knocking characteristics of pure hydrocarbons are strongly dependent upon the length of uninterrupted chain fragment.
2. Both the physical properties and the knocking characteristics of pure hydrocarbons seem to reflect minor changes in the valence electron pattern of the molecule.

Engine Characteristics and Molecular Structure

The foregoing pages have shown a number of ways in which physical constants vary with molecular structure. Petroleum chemists and automotive engineers have come to recognize that the performance of a motor fuel in an internal combustion engine is also dependent upon the structure of the hydrocarbon molecules which the fuel contains. This does not mean that engine performance is a function of the physical constants, but rather that the features of molecular structure which determine the one also determine the other.

It has been repeatedly shown that hydrocarbons differing in molecular structure differ in their rate of combustion (*9*). Proper fuel performance is a matter of adjusting the rate of combustion of the fuel to the engine in which it is to be used.

Chain Length

Gaseous paraffins and olefins with low molecular weight and short chain length have relatively high critical compression ratios. Their octane numbers must all be well above 100. Normal paraffins have the lowest octane numbers of any of the members of their own isomeric group. Highly branched paraffins have high critical compression ratios, higher in many cases than the gaseous paraffins. It is well to examine these facts in greater detail. The engine characteristics of the isoparaffins are listed in Table VIII in much the same manner that their physical constants were listed in Table I.

The melting points of the first members of both the normal and 2-methylalkanes were shown to be anomalous. Methane and ethane are also anomalous with respect to their compression ratios. It is not until *n*-propane is reached that the normal paraffins begin to show the usual series relation. The same is true with respect to the relative rates of oxidation of the normal paraffins. Beginning with propane as one moves from point to point along the critical compression ratio curve for the *n*-paraffins in the direction of increasing carbon content (increasing chain length), the engine characteristics fall by diminishing increments (Table VIII, column 2). The alternation so characteristic of the melting points is not apparent.

When a *n*-paraffin is isomerized to a monomethyl derivative the engine characteristics rise (column 3, Table VIII). If the isomerization is continued with the formation of two methyl groups along the principal chain the deviation from the normal isomer is still greater (columns 7 to 12). As the single methyl group in the 2-position is moved toward the middle of the chain the deviation is increased. In like manner the deviations of the 2,3- and 3,4-dimethyl derivatives are generally greater than for the 2,2-dimethylalkane.

It is of interest to note that the increase in deviation of the monomethylalkane from the normal alkane does not reach its maximum until the hexanes are reached, and for the dimethylhexanes this maximum may be found as high as eight carbon atoms. These facts seem to point to some inherent characteristics of the methyl group, and to indicate that its influence may extend down the chain as many as 3 or 4 carbon atoms.

Unsaturation and Olefin Type

The engine data for the normal olefins, pentenes to octenes inclusive, are recorded in Table IX. The data are stated as octane numbers or critical compression ratios. The table is fragmentary, the work being still incomplete, but it is sufficiently complete to show the trends.

The introduction of a double bond in the 1-position of a *n*-alkane causes a sharp rise in the fuel rating of the hydrocarbon. Again, as in the case of the methyl group, the ratings increase as the double bond is moved from position 1 to 2 to 3 to 4. The ratings decrease as one moves from 1-pentene to 1-octene along the subseries curve of the 1-alkenes. The increment of deviation of the 1-alkene from the *n*-alkane increases up to about six carbon atoms. In other words, the introduction of a double bond into a *n*-paraffin chain producing a *n*-olefin produces a series of changes quite analogous to the isomerization of the *n*-alkane to its monomethyl isomer.

The boiling point, refractive index, and density of the olefin derivative of any paraffin were shown, by use of Table III, to stand in the order of their olefin type. Table X contains the engine data of the olefin derivatives of 2-methylpentane and 3-methylpentane, recorded in the order of their olefin type. No consistent relations between octane numbers or critical compression ratios are obvious—but the blending octane numbers of these branched olefins, as measured by both the research and Motor methods, do generally stand in the order of their type. Two olefins of type III form exceptions, the exceptions being in one case too high and in the other case too low.

A discussion of this relation was contained in a paper presented in April 1951 (7). It was there pointed out that these facts are consistent with the free radical peroxidation theory of combustion, if it is assumed that the free radicals add at the carbon-to-carbon double bond. The assumption is justified on the basis of experimental evidence.

Aromatic Ring Structure

Aromatic hydrocarbons have exceptionally high engine characteristics. The Research octane numbers of all aromatic hydrocarbons thus far measured are above 100. Those measured by the Motor method are a little lower, but in all cases are above 95. The critical compression ratios at 600 revolutions per minute and 212° F., jacket temper-

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Table VIII. Deviation of Engine

Hydrocarbon	Normal Value	Series Deviation	2-Me	3-Me	4-Me
Research octane number					
Butanes	( )	....	....	....	....
Pentanes	61.7	( )	+30.6	....	....
Hexanes	24.8	−36.9	+48.6	+50.0	....
Heptanes	00.0	−24.8	−42.4	+52.0	....
Octanes	−20.3[a]	−20.3[a]	42.0[a]	47.1[a]	47.0[a]
Motor octane number					
Butanes	( )	....	....	....	....
Pentanes	61.9	( )	+28.4	....	....
Hexanes	26.0	−35.9	+47.5	+48.3	....
Heptanes	00.0	−26.0	+46.4	+55.0	....
Octanes	−13.6[a]	−13.6[a]	+37.4[a]	+48.6[a]	52.6[a]
Blending octane number (Research)					
Butanes	113	....	+9.0	....	....
Pentanes	62	−51.0	+37.0	....	....
Hexanes	19	−43.0	+64.0	+67.0	....
Heptanes	00.0	−19.0	+41.0	+56.0	....
Octanes	−19	−19.0	+32.0	+49.0	+50.0
Blending octane number (Motor)					
Butanes	114	....	+7.0	....	....
Pentanes	67	−47.0	+37.0	....	....
Hexanes	22	−35.0	+57.0	+59.0	....
Heptanes	00.0	−22.0	+42.0	+57.0	....
Octanes	−15.0	−15.0	+39.0	+45.0	+63.0
Performance number (Research)[b]					
Butanes	( )	....	....	....	....
Pentanes	42.2	( )	+36.2	....	....
Hexanes	27.1	−15.1	+24.1	+25.2	....
Heptanes	21.9	−5.2	+11.0	+15.2	....
Octanes	18.9[a]	−2.9[a]	+7.4[a]	+7.1[a]	+8.7[a]
Critical compression ratio (600/212° F.)					
Butanes	5.5	....	+2.5	....	....
Pentanes	3.95	−1.55	+1.7	....	....
Hexanes	3.25	−0.70	+1.05	+0.95	....
Heptanes	3.0	−0.25	+0.65	+0.8	....
Octanes	2.9	−0.10	+0.4	+0.5	+0.6
Critical compression ratio (600/350° F.)					
Butanes	5.3	....	+1.15	....	....
Pentanes	3.2	−2.1	+1.9	....	....
Hexanes	3.0	−0.2	+0.65	+0.7	....
Heptanes	....	....	....	....	....
Octanes	....	....	....	....	....

[a] This datum constitutes, or is partly derived from, an extrapolated octane number based on critical compression ratios, measurement of which is not limited to the octane range as defined (0–100).

[b] Calculated from the CFR Research octane number by the Army-Navy Aeronautical Board formula, PN = 2800/(127 − ON).

ature, are all above 10, and those at 600 r.p.m. and 350° F., while somewhat lower, are 6.9 or higher.

The blending octane number of benzene is the lowest for any aromatic hydrocarbon thus far measured. When measured by either the Research or Motor method it seems to form another case where the first member of an homologous series is anomalous.

The blending octane members of the first five members of the monoalkylbenzenes as measured by the Motor method show alternation. The same is true for the four monobutylbenzenes, as the butyl group is telescoped on the aromatic nucleus. This is also true of their critical compression ratios (Table XI).

The engine characteristics of aromatic hydrocarbons seem strongly dependent upon the nature of the side chain. The alignment of the knock resistance of the polymethylbenzenes with structure corresponds quite closely with that found to be characteristic of the physical constants. The vicinal derivatives *o*-xylene, hemimellitine, and prehnitene

Characteristics of Isomeric Alkanes

Isomer Deviation						
3-Et	2,2-Me₂	2,3-Me₂	2,4-Me₂	2,5-Me₂	3,3-Me₂	3,4-Me₂
....	....	....	....	....	....	....
....	+23.8	....	....	....	....	....
....	+67.0	+115.9[a]	....	....	....	....
+65.0	+92.8	+91.1	+83.1	....	+80.8	....
53.8[a]	+92.8[a]	+91.6[a]	+82.5[a]	+75.8[a]	+90.8[a]	+96.6[a]
....	....	....	....	....	....	....
....	+18	....	....	....	....	....
....	+67.4	+68.3	....	....	....	....
+69.3	+95.6	+88.5	+83.8	....	+86.6	....
+66.0[a]	+91.0[a]	+95.5[a]	+83.5[a]	....	+86.6[a]	+95.3[a]
....	....	....	....	....	....	....
....	+38	....	....	....	....	....
....	+70	+77	....	....	....	....
+64	+89	+87	+77	....	+83	....
+83	+86	+90	+84	....	+102.4	....
....	....	....	....	....	....	....
....	+23	....	....	....	....	....
....	+75	+40	....	....	....	....
+73	+93	+90	+78	....	+88	....
+64	+91	+91	+85	....	+81	+95
....	....	....	....	....	....	....
....	+23.7	....	....	....	....	....
....	+50.2	....	....	....	....	....
....	+57.8	+54.9	+40.5	....	+37.4	....
+10.7[a]	+31.6[a]	+30.5[a]	+25.7[a]	+19.7[a]	+34.4[a]	+35.2[a]
....	....	....	....	....	....	....
....	+1.65	....	....	....	....	....
....	+2.70	+5.7	....	....	....	....
....	+3.0	+3.2	+1.9	....	+2.0	....
+0.6	+1.5	+1.6	+1.4	+1.05	+1.75	+1.8
....	....	....	....	....	....	....
....	+1.3	....	....	....	....	....
....	+2.1	+4.45	....	....	....	....
....	....	....	....	....	....	....
....	....	....	....	....	....	....

have the lowest blending octane numbers and critical compression ratios, each within its own group. The symmetrical derivatives—*p*-xylene, mesitylene, and durene—have the highest values, each within its own group. The unsymmetrical derivatives such as *m*-xylene, pseudocumene, and isodurene have intermediate values in each case.

One cannot help being impressed by the dominant character of the methyl group. It would seem that when the electron release of the methyl groups is balanced across the benzene nucleus the knock resistance is increased; this indicates that the velocity of combustion is slowed down. On the other hand, when the electron releases of the methyl groups supplement each other, as in the case of the vicinal derivatives, knock resistance is decreased; this indicates that the combustion velocity is increased. An accumulation of methyl groups either upon the side chain, as in *tert*-butylbenzene, or upon the nucleus, as in isodurene, seems to increase the knock resistance.

Discussion

In the preceding pages, an attempt was made to develop the relation of properties to molecular structure for hydrocarbons. Two methods of approach were used. The first procedure is to follow the evolution of each typical subseries of homologs from point to

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Table IX. Engine Characteristics of Normal Olefins

Hydrocarbon	Paraffin Value	1(=)	2(=) cis	2(=) trans	3(=) cis	3(=) trans	4(=) cis	4(=) trans
Research octane number								
Pentane	61.7	90.9	...	...	...	...	...	...
Hexane	24.8	76.4	...	...	...	...	...	...
Heptane	0	...	...	...	...	...	...	...
Octane	−20.3	28.7	(56.3)		...	72.5	...	73.3
Motor octane number								
Pentane	61.9	77.1	...	...	...	...	...	...
Hexane	26.0	63.4	...	80.8	...	80.1	...	...
Heptane	0	...	...	...	...	...	...	...
Octane	−13.6	34.7	(56.5)		...	68.1	...	74.3
Blending octane number (Research)								
Butane	113	144	155	152	...	...	...	...
Pentane	63	119	154	150	...	...	...	...
Hexane	19	97	...	134	...	137	...	...
Heptane	0	68	...	...	...	...	...	...
Octane	−19	...	(75)		...	95	...	99
Blending octane number (Motor)								
Butane	114	126	130	128	...	...	...	...
Pentane	67	109	137	134	...	...	...	...
Hexane	22	94	...	129	...	120	...	...
Heptane	0	46	...	...	...	...	...	...
Octane	−15	...	(68)		...	85	...	101
Critical compression ratio (600/212° F.)								
Butane	5.5	7.1	7.9	8.7	...	...	...	...
Pentane	3.95	5.55	7.05	7.05	...	...	...	...
Hexane	3.25	4.35	...	5.4	...	7.0	...	...
Heptane	3.0	...	...	...	...	...	...	...
Octane	2.9	3.25	(3.9)		...	4.25	...	4.25
Critical compression ratio (600/350° F.)								
Butane	5.3	5.3	5.95	5.95	...	...	...	...
Pentane	3.2	4.55	5.4	5.4	...	...	...	...
Hexane	3.0	3.6	...	4.5	...	5.2	...	...
Heptane	...	3.0	...	...	...	...	...	...
Octane	...	2.85	(3.25)		...	3.6	...	3.7

point in the direction of increasing carbon content or chain length. The subseries curve takes up a fixed position with respect to the normal series curve, which is determined by its characteristic grouping. The second procedure is to examine in detail the order of intersection of such a bundle of curves as one moves from point to point along a cross-sectional line at any given carbon atom level.

The first procedure is the one usually followed by those investigators who attempt to find a mathematical formula for calculating or predicting physical properties (*14*). The second procedure has the advantage that once the general pattern has been established, it is not too greatly disturbed by missing data. In either case, comparisons may be made between actually measured values or between the increments of deviation from point to point. Both methods of comparison have their value. Some investigators use the second procedure in making predictions and some of them use a combination of both procedures (*15*).

No method of prediction is quite so satisfying as having at hand experimentally determined values, measured on products of high purity. As the experimentally determined data become increasingly accurate and as the data increase in volume, the predictions can be and are made with greater and greater accuracy.

One of the most fundamental elements of molecular structure is chain length. It serves to fix the hydrocarbon's position on its own subseries curve and thus becomes a factor in determining its physical constants. It also is a major factor in determining the hydrocarbon's rate of combustion and hence its octane number and critical compression ratio.

The methyl group and the double bond are two other structural elements which play a dominant role in determining the properties of a hydrocarbon. As a methyl group is moved from carbon to carbon atom along a hydrocarbon chain, it alters the physical properties of the hydrocarbon. How does it do this? It seems obvious that the change in the electronic pattern of the molecule, as the methyl group is moved from point to point, effects these changes. It also interrupts the effective chain length and determines the

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principal point of oxidative attack on the hydrocarbon. The combustion velocity is altered and hence the octane number and critical compression ratio are changed.

The double bond functions in a very analogous manner. It too interrupts effective chain length and determines the principal point of oxidative attack. In a manner quite analogous to the methyl group, through changes in the combustion velocity, the double bond also alters the octane number and critical compression ratio.

The implications of these deductions seem to lead to the conclusion that such structural factors as chain length, methyl groups, and double bonds influence not only the physical properties but the chemical properties of the hydrocarbon as well. Hydrocarbons are limited in their chemical reactivity. The paraffins are compounds having small affinity. The hydrocarbon molecules are armor-plated with hydrogen. Since structure plays so vital a role in the rate of combustion, there must be a fundamental difference in the relative reactivity of the hydrogen atoms. Experimental evidence that such is the case is accumulating. There are reasons to believe that methods are at hand by which the

Table X. Engine Characteristics of Branched Olefins

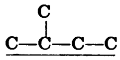
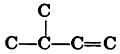
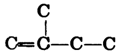
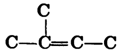
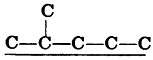
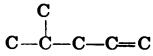
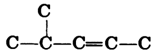
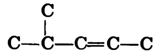
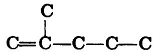
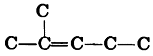
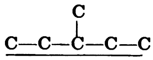
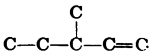
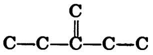
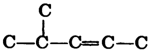
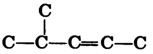
Hydrocarbon Structure	Olefin Type	Research Octane No.	Motor Octane No.	Blending Octane No. (Research)	Blending Octane No. (Motor)	Critical Compression Ratio (600/212° F.)	Critical Compression Ratio (600/350° F.)
2-Methylbutane derivatives							
 $C-\overset{C}{\overset{\vert}{C}}-C-C$	....	92.3	90.3	99.0	104	5.65	5.1
 $C-\overset{C}{\overset{\vert}{C}}-C=C$	I	(volatile)		129	125	8.3	5.45
 $C=\overset{C}{\overset{\vert}{C}}-C-C$	III	+0.3	81.9	146	133	7.7	5.45
 $C-\overset{C}{\overset{\vert}{C}}=C-C$	IV	97.3	87.4	176	141	9.1	6.45
2-Methylpentane derivatives							
 $C-\overset{C}{\overset{\vert}{C}}-C-C-C$	....	73.4	73.5	83	79	4.3	3.65
 $C-\overset{C}{\overset{\vert}{C}}-C-C=C$	I	95.7	80.9	112	108	6.8	5.5
 $C-\overset{C}{\overset{\vert}{C}}-C=C-C$	II *cis*	99.3	84.3	130	128	7.7	5.5
 $C-\overset{C}{\overset{\vert}{C}}-C=C-C$	II *trans*						
 $C=\overset{C}{\overset{\vert}{C}}-C-C-C$	III	95.1	78.9	126	114	6.75	5.15
 $C-\overset{C}{\overset{\vert}{C}}=C-C-C$	IV	97.8	83.0	159	148	7.05	5.25
3-Methylpentane derivatives							
 $C-C-\overset{C}{\overset{\vert}{C}}-C-C$	....	74.5	74.3	86	81	4.2	3.7
 $C-C-\overset{C}{\overset{\vert}{C}}-C=C$	I	96.0	81.2	113	114	7.0	5.4
 $C-C-\overset{C}{\overset{\Vert}{C}}-C-C$	III	98.3	79.4	143	129	7.0	5.4
 $C-\overset{C}{\overset{\vert}{C}}-C=C-C$	IV *cis*	....	....	125	113	7.2	5.0
 $C-\overset{C}{\overset{\vert}{C}}-C=C-C$	IV *trans*	97.2	81.0	130	118	7.15	5.0

Table XI. Engine Characteristics of Monoalkylbenzenes

Hydrocarbon	Research Octane No.	Motor Octane No.	Blending Octane No. (Research)	Blending Octane No. (Motor)	Critical Compression Ratio (600/212° F.)	Critical Compression Ratio (600/350° F.)
Benzene	....	+2.7	99	91	....	....
Toluene	+5.8	+0.3	124	112	15.	11.35
Ethylbenzene	+0.8	97.9	124	107	13.5	8.2
n-Propylbenzene	+1.5	98.7	127	129	11.9	8.7
n-Butylbenzene	....	95.3	114	117	10.2	6.9
n-Propylbenzene	+1.5	98.7	127	129	11.9	8.7
Isopropylbenzene	+2.1	99.3	132	124	14.5	8.9
n-Butylbenzene	....	95.3	114	117	10.3	6.9
Isobutylbenzene	....	....	122	118	13.5	8.6
sec-Butylbenzene	....	....	116	117	12.5	8.25
tert-Butylbenzene	> +3.0	+0.8	138	127	13.2	9.8

relative reactivity pattern of the hydrogen atoms of a hydrocarbon may be determined. If this can be done with accuracy, it should not only give us an insight into the cause of the variation of combustion velocity with structure but also form a foundation for an attack upon the stability of the carbon skeleton of the hydrocarbon.

Table XII. Engine Characteristics of Methylbenzenes

Hydrocarbon	Position Isomers					
	Vicinal		Unsymmetrical		Symmetrical	
Blending octane No. (Research)						
C_6H_6			99			
$C_6H_5CH_3$			124			
$C_6H_4(CH_3)_2$	(1, 2)	120	(1, 3)	145	(1, 4)	146
$C_6H_3(CH_3)_3$	(1, 2, 3)	118	(1, 2, 4)	148	(1, 3, 5)	171
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	..	(1, 2, 3, 5)	154	(1, 2, 4, 5)	..
Blending octane No. (Motor)						
C_6H_6			91			
$C_6H_5CH_3$			112			
$C_6H_4(CH_3)_2$	(1, 2)	103	(1, 3)	124	(1, 4)	127
$C_6H_3(CH_3)_3$	(1, 2, 3)	105	(1, 2, 4)	124	(1, 3, 5)	137
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	..	(1, 2, 3, 5)	128	(1, 2, 4, 5)	..
Critical compression ratio (600/212° F.)						
C_6H_6			..			
$C_6H_5CH_3$			15			
$C_6H_4(CH_3)_2$	(1, 2)	13.0	(1, 3)	15.5	(1, 4)	15.7
$C_6H_3(CH_3)_3$	(1, 2, 3)	12.0	(1, 2, 4)	12.8	(1, 3, 5)	14.0
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	..	(1, 2, 3, 5)	12.7	(1, 2, 4, 5)	..
Critical compression ratio (600/350° F.)						
C_6H_6			..			
$C_6H_5CH_3$			11.35			
$C_6H_4(CH_3)_2$	(1, 2)	7.1	(1, 3)	11.5	(1, 4)	11.5
$C_6H_3(CH_3)_3$	(1, 2, 3)	7.9	(1, 2, 4)	8.7	(1, 3, 5)	10.6
$C_6H_2(CH_3)_4$	(1, 2, 3, 4)	..	(1, 2, 3, 5)	8.7	(1, 2, 4, 5)	..

The structure of cyclic hydrocarbons is very complex. The number of isomers increases rapidly with carbon content. Although the data at hand are extensive, many more are needed to allow a fundamental analysis of the relation between properties and structure.

The aromatic hydrocarbons form a unique case of cyclic structure. The benzene ring, like the methyl group and double bond, exerts a powerful influence upon the properties of any hydrocarbon of which it is a part. All aromatic hydrocarbons have high boiling points, high densities, and high refractive indices. They also have high octane numbers and critical compression ratios.

The hydrogen atoms of the benzene ring are not readily subject to free radical stripping (*8*). Variations in the engine characteristics are, therefore, chiefly due to difference in the structure of the side chains. One of the most striking illustrations of the effect of structure upon properties for aromatic hydrocarbons is to be found in the distribution of polymethyl groups about the benzene ring. The effect is observable in both the physical properties and in the engine characteristics. This effect of symmetry *vs.* dissymmetry, together with the increased reactivity of the hydrogen atoms on the alpha carbon atoms of side chains, seems to lend added support to the belief that these differences are effected through changes in the electron pattern of the molecule.

Conclusions

The conclusions which one draws in consideration of the above facts are that both the physical and chemical properties of hydrocarbon molecules are largely a function of the electron distribution. The structural elements which play a prominent role in this distribution are chain length, chain branching, methyl groups, double bonds, and benzene nuclei.

Much has been accomplished in the synthesis, separation, purification, and careful determination of both physical constants and engine characteristics. Much still remains to be done but the work is progressing.

There still remains to be accomplished a more careful correlation of the chemical properties with structure; a study of the relative rates of reactivity for the hydrogen atoms on different parts of the hydrocarbon structure; and the effects which these differences impose upon the velocity of combustion.

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Physical Chemistry in the Petroleum Industry

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Understanding of the physical and chemical principles relating to the production and refining of petroleum has contributed to the emergence of a truly chemical industry based upon petroleum as a raw material. This transition would have been retarded and its ultimate accomplishment impaired except for the application of experimental data and associated generalizations concerning the physical properties of hydrocarbons by the technical personnel of the industry at large. The contributions of numerous investigators to the background of experimental information and its correlation for the petroleum industry are described and a brief review of the more pertinent literature is presented.

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The scope of physical chemistry as related to the petroleum industry includes regions in which the subject matter crosses other fields of science. The subject is bounded in part by organic chemistry, thermodynamics, mechanics, and structural chemistry. The present treatment of physical chemistry, which is limited to the period from 1925 to 1950, considers only the physical properties of nonionic phases of direct interest to the producing and refining activities of the petroleum industry. Under these circumstances the fields of physical chemistry can be divided broadly into phenomena pertaining to equilibrium and those in which divergences from equilibrium are of primary concern. The treatment of equilibrium has been subdivided into the characteristics of hydrocarbon phases which are concerned with volumetric and phase behavior and the thermal, surface, and optical properties of the systems of interest. Only properties relating to rheological processes and material and thermal transfer have been considered in the nonequilibrium field. This classification is somewhat arbitrary and other subdivisions would be possible. In the interest of brevity, no consideration has been given to electrolytic solutions, which often are of importance in the production of petroleum and in some of the refining operations of the industry.

In the petroleum industry the influence of pressure upon the properties of fluids is important. In production practice, pressures in excess of 10,000 pounds per square inch (*37*) appear to be of interest and the hydrogenation of petroleum (*51*, *69*) may involve even higher pressures. Such pressures materially influence the physical and chemical equilibrium of these systems. The magnitude of this effect results from the fact that the partial volumes (*43*) of many of the components of petroleum are large, thus making their chemical potential (*21*) or fugacity (*42*) markedly susceptible to changes in pressure. For this reason many of the earlier generalizations concerning the effect of pressure upon the volumetric (*6*, *73*) and phase behavior (*55*) of substances did not describe the effect of pressure upon the characteristics of hydrocarbon systems with sufficient accuracy for engineering needs. It is not possible to neglect the effects of pressure on the viscosity of either liquid (*3*, *60*) or gaseous (*74*) hydrocarbon phases or to treat the interfacial tension

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of such phases as functions of temperature and composition only. In many instances the effects of pressure upon the thermal and component diffusion constants (*10, 75*) cannot be neglected.

The early work of Gibbs (*22*) in the field of statistical mechanics, which has been supplemented and extended by many workers (*20, 72*), has assisted in the interpretation and coordination of experimental results. The science of statistical mechanics has been of particular value in establishing the heat capacity of hydrocarbons at infinite attenuation. However, much progress must be made before it will be possible to predict from statistical mechanics the characteristics of a phase from a knowledge of its state. The period between 1925 and 1950 has been characterized by substantial progress in the accumulation of experimental data from which concordant theories or generalizations may be developed.

The petroleum industry is interested in processes involving both physical and chemical changes. The present discussion is limited to situations where no change in the molecular species is involved. A substantial part of the experimental facts which are reviewed often is of direct use in the prediction of the tendencies toward and the rates of chemical reaction. Transfer processes are of importance, particularly a detailed knowledge of the effects of the motion of fluid (*1, 34*). During the period covered by this discussion some progress has been made in the field of fluid mechanics. However, much still is to be learned about the basic nature of turbulence and its influence upon transfer processes. Work is required in the analysis of fluid flow under conditions where large changes in the properties of the phases are encountered within a given flowing system.

The groundwork of thermodynamics was well systematized by Gibbs (*21*), who based his work upon the earlier considerations of Clausius and Carnot. The principal relations of interest in multicomponent systems have been systematically presented by Goranson (*23*). The close interrelation of heat and work in flowing systems of changing composition, velocity, and elevation under conditions where irreversible processes are of controlling importance has been considered in some detail by Eckart (*18*). Onsager (*52*) has made unusual contributions in pointing out the interrelation of the several transfer coefficients involved in such processes.

The importance of the changes in thermodynamic, rheological, and transfer characteristics of fluids with position can be exaggerated only with difficulty. In a large number of processes encountered in the petroleum industry, the variations in state within a single flowing stream result in significant changes in many of the intensive properties of the phases. The average values of these properties often do not yield results sufficiently descriptive of actuality for engineering needs. It is probable that the petroleum industry will become increasingly interested in the microscopic approach to the characteristics of systems which are not at mechanical or thermodynamic equilibrium. An adequate experimental background of facts concerning the rheological properties of hydrocarbon fluids appears to be increasingly desirable, as more interest is given to the microscopic aspects of momentum, thermal, and material transfer processes.

Equilibrium Phenomena

For present purposes discussion of equilibrium phenomena is divided into the fields of phase equilibria, volumetric behavior, thermal properties, and surface characteristics. The subject matter is limited to a number of the components and their mixtures which are found in petroleum. The phenomena are restricted to those involving properties in which time does not enter as a variable. The elimination of time follows from the basic characteristic of an equilibrium state in which the properties of the system are invariant.

The phase equilibrium of mixtures is characterized by the following equalities:

$$T^{(1)} = T^{(2)} = T^{(3)} \tag{1}$$

$$P^{(1)} = P^{(2)} = P^{(3)} \tag{2}$$

$$f_k^{(1)} = f_k^{(2)} = f_k^{(3)} \tag{3}$$

In these equations the superscript parenthetical figures refer to individual phases.

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T is temperature, *P* is pressure, and *f* is the fugacity of the component. In Equation 3 subscript *k* refers to each component of the system. In the present discussion the fugacity (*42*) is employed in preference to the chemical potential (*21*). Earlier in the history of the petroleum industry, Raoult's (*55*) and Dalton's laws were applied to equilibrium at pressures considerably above that of the atmosphere. These relationships, which assume perfect gas laws and additive volumes in the gas phase and zero volume for the liquid phase, prove to be of practical utility only at low pressures. Henry's law was found to be a useful approximation only for gases which were of low solubility and at reduced pressures less than unity.

Beattie (*2*) and coworkers opened a new approach to the description of the phase behavior of pure substances and mixtures through more accurate equations of state. An extension of the Beattie-Bridgeman equation (*2*) has been developed by Benedict, Webb, and Rubin (*4*). It describes the volumetric behavior of mixtures of the lighter hydrocarbons in both the liquid and gas phases with sufficient accuracy to permit its employment in evaluating the fugacity as a function of state. It appears that the equation of state offers one of the most useful methods of generalizing the phase behavior of mixtures of the lighter paraffin hydrocarbons. The chief difficulty in the application of such equations lies in establishing the requisite constants for the components of high molecular weight. Recent work (*11*) has indicated the feasibility of utilizing commercially available automatic digital computing equipment to evaluate the properties of the coexisting phases in heterogeneous hydrocarbon mixtures by use of the Benedict equation of state.

Table I presents a summary of some of the literature pertinent to the phase behavior of a number of the lighter components of petroleum, listing publications. In this table the specific references for each subject are identified by an index number applicable to an American Documentation Institute reference (*59*). The large number of entries involved does not permit the inclusion of the specific references as part of this discussion. The marked increase in publication found in the past five years appears typical of the general growth of research activities, although in part it may result from a more complete literature search in this period.

Table I. Publications Concerning Phase Equilibria

	Status[a]		Cumulative Total Number[b]						
Subject	Component	Mixture	1925	1930	1935	1940	1945	1950	Index Number[c]
Azeotropes		6	0	0	0	0	1	8	I-1
Correlations	9	7	1	3	5	12	19	40	I-2
Critical state	7	4	7	8	11	21	27	29	I-3
Miscellaneous	–	–	0	2	2	3	10	15	I-4
Carbon dioxide	10	4[d]	0	1	2	3	4	6	I-5
Hydrogen sulfide	7	3	0	0	1	2	2	3	I-6
Nitrogen	8	3	0	0	0	1	1	5	I-7
Water	10	4	0	2	8	10	16	21	I-8
Natural gas		5	0	1	2	4	12	17	I-9
Crude oil		6	0	1	2	5	9	15	I-10
Hydrocarbons, general	–	–	0	2	6	7	8	14	I-11
Methane	9	7	0	0	2	16	20	32	I-12
Ethane	8	4	1	2	2	4	7	12	I-13
Propane	9	5	2	2	5	12	15	17	I-14
Propene	7	4	0	0	0	0	1	3	I-15
n-Butane	8	7	0	1	3	6	9	22	I-16
Isobutane	7	3	0	0	0	0	2	5	I-17
1-Butene	6	4	0	1	1	2	5	8	I-18
n-Pentane	8	6	0	0	2	3	4	7	I-19
Pentene	4	2	0	0	0	0	0	3	I-20
n-Hexane	6	3	1	1	1	6	7	11	I-21
Benzene	8	5	0	0	2	12	13	20	I-22
n-Heptane	6	2	0	0	2	7	9	14	I-23
n-Octane	5	3	1	1	2	4	5	11	I-24
Nonane	4	4	0	0	0	3	4	6	I-25
Decane	6	6	0	0	0	2	2	11	I-26
Heavier	–	–	0	0	0	0	1	0	I-27
Total			13	28	61	145	213	355	

[a] Author's estimate of status of studies in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[b] Publications are predominantly American; foreign references which have come to author's attention have been included.

[c] American Documentation Institute (*59*).

[d] Mixtures reported under each of pure substances listed.

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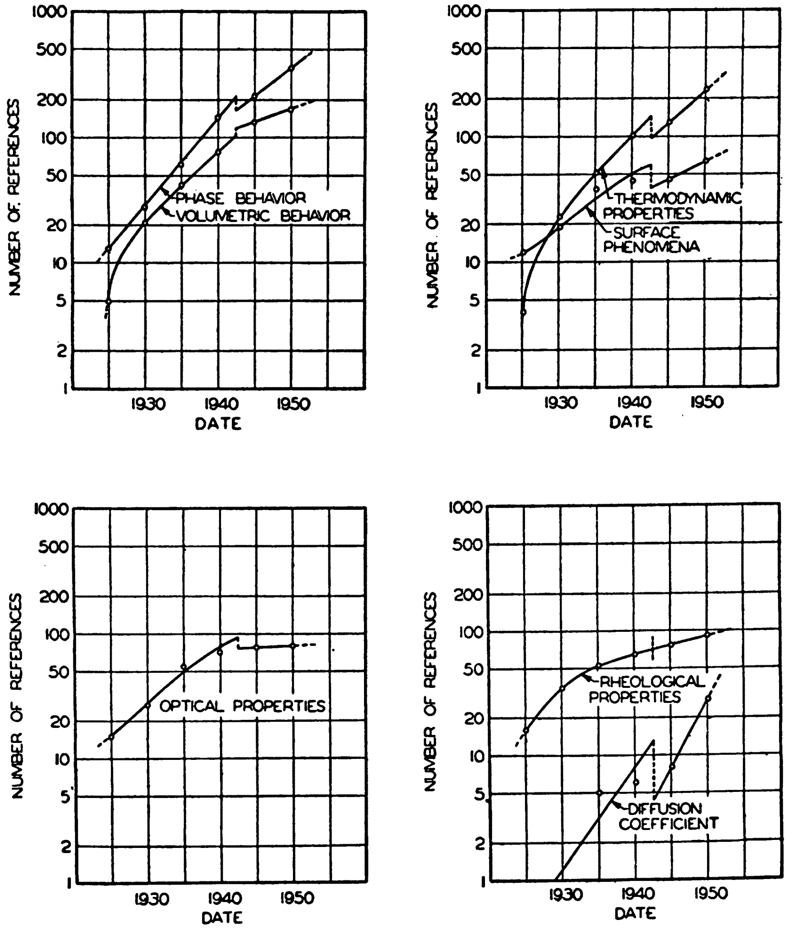

Figure 1. Cumulative References Pertaining to Several Fields in Physical Chemistry

Figure 1 presents the cumulative totals of references found in the several fields of physical chemistry considered here. The literature listing is not exhaustive, but represents only references that have come to the attention of the author.

Azeotropes have become of increasing industrial importance. The basic theory concerning their behavior presented by Kuenen (*39*) and Roozeboom (*56*) remains the classic contribution. Horsley (*28*, *29*) and Lecat (*40*) have summarized the recent advances in this field. It is probable that much additional experimental work must be completed to establish the details of the behavior of azeotropic mixtures of industrial interest. The absence of adequate experimental data is particularly acute at elevated pressures. The behavior of azeotropes at elevated pressures is becoming increasingly important to the petroleum industry and will necessitate meticulous experimental investigations, as the generalization of the behavior of azeotropes is more difficult than for normal systems.

The concept of ideal solutions (*41*) was used by the industry early in the period covered by this discussion. Hydrocarbons follow this type of behavior with reasonable accuracy at pressures somewhat above their vapor pressures. However, important divergences occur at higher pressures. Serious deviations from ideal solutions are experienced for components at reduced temperatures markedly greater than unity. Lewis (*48*) proposed a modified type of ideal solution by neglecting the volume of the liquid phase. This modification simplified the application of the concept. The Lewis generalization has been widely employed by the industry.

Brown and coworkers (*35, 54*) contributed to the correlation of the phase behavior of hydrocarbons by considering that the ratio of the fugacity of a hydrocarbon component in a phase to the mole fraction of that component is a single-valued function of pressure and temperature. This ratio is not necessarily equal to the fugacity of the component in the pure state at the same pressure and temperature. This equality would be required for an ideal solution. Generalization of this ratio as a function of the reduced temperature and pressure has been the basis of many of the correlations which are referred to in Table I. The concept of the pseudocritical state (*38*) has assisted materially in the generalization of the behavior of mixtures. However, the estimation of the pseudocritical temperature and pressure proves to be troublesome unless recourse is had to the volumetric methods originally proposed by Kay (*38*). The equilibrium ratio defined as the ratio of the mole fraction of a component in the gas phase to that in the coexisting liquid phase (*36*) has proved to be a useful means of correlating the phase behavior of hydrocarbons. However, it has been found (*61*) that the equilibrium ratios at a given temperature and pressure are markedly influenced by the nature and amount of the other components present.

The Benedict (*4*) equation of state has opened a new avenue to the correlation of the phase behavior of hydrocarbons. However, the extent of the iterative calculations required to determine the properties of the coexisting phases has prevented its widespread adoption. Recently the concept of convergence pressures (*58, 76*) has gained acceptance in the industry. This pressure is presumed to be that at which the equilibrium ratios approach unity. However, for a given mixture a true convergence pressure exists only at the critical temperature of the mixture.

At present, by appropriate choice of one of the aforementioned methods, the phase behavior of hydrocarbons can be predicted with reasonable accuracy under most of the conditions of interest. An important exception occurs in the case of retrograde dew point states, when the nature and amount of the heavier hydrocarbons present in small quantities may be of controlling importance. This uncertainty in predicting the behavior of a system may well prevail until the large number of compounds of intermediate and high molecular weight can be identified. The use of characterization factors to identify the group of hydrocarbons of greater molecular weight than decane has proved satisfactory for predicting the bubble point state, but those factors are not adequate for correlating the experimental dew point data.

The final part of Table I is devoted to a summary of the available data concerning specific components and their mixtures. Recently there has been a material increase in the available data concerning isomers of the lighter hydrocarbons. However, the field is large and many mixtures still exist for which no experimental data are available and for which the existing methods of prediction still are inadequate.

Volumetric Behavior

The early application of volumetric data for hydrocarbons made use of the perfect gas laws. They were not sufficiently descriptive of the actual behavior to permit their widespread use at pressures in excess of several hundred pounds per square inch. The need for accurate metering aroused interest in the volumetric behavior of petroleum and its products at elevated pressures. Table II reviews references relating to the volumetric behavior of a number of components of petroleum and their mixtures. For many purposes the ratio of the actual volume to the volume of a perfect gas at the same pressure and temperature has been considered to be a single-valued function of the reduced pressure and temperature or of the pseudo-reduced (*38*) pressure and temperature. The proposals of Dodge (*15*), Lewis (*12*), and Brown (*8*) with their coworkers serve as examples of the nature of these correlations. The Beattie-Bridgeman (*2*) and Benedict (*4*) equations of state describe the volumetric behavior of many pure substances and their mixtures with an accuracy adequate (*31*) for most purposes. However, at pressures above 3000 pounds per square inch the accuracy of representation with existing constants leaves something to be desired.

With regard to the nonhydrocarbon components, the references listed in Table II are

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Table II. Publications Concerning Volumetric Behavior

Subject	Status[a]		Cumulative Total Number[b]						Index Number[c]
	Component	Mixture	1925	1930	1935	1940	1945	1950	
Compressibility	8	7	0	1	3	5	7	8	II-1
Correlations	7	7	0	0	1	4	11	12	II-2
Equations of state	8	6	0	5	5	10	12	20	II-3
Miscellaneous	–	–	0	0	3	6	10	12	II-4
Carbon dioxide	10	5[d]	0	0	1	1	3	3	II-5
Hydrogen sulfide	6	3	0	1	2	3	3	4	II-6
Nitrogen	10	5	0	6	7	8	8	8	II-7
Water	10	6	0	0	2	3	3	3	II-8
Natural gas		8	2	3	4	5	8	13	II-9
Crude oil		8	0	0	0	0	3	6	II-10
Methane	9	8	0	2	4	8	16	22	II-11
Ethane	8	4	0	0	2	4	6	6	II-12
Propane	9	6	0	0	2	4	5	7	II-13
Propene	6	3	0	0	2	4	4	5	II-14
n-Butane	8	6	1	1	1	6	9	11	II-15
Isobutane	5	3	0	0	0	0	2	2	II-16
1-Butene	5	3	0	0	0	0	1	2	II-17
n-Pentane	6	4	2	2	3	4	4	4	II-18
n-Hexane	5	4	0	0	0	0	1	1	II-19
Benzene	8	6	0	0	0	1	2	6	II-20
n-Heptane	6	4	0	0	0	1	1	1	II-21
n-Octane	5	4	0	0	0	0	0	2	II-22
Decane	6	6	0	0	0	0	3	3	II-23
Total			5	21	42	77	122	161	

[a] Author's estimate of status of studies in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[b] Publications are predominantly American; foreign references which have come to author's attention have been included.

[c] American Documentation Institute (*59*).

[d] Mixtures are reported under each of components.

only those considered most pertinent. A review indicates adequate data for nearly all of the lighter hydrocarbons containing less than five atoms. However, for the compounds of high molecular weight, with the exception of benzene, there is a serious absence of data, particularly for the gas phase. The absence of data at the higher molecular weights probably results from the difficulties of measurement associated with adsorption of the heavier molecules even at low pressures. The need for additional information for states at which rates of chemical decomposition are significant serves as a challenge to the experimenter. Under such conditions it will be necessary to make rapid measurements of good precision.

Some consideration has been given to the partial volumetric (*43*) behavior of the lighter components of petroleum in both the liquid (*62*) and gas (*65*) phases. The use of these quantities in predicting the volumetric behavior of hydrocarbon mixtures is particularly valuable in estimating the effect of components present in small quantities, but is somewhat more difficult than that of a correlation based upon the pseudocritical concept (*19*) and the assumption of the law of corresponding states. It is commonly assumed that pseudocritical temperature or pressure may be taken as the molal average of the critical temperatures or pressures of the components. Except for states near retrograde dew point, the volume of a hydrocarbon mixture in the gas phase may be predicted within a few per cent at pressures up to 3000 pounds per square inch. At higher pressures the uncertainty is somewhat greater. The volumetric behavior of hydrocarbon liquids also may be estimated with comparable accuracy (*62*), if the requisite data concerning the composition and characterization factors of the phase are available.

Thermodynamic Data

The interest in thermal data for hydrocarbons stems from two sources. The first relates to a need to establish the chemical potential (*21*) or the free energy (*44*) of pure compounds from measurements of the heat capacity from low absolute temperatures to the temperatures of interest. Such measurements and the third law of thermodynamics permit the evaluation of the free energy. The second industrial interest in thermodynamic properties arises from a need to evaluate the heat and work associated with changes in state of hydrocarbon systems. The measurements by Rossini (*57*), Huffman (*17*), and Parks (*32, 53*) are worthy of mention in a field replete with a host of careful investigators. Such thermal measurements have been of primary utility in predicting chemical equilib-

Table III. Publications Concerning Thermodynamic Properties

Subject	Status[a]		Cumulative Total Number[b]						Index Number[c]
	Component	Mixture	1925	1930	1935	1940	1945	1950	
Correlations	7	6	0	0	0	0	1	2	III-1
Miscellaneous	–	–	1	6	8	12	16	26	III-2
Carbon dioxide	8	4[d]	0	0	0	2	2	2	III-3
Hydrogen sulfide	5	2	0	0	1	4	5	6	III-4
Nitrogen	8	4	0	1	5	5	6	6	III-5
Water	10	5	1	1	1	4	5	6	III-6
Natural gas		7	0	0	0	0	2	3	III-7
Crude oil		5	0	0	1	1	1	3	III-8
Hydrocarbons, general	–	–	0	1	3	11	12	42	III-9
Methane	9	6	0	3	6	8	10	15	III-10
Ethane	7	3	1	2	2	4	5	7	III-11
Ethene	3	–	1	1	1	1	1	1	III-12
Others[e]	2	–	0	0	0	2	2	2	III-13
Propane	7	6	0	1	2	4	5	7	III-14
Propene	5	–	0	0	0	2	2	6	III-15
Others[e]	3	–	0	0	1	2	2	2	III-16
n-Butane	7	5	0	1	2	10	10	14	III-17
Isobutane	5	3	0	0	0	2	2	3	III-18
1-Butene	3	–	0	1	1	1	3	9	III-19
Others[e]	1	–	0	0	1	1	1	1	III-20
n-Pentane	7	3	0	0	9	12	18	26	III-21
Pentene	3	–	0	0	0	0	0	3	III-22
Others[e]	2	–	0	0	1	2	2	6	III-23
n-Hexane	5	–	0	0	0	2	3	8	III-24
Benzene	6	3	0	0	0	2	2	4	III-25
Others[e]	3	–	0	0	0	1	1	5	III-26
n-Heptane	3	–	0	0	0	0	2	7	III-27
Others[e]	1	–	0	0	0	0	0	2	III-28
Octane	4	2	0	2	3	3	5	5	III-29
Others[e]	1	–	0	0	0	0	0	2	III-30
Nonane	1	–	0	1	2	2	2	2	III-31
Decane	4	2	0	2	3	3	3	5	III-32
Total			4	23	53	103	131	238	

[a] Author's estimate of status of studies in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[b] Publications are predominantly American; foreign references which have come to author's attention have been included.

[c] American Documentation Institute (*59*).

[d] Mixtures are reported under each of components.

[e] Compounds containing same number of carbon atoms as those in main paraffinic heading have been included in this category.

rium at elevated temperatures. The thermodynamic properties of many substances were summarized at atmospheric pressure by Lewis and Randall (*44*) and by Bichowsky and Rossini (*7*) without particular attention to petroleum. Similar data have been accumulated by Rossini (*57*) in connection with his work for the American Petroleum Institute. When combined with information concerning the effects of pressure and temperature upon the specific volume of pure substances and their mixtures, these data furnish the requisite thermodynamic background from which the heat and work associated with changes in state may be evaluated. Edmister (*19*) has prepared numerous correlations of the thermodynamic properties of hydrocarbons on the basis of composition, characterization factors, and the reduced state of the system. This method of correlation has received wide acceptance in the petroleum industry.

Table III presents the references covering the thermodynamic properties of a number of hydrocarbons and their mixtures. No effort has been made to include the broad background of thermal data considered by Rossini (*57*). In many instances the references involved such a large number of compounds that detailed cataloging was difficult; for this reason there are many references under the heading of "Hydrocarbons, general." Thermodynamic studies of the pure nonhydrocarbon compounds have been sufficiently extended to indicate that the available data are adequate for the needs of the industry. It is surprising that ethane has received so little attention as compared to the hydrocarbons of higher or of lower molecular weight. The butanes and pentanes have been investigated in sufficient detail for present purposes, and a wealth of information is at hand concerning the thermodynamic properties of methane. A recent tabulation (*66*) presents the effects of pressure and temperature upon the enthalpy, entropy, and specific volume of a number of the lighter paraffin hydrocarbons and their binary mixtures. Such data also are available in many of the common handbooks.

The volume of tabular information necessary to record in detail the thermodynamic data for the paraffin hydrocarbons and their mixtures, as was done for steam, is excessive. It appears hopeful that graphical generalizations typified by the work of Edmister (*19*) will prove adequate for the less rigorous requirements of design, whereas the Benedict equation of state (*4*) may be employed where precision is necessary. However, the effective application of this equation of state to compounds containing more than four carbon atoms per molecule still awaits the evaluation of the constants. After the composition and specific volume have been established for a particular state, the solution of equations of state to establish enthalpy and entropy is a straightforward process.

Surface Properties

The energy associated with the interfaces between phases plays an important part in certain aspects of the migration of petroleum in underground reservoirs. For this reason there has long been interest in the interfacial tension between the phases of petroleum. The work of Swartz (*71*) was one of the early efforts to determine the effect of changes in pressure and composition upon the interfacial tension between the liquid and gas phases of petroleum. The methods of determining the interfacial tension between phases have been improved and the pendant drop method (*16, 25*) appears to be one of the more useful approaches to such measurements, particularly at elevated pressures.

Table IV. Publications Concerning Surface Phenomena

Subject	Status[a]		Cumulative Total Number[b]						Index Number[c]
	Component	Mixture	1925	1930	1935	1940	1945	1950	
Adsorption	1	1	0	0	0	0	0	9	IV-1
Prediction	3	3	0	0	0	3	3	6	IV-2
Miscellaneous	–	–	0	1	4	4	4	4	IV-3
Water	8	3[d]	0	0	0	1	1	3	IV-4
Crude oil		5	0	1	3	5	6	5	IV-5
Ethane	3	2	1	1	1	1	1	1	IV-6
Ethene	2	–	1	1	1	1	1	1	IV-7
Propane	6	3	2	2	2	2	2	7	IV-8
Propene	3	–	1	1	1	1	1	1	IV-9
Butane	3	1	0	0	1	1	1	1	IV-10
Isobutane	3	1	0	1	1	1	1	1	IV-11
Butene	2	–	0	1	2	2	2	2	IV-12
Pentane	3	1	0	0	1	1	1	1	IV-13
Isopentane	3	–	0	0	1	1	1	1	IV-14
Pentene	3	–	0	0	1	1	1	1	IV-15
n-Hexane	5	2	2	3	3	3	3	3	IV-16
Hexene	2	–	0	0	0	1	1	1	IV-17
Heptane	5	2	1	2	3	3	3	3	IV-18
Octane	6	2	3	3	4	4	4	4	IV-19
Octene	3	–	0	0	1	1	1	1	IV-20
Nonane	3	–	1	2	3	3	3	3	IV-21
Nonene	2	–	0	0	1	1	1	1	IV-22
Decane	4	2	0	0	3	3	3	3	IV-23
Decene	3	–	0	0	1	1	1	1	IV-24
Total			12	19	38	45	46	64	

[a] Author's estimate of status of studies in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[b] Publications are predominantly American; foreign references which have come to author's attention have been included.

[c] American Documentation Institute (*59*).

[d] Mixtures are reported under each of components.

In Table IV is presented a brief review of the literature relating to surface phenomena. In recent years much interest has been shown in the adsorption of hydrocarbons upon solids. No effort has been made to include references to analytical methods based upon selective adsorption. This process is often employed in the purification of hydrocarbons and in some cases is superior to fractionation. The work of Lewis and Gilliland (*45–47*) reviews the status of the techniques and data relating to the adsorption of petroleum upon solid surfaces. The increasing importance of such techniques is evidenced by the recent development of commercial processes (*5, 30*) for the separation of hydrocarbons based on adsorption.

Optical Properties

The optical properties of the components of petroleum have been of major importance in connection with their identification and in the determination of purity. The primary effort has been directed to the study of pure hydrocarbons and only limited work has been concerned with the prediction of the index of refraction and the specific rotation of hydrocarbon mixtures. Table V summarizes the optical properties of a number of the principal components of petroleum. Only a few references to the optical properties of pure hydrocarbons of primary interest to the analyst have been included. Developments (*9*) in refractometers have materially increased the potentialities of the index of refraction measurements at atmospheric pressure as an analytical method. Consideration of the pertinent data in this field is beyond the scope of the present discussion. Reviews of developments in infrared (*24, 26*) and mass spectrometry (*68*) are available.

Nonequilibrium Processes

In connection with nonequilibrium processes, attention is directed to rheological characteristics and transfer phenomena, which are important in a consideration of momentum, thermal, and material transfers.

From the standpoint of rheology, the viscosity of hydrocarbons is one of the more important properties (*67*). For many of the conditions of interest in petroleum processing and production, it is not necessary to consider the effect of pressure upon the viscosity of the hydrocarbon phases. However, in many situations involving elevated pressures the effect is of great importance. The marked influence of state upon the viscosity of hydrocarbons is illustrated by measurements for propane (*63*). The pressures encountered in petroleum reservoirs exert a marked effect (*64*) even upon the viscosity of liquids. In Table VI the available references concerning viscosity, plasticity, and other rheological properties are summarized. As may be seen from Figure 1, the rate of accumulation of data concerning the rheological properties of petroleum and its components has been somewhat more constant than in most of the other fields considered.

Data considered here for thermal transfer processes have been limited to the intensive properties of the phases. They have not included the large background of information associated with radiant and convective thermal transfer which has accumulated (*33, 49*)

Table V. Publications Concerning Optical Properties[a]

Subject	Status[b]		Cumulative Total Number[c]						Index Number[d]
	Component	Mixture	1925	1930	1935	1940	1945	1950	
Critical state	3	–	0	0	0	0	1	1	V-1
Prediction	2	–	0	0	0	0	0	1	V-2
Hydrocarbons, general	–	–	0	0	0	1	6	6	V-3
Methane	3	2[e]	1	1	1	1	1	1	V-4
Propane	4	3	0	0	0	1	1	1	V-5
Propene	4	2	1	1	1	1	1	1	V-6
Butane	3	2	0	0	0	1	1	1	V-7
Isobutane	3	–	0	0	0	1	1	1	V-8
Pentane	4	3	0	0	1	1	1	1	V-9
Isopentane	5	2	0	1	1	1	1	1	V-10
Pentene	5	2	0	0	1	2	2	2	V-11
Hexane	7	3	0	0	1	1	1	1	V-12
Hexene	8	–	2	3	6	6	6	6	V-13
Benzene	5	3	0	0	0	2	2	2	V-14
Heptane	5	2	0	1	1	2	2	2	V-15
Heptene	8	–	3	4	7	7	7	7	V-16
Octane	8	3	1	4	7	10	10	10	V-17
Octene	8	–	1	1	7	8	8	8	V-18
Nonane	8	4	3	5	7	8	8	8	V-19
Nonene	8	–	1	2	5	6	6	6	V-20
Decane	8	3	2	3	6	8	8	8	V-21
Decene	6	–	0	1	3	3	3	3	V-22
Total			15	27	55	71	77	78	

[a] Optical properties of carbon dioxide, hydrogen sulfide, nitrogen, and water have not been considered.

[b] Author's estimate of status of studies in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[c] Publications are predominantly American; foreign references which have come to author's attention have been included.

[d] American Documentation Institute (*59*).

[e] Mixtures are reported under each of components.

Table VI. Publications Concerning Rheological Properties

Subject	Status[a]		Cumulative Total Number[b]						Index Number[c]
	Component	Mixture[d]	1925	1930	1935	1940	1945	1950	
Critical state	4	2	0	0	2	3	3	3	VI-1
Prediction	4	6	0	1	1	2	2	5	VI-2
Carbon dioxide	8	3[e]	2	4	5	5	6	6	VI-3
Nitrogen	8	3	0	1	3	4	4	5	VI-4
Water	9	4	1	2	6	7	7	7	VI-5
Natural gas		7	2	2	2	2	4	5	VI-6
Crude oil		9	0	5	5	7	8	12	VI-7
Methane	7	6	4	4	4	6	8	11	VI-8
Ethane	4	3	0	1	1	2	2	3	VI-9
Ethene	3	–	0	0	1	1	1	1	VI-10
Propane	8	7	0	0	4	5	7	7	VI-11
Propene	3	–	0	0	1	1	1	1	VI-12
n-Butane	6	6	1	2	2	2	3	4	VI-13
Isobutane	3	3	0	0	0	0	1	2	VI-14
Pentane	6	4	0	4	4	4	4	4	VI-15
Isopentane	4	–	1	1	1	1	1	1	VI-16
Pentene	4	–	1	1	1	1	1	1	VI-17
Hexane	4	3	1	2	2	2	2	2	VI-18
Hexene	3	–	1	1	1	1	1	1	VI-19
Benzene	4	–	0	0	0	0	1	1	VI-20
Heptane	3	3	1	2	2	2	2	2	VI-21
Heptene	4	–	1	1	1	2	2	2	VI-22
Octane	3	2	0	1	1	1	1	1	VI-23
Octene	4	–	0	0	0	0	1	1	VI-24
Nonane	5	–	0	0	2	3	3	3	VI-25
Decane	3	–	0	0	1	1	1	1	VI-26
Total			16	35	53	65	77	92	

[a] Author's estimate of status of studies in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[b] Publications are predominantly American; foreign references which have come to author's attention have been included.

[c] American Documentation Institute (*59*).

[d] Only rheological properties of homogeneous phases are considered here.

[e] Mixtures are reported under each of components involved.

in the past quarter century. The measurement of thermal conductivity of gases is difficult, and the recent work of Hirschfelder (*27*) has extended the application of statistical mechanics to this problem. Eddy conductivity and its important analogy with the turbulent transfer of momentum (*13, 34*) have not been considered. The rapid advances in the field of fluid mechanics, particularly as applied to compressible fluids, should add much to the ability of the technician to predict thermal transfer in flowing systems. Table VII presents a brief review of available information about thermal diffusion in petroleum. This review is not complete and has been limited primarily to the recent past. For this reason the references which have been included in Table VII do not appear in Figure 1.

Material Transfer

Diffusion is of importance in a number of operations associated with the production and refining of petroleum. Because the diffusion "constant" of a component is influenced markedly by the state of the system, the pressure and composition of a phase exert a material influence upon its diffusion. Again statistical mechanics has been of assistance in outlining the interrelation of the several diffusion coefficients. In this regard the reciproc-

Table VII. Recent Publications Concerning Thermal Diffusion

Subject	Status[a]	Total[b]	Index Number[c]
Prediction	2	1	VII-1
Carbon dioxide[d]	2	2	VII-2
Nitrogen	4	2	VII-3
Crude oil	4	1	VII-4
Hydrocarbons, general	–	1	VII-5
Methane	2	3	VII-6
Total		10	

[a] Author's estimate of status of studies in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[b] Publications are predominantly American; references which have come to author's attention have been included.

[c] American Documentation Institute (*59*).

[d] These data relate only to pure substances and no consideration has been given to mixtures.

Table VIII. Publications Concerning Diffusion Coefficients

Subject	Status[a] Component[d]	Status[a] Mixture	Cumulative Total Number[b] 1925	1930	1935	1940	1945	1950	Index Number[c]
Gases	–	–	0	0	0	0	0	1	VIII-1
Liquids	2	4	0	0	0	0	0	3	VIII-2
Theory and prediction	4	3	0	0	0	0	1	7	VIII-3
Miscellaneous	–	–	0	0	2	2	3	4	VIII-4
Water	–	2[e]	0	0	0	0	0	2	VIII-5
Natural gas		3	0	0	0	0	0	4	VIII-6
Crude oil		3	0	0	0	0	0	1	VIII-7
Methane	–	4	0	0	2	3	3	4	VIII-8
Propane	–	3	0	0	1	1	1	1	VIII-9
Total			0	0	5	6	8	27	

[a] Author's estimate of status in comparison with potential use by industry expressed on a probability scale extending from 0 to 10.

[b] Publications are predominantly American; foreign references which have come to author's attention have been included.

[c] American Documentation Institute (*59*).

[d] Data for components pertain to self-diffusion and techniques for measurements of this quantity have been developed only recently.

[e] Mixtures are reported under each of components.

ity expressions designated by Onsager (*52*) have indicated the basic relationships in a field which has received but little attention since the early work of Maxwell (*50*). Recently a summary of the diffusion constants of a large number of actual gases and liquids (*70*) became available. Hirschfelder (*14*) has considered multicomponent diffusion from the viewpoint of statistical mechanics.

The microscopic consideration of diffusional processes has not received the attention given to the analogous aspects of the thermal transfer of energy. The large variations in the diffusion coefficient with change of state and the marked changes in volume during diffusion have complicated the analysis of these processes from the microscopic standpoint. As in the discussion of thermal transfer, no consideration has been given to the effects of flow processes or convective influences upon material transfer. Table VIII summarizes the references that relate to diffusion coefficients of interest to the petroleum industry.

Conclusions

Physical chemistry and related sciences have played an increasingly important role in the explanation and prediction of physical phenomena which are useful in the production and processing of petroleum. Knowledge of the volumetric and phase behavior of hydrocarbons has so developed that such properties may be predicted with reasonable accuracy at most of the states of interest except those near retrograde dew point. The inability to describe with certainty the composition of many hydrocarbon mixtures in terms of their components places a severe limitation on the prediction of the volumetric and phase behavior of petroleum and of mixtures of its components.

Thermodynamics has been a useful tool in predicting physical and chemical equilibria and in determining the heat and work associated with actual processes. Progress has been made in the application of the third law of thermodynamics in conjunction with heat capacity data at low temperatures to predict the chemical potential or free energy of numerous pure hydrocarbons. The background of thermodynamic data at elevated pressures for both the gas and liquid phases has increased materially and useful equations of state now are available. They permit the accurate estimation of the volume, enthalpy, and entropy of the lighter hydrocarbons and their mixtures over the greater part of the range of pressures and temperatures of industrial interest. Predictions of thermodynamic properties based on the law of corresponding states also have proved useful.

The optical characteristics of many of the pure hydrocarbons have been investigated extensively. This situation is particularly true in regard to the index of refraction under ambient laboratory conditions, as this property has proved to be a useful analytical tool.

The background of experimental work remains insufficient to permit estimations of the interfacial tension between hydrocarbon phases and between hydrocarbon and solid or aqueous phases. However, satisfactory experimental techniques have been developed and the pertinent experimental facts should be forthcoming if the industrial need continues.

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Limited information concerning surface tensions under atmospheric conditions is available for a variety of hydrocarbons.

In the field of rheology, primary emphasis has been placed upon Newtonian fluids. At low pressures there are adequate viscosity data concerning hydrocarbon phases to permit useful generalizations. Only limited information on the effect of pressure on the viscosities of liquids and gases has been obtained. However, the rapid changes in viscosity with state in the critical region make difficult the prediction of viscosity in many flowing systems of interest in the production of petroleum. Advances in fluid mechanics have increased the importance of knowledge of rheological properties of petroleum, for it is now possible to predict with some certainty the velocity in a flowing fluid as a function of time and spatial position if requisite physicochemical properties have been measured.

The increased understanding of turbulence and the extension of the analysis of potential flow have made possible the consideration of many thermal and material transfer problems which formerly were not susceptible to analysis. However, at present the application of such methods is hampered by the absence of adequate information concerning the thermal conductivities and diffusion coefficients of the components of petroleum. The diffusion coefficient in particular is markedly influenced by the state of the phase. For this reason much experimental effort will be required to obtain the requisite experimental background to permit the quantitative application of the recent advances in fluid mechanics and potential theory to dynamic transfer problems of practical interest.

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Analysis of Petroleum

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The history, progress, and development in the field of analysis and testing of petroleum, its products and auxiliaries, are reviewed and an attempt is made to forecast the likely avenues of future developments in this field. The survey considers the simple physical methods that have long been used and the technically involved instrumental and chemical methods that have been developed over these years. These include but are not limited to microchemistry, adsorption, refractometry, radiation methods of analysis, and analytical methods and devices used on plant units and streams.

The papers in this symposium on "25 Years of Progress in Petroleum Technology" present an impressive picture of development in manufacturing and processing operations on old and new products from, and relating to, petroleum. These new processes and products created needs on the one hand for new analytical methods and devices, while on the other hand the very development of some of those products and processes has been dependent upon methods of analysis which are precise enough and fast enough to evaluate progress in those developments.

Exhaustive comparisons between the developments that constitute steps in the progress of analysis and testing of petroleum and its products for the past quarter century are impossible; therefore, only those developments that impressed this author as being milestones in that progress or which serve to illustrate the magnitude and quality of that growth are discussed. For a more detailed account of progress in analysis of petroleum in the last decade, the reader is referred to the reviews by Levin (*35–37*).

Twenty-five years ago a unit of 100 men was a very large petroleum laboratory staff. Today numerous major oil companies have over 700 men in the groups that grew from those older laboratories. The number of men engaged in analysis and testing has grown proportionately.

The analytical and testing facilities of a petroleum laboratory of that time look mighty meager by the standards of today. A comparison of the report and standards of the petroleum section of the American Society for Testing Materials (ASTM) for 1925 (*3*) and 1950 (*4*) reflect the expansion that has taken place. In 1925 there were 100 pages comprising 8 chemical procedures and 18 physical testing methods. In 1950 there were 700 pages devoted to 48 chemical procedures and 77 physical testing methods, exclusive of an additional 100 pages in a separate volume devoted to asphalt. Qualitatively, the expansion is even more impressive. The 1925 text contains chemical procedures only for water, sulfur, detection of free sulfur, acidity, saponification number, and grease analysis. In 1950 there were included such intricate analyses as the precise determination of aromatics by chromatography, benzene by ultraviolet absorption, phosphorus by spectrophotometry, oil in wax by microchemistry. Methods for the determination of tetraethyllead in gasoline by polarography, hydrocarbon analysis by infrared and mass spectrometry, etc., are under study.

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Hydrocarbon Gas Analysis

Industrial analysis of hydrocarbon gases 25 years ago was limited almost to Orsat-type absorptions and combustion, resulting in crude approximations and inadequate qualitative information. The more precise method of Shepherd (*56*) was available but too tedious for frequent use. A great aid to the commercial development of hydrocarbon gas processes of separation and synthesis was the development and commercialization of high efficiency analytical gas distillation units by Podbielniak (*50*). In these the gaseous sample is liquefied by refrigeration, distilled through an efficient vertical packed column, the distillation fractions collected as gas and determined manometrically at constant volume. The operation was performed initially in manually operated units, more recently in substantially automatic assemblies.

Unsaturated constituents of gaseous hydrocarbon mixtures were generally determined as a unit, most frequently by absorption in sulfuric acid—with all the complications of solution of saturated constituents in the acid and in the undissolved polymers which resulted. The apparatus and procedure of McMillan *et al.* (*42*) for determining total olefinic unsaturation by hydrogenation over a nickel catalyst was a real improvement in hydrocarbon gas analysis, as was his (*41*) scheme for analyzing a mixture of C_4 hydrocarbons for individual members. He employed distillation to produce two cuts and by hydrogenation and hydrochlorination determined isobutane, isobutene, and 1-butene in the first cut; and by hydrogenation for total butenes, bromination and determination of refractive index of the dibromides, determined *cis-* and *trans-*butenes and *n*-butane in the second cut. The hydrochlorination for isobutene was accomplished in a special apparatus, the gaseous sample and hydrogen chloride being condensed together, then evaporated to leave the chloride as a residue of insignificant vapor pressure under the conditions of the test. With application (*61*) of the Diels-Alder reaction to the determination of 1,3-butadiene in hydrocarbon gas by absorption in molten maleic anhydride at 100° C., the analysis of C_4 hydrocarbons by chemical means was accomplished.

Instrumental Methods of Analysis

In reviewing the literature one becomes aware that about 12 years ago the petroleum industry was undergoing partial transition into a synthetic chemicals industry and this is reflected in the variety of analyses required. Production of synthetic rubber, 1,3-butadiene, isobutene, isobutane, styrene, diisobutene, alkylate, iso-octane, copolymer, cumene, and toluene was greatly aided by instrumental analysis including ultraviolet, infrared, mass and emission spectrometry. Without these methods many of the analyses would be entirely impractical because of tediousness, long elapsed time for results, and general expense of operation.

Although infrared absorption analysis of hydrocarbon mixtures was described by Lecomt and Lambert (*34*), the extensive application of this technique to the examination of petroleum products awaited the commercial availability of a practical instrumental unit and adequately described methods such as those of Brattain and Beeck (*11*) for a two component mixture and Brattain *et al.* (*12*) for a multicomponent mixture of hydrocarbon gases. By such methods the possible qualitative constituents of the sample must, of course, be known and their number limited to a maximum probably simultaneously present.

Ultraviolet absorption is particularly useful for the determination of compounds possessing conjugated unsaturation and as far as hydrocarbon gases are concerned, this includes diolefins such as 1,3-butadiene and its five carbon equivalents.

The development of a commercial mass spectrometer and its application to hydrocarbon gas analysis by the method of Washburn *et al.* (*63*) made gas analysis rapid, economical, and, what is even more important, inspired a confidence in the results of routine hydrocarbon gas analysis which was badly lacking. A complex gaseous mixture comprising the atmospheric gases, carbon monoxide, and C_1 to C_5 hydrocarbons required more than 20 hours of applied time by the previous methods of low temperature fractional distillation coupled with chemical absorption methods. With the mass spectrometer such an analysis is completed in 2 hours or less, about 15 minutes of which is consumed in the

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preparation of the mass spectrogram, the balance being devoted to computation. The computations are greatly aided by mechanical calculators, electrical computers, and more recently by machinery of International Business Machines Corp.

The analytical chemist in the field of petroleum owes much to the projects of the American Petroleum Institute (API). As a result of this work reliable physical properties, ultraviolet absorption, infrared absorption, Raman, and mass spectra of a large number of hydrocarbons are now available. Many of these hydrocarbons can be obtained through the API and are pure enough to be used to calibrate spectrometers. This has been tremendously helpful in extending the usefulness of the newer instrumental methods of analysis. The high purity of these hydrocarbons—many better than 99.5%—deserves special mention. So does the outstanding freezing point procedure developed by Mair *et al.* (*45*) and Glasgow *et al.* (*22*) which provides a practical precision method for determining the quality of such high purity hydrocarbon gases and liquids.

Analysis of Liquid Hydrocarbons

Compared with the methods of today, the procedures that were available 25 years ago for the analysis of liquid hydrocarbons—for example, in the gasoline range—were limited indeed. The method of Egloff and Morrell (*17*) represented a substantial improvement over the then current practices. It provided a moderately reliable method for determining unsaturated and aromatic hydrocarbons in gasoline by taking distillation cuts, treating them with 80% sulfuric acid, measuring the absorption, distilling the unabsorbed layer to a predetermined temperature, and measuring the increase in residue due to polymerization of some unsaturated hydrocarbons. The sum of that which was absorbed and that which was polymerized was considered the unsaturation of the sample. The aromatics were determined in the acid-treated distillate by treatment with a special mixture of nitric and sulfuric acids which produced three layers, the intermediate one being the nitro derivatives of the aromatic hydrocarbons. By changing the concentration of acid, Towne (*60*) modified this method to reduce errors due to alkylation which caused some of the aromatics and unsaturated hydrocarbons to combine to form high boiling aromatics which raised the value for aromatic content and lowered that for unsaturated constituents. Before these methods were published it was common practice to determine unsaturated plus aromatic hydrocarbons by direct absorption in strong acids and to determine unsaturation by absorption in a weaker acid or; indirectly, by iodine or bromine number.

The development of radiation methods such as ultraviolet absorption, infrared absorption, Raman and mass spectrometry tremendously increased the analytical possibilities on liquid hydrocarbons, particularly in the gasoline boiling range. However, these instrumental procedures are frequently lacking in specificity; therefore, the development of precision distillation columns which permitted isolation of narrow distillation fractions containing small numbers of hydrocarbon constituents was a prerequisite to their extensive application and utility. Among such distillation units should be specially mentioned the practical and efficient random helices packing of Fenske *et al.* (*18*), the wire screen packing of Stedman (*58*), and the formed wire packing of Podbielniak (*51*). Willingham and Rossini (*69*) described the application of columns of high efficiency to the analysis of petroleum by ordinary as well as azeotropic and extractive distillation. Selker's *et al.* (*55*) low hold-up concentric glass tube column of high efficiency and capable of handling small samples is finding extensive application.

The development of distillation columns with rotating elements, described by Baker *et al.* (*5*) and Willingham *et al.* (*70*), indicates a trend which probably will be followed in future developments to reduce the time required to reach equilibrium and hence the time for an efficient fractionation. Hickman's (*27*) type of molecular distillation will certainly acquire increasing importance for analytical uses as one becomes more concerned with the higher boiling constituents.

Chromatography. The outstanding possibilities of chromatography in hydrocarbon analysis were demonstrated by Mair and Forziati (*43*) who determined aromatic hydrocarbons in gasoline by percolating it through a column of silica gel, following the change in nature of the percolate by refractive index on small successive fractions leaving

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the bottom of the column, and extended the technique to higher boiling hydrocarbon mixtures like kerosene for which they (*44*) employed a 52-foot adsorption column. Although developed to a point where aromatic constituents can be determined very accurately and precisely, the method is nevertheless quite simple as regards manipulation and practical enough to be in frequent competition in many laboratories with the earlier, less precise and less reliable, faster procedures such as acid absorption, aniline point change, and specific dispersion.

Radiation Methods of Analysis. The problem of determining individual hydrocarbons in liquids is much more complex than in gases because of the possible greater complexity of the former; therefore, radiation methods of analysis are even more important here. Without them, analysis of liquid mixtures for individual hydrocarbons generally would be prohibitive.

Infrared absorption methods of analysis for hydrocarbon mixtures in the gasoline range, which entailed preliminary distillation into narrow boiling fractions each of which contains a relatively small number of constituents, have been described by Kent and Beach (*32*), Heigl *et al.* (*25*), and Webb and Gallaway (*64*). Such methods have been extensively employed in the analysis of alkylate, polymer, commercial iso-octane, *n*-heptane, and many other hydrocarbon mixtures in the gasoline boiling range. Weizmann *et al.* (*65*) used ultraviolet absorption to determine benzene, toluene, xylene, naphthalene, phenanthrene, and anthracene in petroleum and shale oil. The introduction of a commercial ultraviolet spectrophotometer, such as that described by Cary and Beckman (*16*), initiated the extensive application of this technique for the determination of aromatic hydrocarbons. A procedure in much greater detail was presented by Fulton (*20*) for determining individual members of a multicomponent aromatic hydrocarbon mixture both in the presence and absence of nonaromatic hydrocarbons. Raman spectroscopy has not been as extensively applied as ultraviolet nor infrared absorption but an excellent description of the method was given by Grosse *et al.* (*23*) and Rosenbaum (*53*).

Unsaturation of Liquid Hydrocarbons. Estimating unsaturation of liquid hydrocarbons from their capacity for adding halogens—for example, by iodine number and bromine number methods—frequently leaves much to be desired because with mixtures such as gasoline, assumptions must be made for molecular weight of the olefins. This is frequently a source of considerable error, in addition to errors due to substitution, diolefins, etc. An interesting approach for determining unsaturation by a less indirect chemical method was taken by Bond (*9*) who employed nitrogen tetroxide which reacts with unsaturated hydrocarbons to form products of low volatility; unreacted hydrocarbons are removed by steam distillation and measured. Such less indirect methods for determining unsaturation are attractive and will doubtlessly see further development.

Composition Analysis. The problem of determining individual hydrocarbons and classes of hydrocarbons in petroleum mixtures becomes progressively more difficult with increasing boiling point, but progress is being made by using methods involving consideration of sets of physical properties and more directly as described by Lipkin *et al.* (*40*) who modified the silica gel adsorption method of Mair (*45*) by percolating a pentane solution of lubricating oil sample through the gel, desorbing aromatics with a mixture of benzene and methanol, and evaporating the solvent to leave aromatics as residue for weighing.

With still higher boiling petroleum products, composition analysis is difficult indeed, although on asphalt, for example, progress is being made. The methods are still far from satisfactory analytically, but separation into classes of constituents provides useful information for placing asphalts into groups of practical significance to service performance.

The early methods for determining wax in asphaltic products employed high temperature distillation, vigorous chemical treatment, or selective adsorption to eliminate interference of asphaltenes and resins before the wax could be determined by crystallization methods (*2*). The Holde method, involving destructive distillation of sample to coke, was best known and most widely used. Since solid paraffins may be decomposed or altered by such vigorous treatment, the reliability of the results was in doubt. A new approach to the elimination of the interfering asphaltenes-resin fraction was described by Knowles and Levin (*33*) who made a nondestructive separation with liquid propane at 70° C. The methods of Strieter (*59*), Hoiberg and Garris (*28*), and Hubbard and Stanfield (*29*) who modified and extended Marcusson's (*46*) principle of empirical group separations, and the much more comprehensive separations of O'Donnell (*48*) based on molecular size and type, involving solvent fractionation, distillation, silica gel adsorption using a graded series of eluants, thermal liquid diffusion, and urea complexing, may be the encouragement needed for more extensive development in this difficult field of analysis.

Viscosity Determinations. Not all developments have been so glamorous as hydrocarbon analysis. Even so prosaic a test as viscosity determination has undergone significant variations. The Saybolt Universal viscometer was the universal standard in petroleum laboratories for some 50 years, despite its limitations. With it the viscosity of lubricating oil is determined and reported in seconds required for 60 ml. of sample to flow from the thermostated reservoir into a calibrated receiver kept at room temperature. More stringent requirements caused the ASTM about 14 years ago to standardize and adopt an alternative method of greater precision and reliability involving an all-glass apparatus in which the arms of a U-tube constitute the reservoir and receiver, both of which are within the thermostated bath. The Saybolt instrument requires about 75 ml. of sample and the kinematic viscometer about 10 ml. Micro viscometers, requiring a drop or two of sample, have been described by Levin (*38*), Cannon and Fenske (*15*), and Sommer and Wear (*57*). Instruments that continuously indicate viscosity are available for installation on plant streams and Franzen (*19*) reported the use of one for motor oil distillates. Even the possibilities of a torsionally vibrating crystal as a rapid means of determining viscosity of lubricating oils have been investigated (*47*).

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Tetraethyllead in Gasoline. The determination of tetraethyllead in gasoline is another good example of the ever-broadening approach to the determination of constituents in petroleum products. The earlier methods involved precipitation with chlorine or bromine. Then came improvements in the chemical methods, such as Baldeschwieler's (*6*) use of nitric acid to extract the lead in a rapid method for the determination of tetraethyllead in gasoline and then Schwartz's (*54*) improvement upon this procedure by use of a solution of potassium chlorate in nitric acid to extract the lead, the determination being completed gravimetrically as sulfate or chromate. The most extensively used chemical method is doubtlessly that of Calingaert and Gambrill (*13*) which uses a special apparatus combining the features of a reflux still and a separatory funnel to digest the sample with concentrated hydrochloric acid, completing the determination gravimetrically as chromate or volumetrically by molybdate titration. This method became the ASTM standard which is still in use.

More recently instrumental methods have been gaining popularity for this determination. Borup and Levin (*10*) applied the polarograph to the hydrochloric acid extract of the sample. Hansen *et al.* (*24*) determined tetraethyllead polarographically after dissolving the gasoline sample in Cellosolve containing hydrogen chloride; however, unsaturated hydrocarbons interfere. Offutt and Sorg (*49*) employed a direct reading polarograph applied to the acid extract of the sample, using antimony as pilot ion. Recently Hughes and Hochgesang (*30*), Calingaert *et al.* (*14*), Liebhafsky and Winslow (*39*), and Vollmar *et al.* (*62*) described x-ray absorption methods and Birks *et al.* (*7*) employed x-ray fluorescence for the determination of tetraethyllead in gasoline. The use of x-ray absorption for determining tetraethyllead in gasoline, because of its speed and relative simplicity, is finding growing favor. Surprisingly, Aborn and Brown (*1*) in 1929 described an x-ray absorption method for determining lead in gasoline and claimed an accuracy of 0.1 cc. of tetraethyllead per gallon. The failure of industry to utilize the teachings of this paper earlier is doubtlessly attributable to the lack of a commercially available x-ray unit and of adequately trained personnel to construct such units before they became commercially available.

Determination of Auxiliary Products. In addition to more conventional petroleum products, petroleum companies today are concerned with miscellaneous organic and inorganic materials either as auxiliary products of their own manufacture or items of purchase relating to their operations. Twenty-five years ago inorganic analysis was a very minor phase of analytical work in the petroleum laboratory. The advent of catalytic cracking, hydrocarbon synthesis, additives to modify the properties of lubricating oil, etc., has changed the picture so that now a large number of chemists and practically all methods of analysis are used for this purpose. In addition to wet chemical procedures, emission spectrometry, flame photometry, electrodeposition, polarography, and x-ray diffraction are regularly employed.

Further indication of how much more chemical the analytical requirements of the petroleum industry have become is evident from the nature of the problems on which the Committee on Analytical Research of the American Petroleum Institute is engaged. These problems include precise determinations of oxygen, nitrogen, and trace metals in crude oils, charge stocks, and cracking catalysts.

Microchemical Analysis

Until a few years ago, in petroleum laboratories, it was a happy or unhappy "out," depending on the temperament of the investigator, too often to report "sample too small for analysis." There is little excuse for this today. Though it is of course impossible to make an empirical test on a few drops of oil when the empirical method specifies that a liter should be used, it is surprising how often one skilled in microchemical methods can modify an existing method or develop an equivalent one that will enable him to obtain, on a few drops of sample, information that can be expressed directly, or at least interpreted, in terms of the results from the large sample and the standard method.

Semimicro methods of analysis have been extended to the application of such a "down to earth" problem as the determination of oil in wax by Wiberly and Rather (*67*). This procedure is certainly no academic development and is at the present time undergoing standardization in the ASTM. It will probably replace the existing macro method. These authors (*68*) adapted and employed analysis under the microscope to analyze sediments and deposits collected from systems employing petroleum lubricants. The petrographic and binocular microscopes are used for this purpose.

Miscellaneous physical chemical measurements, some quite empirical, are of great importance to the petroleum industry because they are used for control in manufacture and are included in customer's specifications. Macro methods are of course available, but occasionally the sample is too small and this is frequently the case when the problem is particularly important. Micro modifications of these macro methods have often proved extremely helpful. Microchemistry is not a fad but it is not a panacea either. It should be employed where it is necessary, as where the sample is very small or where it offers a definite and substantial advantage in accuracy, precision, or economy of time or materials. If in a particular case it offers none of these advantages there is no good reason to employ it.

Future of Petroleum Analysis

Reviewing the progress of the past 25 years was easy compared to speculating on what the next 25 years will bring in the field of analysis related to petroleum. But the paths of advances in analysis and testing for the next few years is indicated by the current trend. Instrumentation will be extended not only in the laboratory but also in the plant. Analytical and testing devices to continuously indicate, record, or control manufacturing or refining operations will surely increase in number. A few are already available but the reluctance of production superintendents to rely on such devices is still to be overcome by performance. Commercial laboratory instrument makers are developing devices for continuously determining and indicating the vapor pressure of gasoline and, on the basis of the indication, controlling the proportions of constituents going into the blend—a continuously indicating refractometer equipped to control a manufacturing operation on the basis of its indications; an automatic and recording distillation unit for reproducing the performance of the conventional ASTM Engler distillation on gasoline, kerosene, etc. Several automatic titrimeters, one recording, are already on the market. A number of such devices have been described in the literature. A continuously recording refractom-

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eter for industrial control was described by Jones *et al.* (*31*). Heigl *et al.* (*26*) described a recording Raman spectrometer for analysis of hydrocarbon mixtures and White *et al.* (*66*) described a recording infrared spectrometer for continuous determination of six components in a stream.

Instruments will doubtlessly be simplified in performance requirements so that less skilled personnel will be able to utilize them effectively and efficiently.

Further development of direct reading instruments for analysis may be expected, for example in polarographs, x-ray and emission spectrometers.

One type of chemical approach to the analysis of liquid and solid hydrocarbons that will probably see considerable development is that involving reaction or complex formation to yield precipitates that can be separated from the unreacted mass and subsequently be treated to regenerate the hydrocarbons or class of hydrocarbons so precipitated. This field is certainly not extensively developed. In fact very few examples come to mind but among these are Gair's (*21*) determination of naphthalene by precipitation with picric acid; determination of benzene by Pritzker and Jungkunz (*52*) by an aqueous solution of specially prepared nickel ammonium cyanide; Bond's (*8*) nitrous acid method for styrene; and more recently the determination of normal alkanes in hydrocarbons of more than 15 carbon atoms by adduct formation with urea as described by Zimmerschied *et al.* (*71*).

Inevitably developments in all fields of analytical chemistry find their applications to the problems of the chemist in the field of petroleum. Thus ion exchange, microwave techniques, nuclear resonance, radioactive isotopes, activation analysis, high frequency vibrations, and other developments of fundamental research should find applications in the field of petroleum analysis.

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