FUELS FOR INTERNAL-COMBUSTION ENGINES

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CONTENTS

I. INTRODUCTION

The volume of motor fuels available is an astronomical figure. At the present time motor fuels are produced primarily from crude oil, natural gas, and coal. The fuels are derivable from gases such as methane, ethane, propane, and butanes of octane numbers from 90 to 125, from fuels produced from the polymerization of gaseous olefins and paraffinic hydrocarbons of octane ratings from 75 to 100, and from alcohols, isopropyl ether, or mixed ethers and ketones of high octane numbers. As a comparison, natural gasolines have octane ratings of from 70 to over 80, and the octane ratings of gasolines from the atmospheric distillation of crude oils vary between 15 and 70, while cracked gasolines have antiknock values ranging between 60 and 80 octane. The gaseous motor fuels can also be produced from gases obtained from the cracking process as well as from natural gas. Cracked or natural gases can be converted into high-octane liquid motor fuels by the thermal or catalytic polymerization processes. Motor fuels containing alcohols, ethers, and ketones are being produced from the gases of the cracking process.

The increasing demand for motor fuel has led to ingenious methods of supplying the demand, depending upon whether a country has oil supplies or not. Hydrogenation of coal, carbon monoxide, and heavy oils has made available enormous sources of motor fuel from the coal deposits of the world. The motor fuel produced by the hydrogenation of coal has an octane rating of 72. Motor fuel produced from carbon monoxide has an octane rating of 40; by the cracking process this fuel is converted into high-octane gasoline. The hydrogenation of petroleum oils is carried out primarily for the purpose of producing solvents and lubricants.

Motor fuel is being produced by the distillation of oil shale, followed by cracking the hydrocarbons produced therefrom into gasoline of octane ratings from 60 to 75. Countries having little or no crude oil sources are converting plants such as corn, wheat, barley, and potatoes into alcohol by the fermentation process. The alcohol thus produced is used in part as motor fuel. Wood is converted into a gaseous motor fuel which is used in busses and trucks, of which there are many hundreds in Italy, Germany, and France. The wood is burned in equipment which is a part of the motor bus or truck in the engine of which the gas is burned.

The antiknock values of the motor fuels producible by the above methods and from the sources mentioned may be still further improved by solvent extraction of hydrocarbons and by the addition of tetraethyl lead. The low-octane hydrocarbons extracted by solvents are readily converted into high-octane fuel by the cracking process.

By chemical and physical means it is possible to produce motor fuels of the desired octane rating in any volume required.

II. MOTOR FUEL FROM CRUDE OIL

A. General

During the past twenty years a tremendous amount of research work has been carried out on the art of distilling crude oil. Distillation units with capacities ranging from a few hundred to over sixty-five thousand barrels of crude oil per day have been developed to fractionate the gasoline present with such nicety that almost no further refining is required. The gasoline produced in the earlier days of distilling petroleum was treated with sulfuric acid and caustic soda and then redistilled to a commercial product. Today acid treatment is no longer necessary, for gasoline derived by distillation of crude requires, in general, no refinement beyond sweetening.

The antiknock value of straight-run gasoline varies widely, its octane number ranging from approximately 15 to over 70 (very little of the latter is available) and averaging about 53. This average value is too low for modern high-compression engines and is in part reformed or cracked, i.e., the straight-chain paraffins which have low octane ratings are converted by heat and pressure into olefinic, aromatic, and naphthenic hydrocarbons which have greater antiknock properties.

The cracking of hydrocarbon oils, such as gasoline, naphtha, kerosene, gas oil, fuel oil, or crude oil, produces gasolines the octane numbers of which range from approximately 60 to over 80, with an average of about 68. The quality of the cracked gasoline depends upon the type of oil processed and the time, temperature, pressure, and principle of operation used.

The volumes of straight-run and cracked gasolines produced from the various oil fields in the United States (73) for the year 1936 are shown in table 1. For the first time in history, the production of cracked gasoline, representing 50.9 per cent of the total, surpassed that of straight-run gasoline.

B. Straight-run gasoline from distillation of crude oil

The distillation of crude oil at atmospheric pressure may be carried out in a unit (76, 17) such as shown in figures 1 and 2, using Pennsylvania crude as an illustration. The crude oil, before passing through the heating coil of the furnace, is pumped through a series of heat exchangers counterflow to the hot vapors and liquids leaving the bubble tower fractionator.

The temperature of the oil is about 800°F. as it leaves the heating coil and flows into the fractionating column. The products derived from this primary distillation of Pennsylvania crude oil (42–43° A.P.I. gravity) are gasoline, naphtha, kerosene, furnace oil, fuel oil, wax distillate, and heavy lubricating oil stock and bottoms. The percentages and properties of these products are shown in tables 2 and 3.

Octane ratings and laboratory inspection data for a number of motor fuels derived from the distillation of crude oils, as produced in the Appalachian, Michigan, Indiana, Illinois, Kentucky, Mid-Continent, Gulf Coast, Rocky Mountain, and California fields, are shown in table 4. With the exception of those obtained from White Castle, Louisiana, and Smackover, Arkansas (octane ratings 69 to 70), the straight-run gasolines have relatively low octane ratings; yields range from 2.0 per cent for the crude from Placedo, Texas, to over 81 per cent of a 400°F. end-point gasoline from a crude in Medicine Bow, Wyoming. Additional data on octane ratings and yields of the straight-run gasolines from different crude oils are given as follows: (*1*) Appalachian:—straight-run gasolines from Pennsylvania crude have octane ratings ranging from 35 to 50. (*2*) Michigan, Indiana, Illinois, and Kentucky:—Michigan straight-run

TABLE 1

Volumes of straight-run and cracked gasoline produced in various sections of the United States (73) during 1936

REFINERY LOCATION*	CRUDE OIL		STRAIGHT-RUN GASOLINE		CRACKED GASOLINE	
	Thousand barrels	Per cent of total	Thousand barrels	Per cent of total	Thousand barrels	Per cent of total
1. Pennsylvania East Coast	27,072	2.5	39,145	16.9	52,610	22.0
2. Indiana, Illinois, Michigan, Kentucky, etc	25,074	2.3	35,252	15.3	46,794	19.5
3. Mid-Continent:						
Texas Inland	256,695	23.4	20,902	9.0	13,015	5.4
Oklahoma and Kansas	376,212	34.2	33,605	14.5	25,866	10.8
Arkansas and Louisiana Inland	37,364	3.4	5,554	2.4	4,320	1.8
4. Gulf Coast	139,160	12.7	50,057	21.7	67,858	28.3
5. Rocky Mountain	22,166	2.0	5,811	2.5	5,113	2.1
6. California	214,773	19.5	40,961	17.7	24,044	10.1
Total	1,098,516	100.0	231,287	100.0	239,620	100.0

* It should be noted that the figures for the production of gasoline are based on the location of the refinery rather than on the source of the crude.

gasolines range in antiknock value from 17 to 43. (*3*) Mid-Continent:—Texas straight-run gasolines have octane ratings between 55 and 61; the amounts recovered from various crudes have ranged from 22 to 35 per cent. (*4*) Gulf Coast:—crudes obtained from White Castle (Louisiana) and Placedo (Texas) are typical of the general run of Gulf Coast crudes. They usually contain small amounts of high-octane (of the order of 70

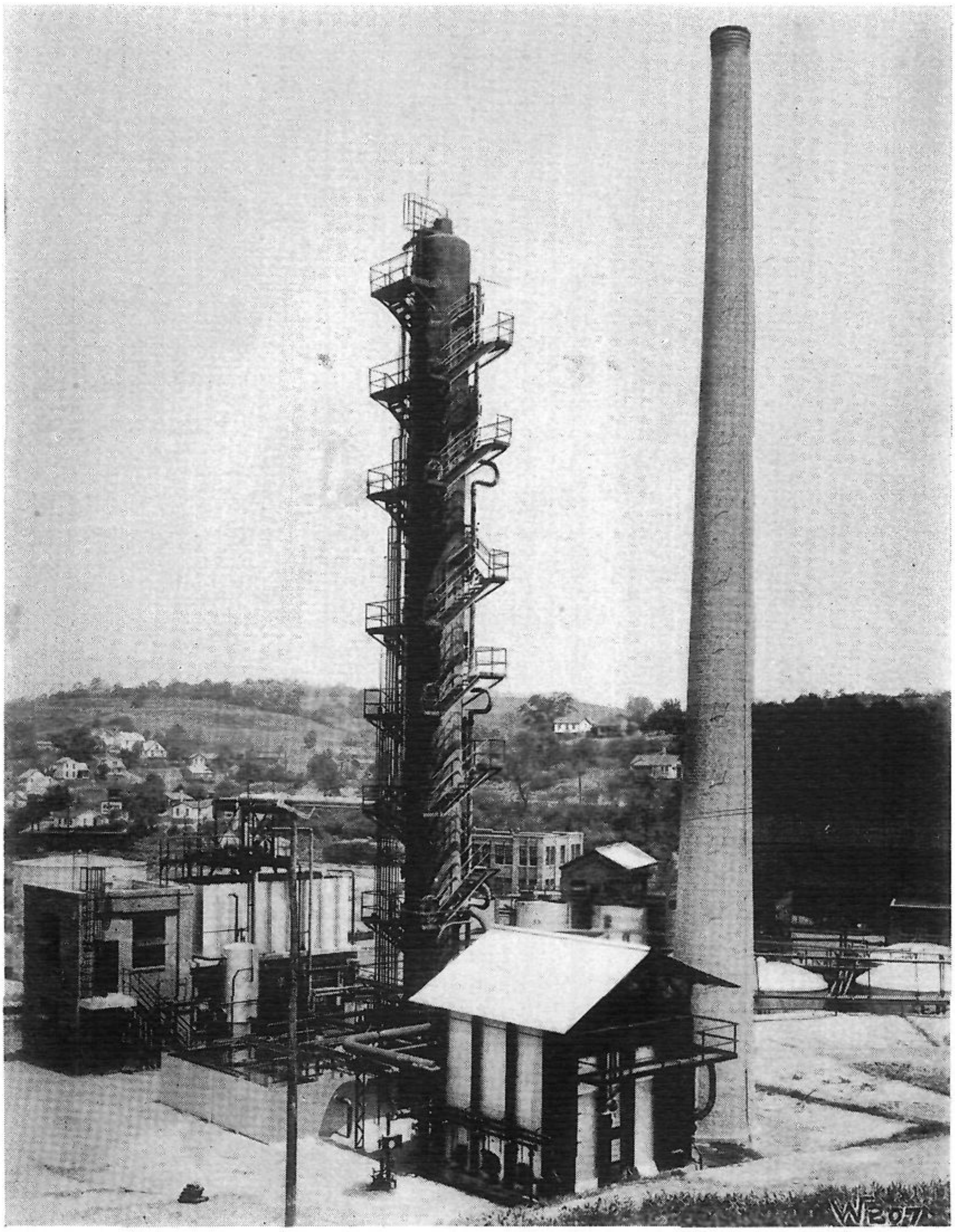
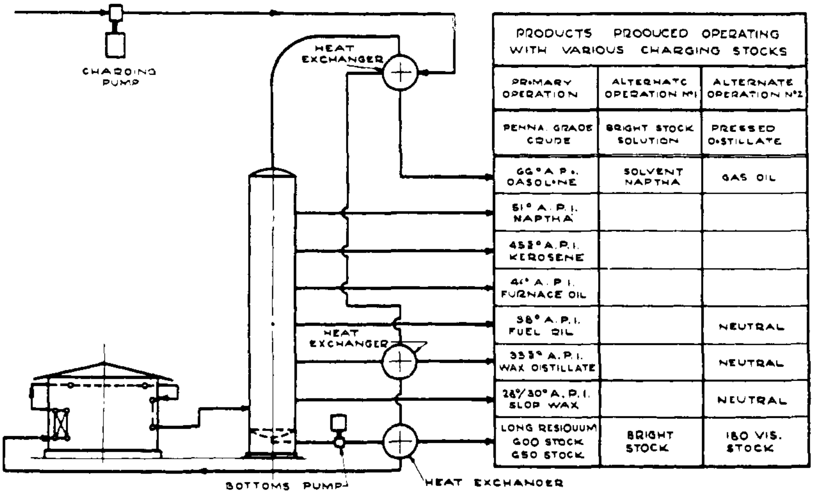


FIG. 1. Crude-oil distillation unit in Pennsylvania

octane) straight-run gasoline. The newer fields in the Gulf Coast area, such as Flour Bluff (Texas) and La Fitti and Gillis (Louisiana) yield straight-run gasolines of lower octane number, the range being from 45



PRODUCTS PRODUCED OPERATING WITH VARIOUS CHARGING STOCKS		
PRIMARY OPERATION	ALTERNATE OPERATION N°1	ALTERNATE OPERATION N°2
PENNA. GRADE CRUDE	BRIGHT STOCK SOLUTION	PRESSED DISTILLATE
66° A.P.I. GASOLINE	SOLVENT NAPTHA	GAS OIL
51° A.P.I. NAPTHA		
45½° A.P.I. KEROSENE		
40° A.P.I. FURNACE OIL		
38° A.P.I. FUEL OIL		NEUTRAL
33½° A.P.I. WAX DISTILLATE		NEUTRAL
28/30° A.P.I. SLOP WAX		NEUTRAL
LONG RESIDUUM 600 STOCK 650 STOCK	BRIGHT STOCK	150 VIS. STOCK

FLEXIBILITY IN DISTILLATION UNIT

FIG. 2. Flow chart of crude-oil distillation unit

TABLE 2

Products derived from primary distillation of Pennsylvania 42–43° A.P.I. gravity crude oil (76, 17)

PRODUCT	GRAVITY AT 60°F.		MAKING 600 FIRE STOCK		MAKING 665 FIRE STOCK	
	°A.P.I.	Specific	Barrels per day	Per cent	Barrels per day	Per cent
Gasoline*	66.0	0.717	633	25.3	625	25.0
Naphtha	51.1	0.775	242	9.7	250	10.0
Kerosene	45.7	0.799	362	14.5	375	15.0
Furnace oil	40.0	0.825	213	8.5	125	5.0
Fuel oil	38.0	0.835	100	4.0	175	7.0
Wax distillate	33.4	0.858	475	19.0	550	22.0
Bottoms†	25.0	0.904	475	19.0	400	16.0
Total			2500	100.0	2500	100.0

* The light gasoline shown, having an A.P.I. gravity of 80 and representing 3.5 per cent of the crude or 13.8 per cent of the total gasoline, was preflashed and not fractionated. This product is usually blended with the heavy gasoline to produce the 66° A.P.I. gravity shown.

† While the unit was designed for taking off a slop wax, the fraction usually is sufficiently sharp to eliminate the necessity of this cut.

to 47. (*5*) Arkansas and Northern Louisiana:—The Smackover field is the largest producer in Arkansas. The crude is of low gravity and contains small amounts of high-octane straight-run gasoline. The Rodessa field in Northern Louisiana, the largest producer in that area, yields a low-octane straight-run gasoline. (*6*) Rocky Mountain:—This area produces all types of crudes, the most unusual being that from Medicine Bow (Wyoming) which has yielded 81 per cent of 400°F. end-point straight-run gasoline having an octane rating of 58. The straight-run gasolines in the entire field range in octane number from 17 to 58. The gasoline having an octane number of 17 comes from Baker (Montana) crude oil. (*7*) California:—The octane numbers of straight-run gasolines from California crude oil generally range from 52 to 66. The lighter crude oils are produced in the Signal Hill district and the heavier crudes come from the Los Alamos and Santa Maria fields. The heavier crudes are usually higher in sulfur content.

TABLE 3

Properties of products from primary distillation of Pennsylvania 42-43° A.P.I. gravity crude oil (76, 17)

PROPERTIES	GASOLINE*		NAPHTHA	KEROSENE	FURNACE OIL†	FUEL OIL†	BOTTOMS, 665 FIRE STOCK‡
	Light	Heavy					
Gravity, °A.P.I.	80.0	64.0	51.1	45.7	40.0	38.0	25.0
Distillation characteristics:							
Initial boiling point, °F.	70	120	305	400	340	540	
10 per cent	100	175	330	413	491	583	
20 per cent	115	196	334	418	512	589	
50 per cent	158	237	344	433	528	601	
90 per cent	258	293	375	468	550	622	
End point, °F.	270	320	419	498	574	635	
Flash point, °F.				185			590
Fire point, °F.				205			665
Flash point P.M., °F.							590
Viscosity, S.U. at 210°F.							202

* The light gasoline shown, having an A.P.I. gravity of 80 and representing 3.5 per cent of the crude or 13.8 per cent of the total gasoline, was preflashed and not fractionated. This product is usually blended with the heavy gasoline to produce the 66° A.P.I. gravity gasoline shown in table 2.

† Furnace oil and fuel oil may be varied as the market demands.

‡ While the unit was designed for taking off a slop wax, the fraction usually is sufficiently sharp to eliminate the necessity of this cut.

TABLE 4

Octane ratings and inspection data for straight-run gasolines from various crude oils

CRUDE OIL-PRODUCING FIELDS AND DISTRICTS	APPALACHIAN	CALIFORNIA		GULF COAST			MICHIGAN, INDIANA, ILLINOIS	MID-CONTINENT			ARKANSAS AND NORTHERN LOUISIANA		ROCKY MOUNTAIN	
	Corning, Ohio	Signal Hill light crude	Los Alamos heavy crude	White Castle, Louisiana	Placedo, Texas	Flour Bluff, Texas	Mt. Pleasant, Michigan	Kansas	East Texas	West Texas (Howard-Glasscock)	Smackover, Arkansas	Rodessa, Louisiana	Rex Lake, Wyoming	Pondera, Montana
Crude oil:														
Gravity, °A.P.I.	35.0	25.2	14.1	24.0	24.4	43.2	40.7	38.9	39.9	29.5	20.5	42.7	34.9	31.6
Straight-run gasoline:														
Yield, per cent of crude	25.2	20.7	12.7	4.6	2.0	26.0	35.9	35.0	35.0	22.3	10.5	36.6	28.1	34.5
Gravity, °A.P.I.	58.5	52.8	54.3	46.4	No analysis because of low gasoline content	59.9	62.5	60.5	64.3	55.0	47.3	59.6	59.9	58.9
Octane No., C.F.R. motor method	Approx. 42	58	61	Approx. 70		46	22	45	55	61	69	33	58	43
Sulfur, per cent	0.03	0.10		0.02		0.02		0.03	0.02		0.06	0.04	0.01	
Distillation characteristics:														
Initial boiling point, °F.	140	144	118	127		120	107	110	89	106	183	130	99	142
5 per cent	170	202	166	214		170	142	154	122	149	221	167	141	170
10 per cent	193	220	188	240		186	162	171	142	174	233	186	160	188
20 per cent	222	240	217	266		212	193	196	172	208	255	210	187	214
50 per cent	276	282	280	301		267	269	259	236	276	312	280	251	273
90 per cent	350	349	355	358		325	364	347	348	358	375	360	352	362
End point, °F.	400	400	400	400		374	401	398	401	400	428	399	398	402
Per cent over	98.5	99.0	98.0	98.5		98.0	98.5	98.0	97.5	98.0	98.5	98.5	98.0	98.0
Per cent bottoms	1.0	1.0	1.0	1.0		1.0	1.0	1.0	1.0	1.0	1.5	1.0	1.0	1.0
Per cent loss	0.5	0.0	1.0	0.5		1.0	0.5	1.0	1.5	1.0	0.0	0.5	1.0	1.0

C. Cracking

1. Straight-run gasolines and naphthas

In view of the increasing number of high-compression motors in use, straight-run gasoline is no longer suitable as a fuel. It is necessary to convert it into suitable hydrocarbons which possess greater antiknock properties. The branched-chain paraffins are the most desirable type at this time (September, 1937); however, olefins, naphthenes, and aromatics are suitable. To convert the knocking gasolines into non-knocking ones, they are subjected to temperatures of the order of 1025°F. and pressures of the order of 750 lb. It is estimated that 25 per cent of the 231,587,000 barrels of straight-run gasoline and naphtha produced during 1936 was reformed (cracked) into gasoline of higher octane numbers. The reforming of gasoline is increasing in order to meet the demand for high-octane gasoline.

Octane ratings and laboratory inspection data for reformed and cracked gasolines, as produced from various crudes, are given in tables 5 and 6.

As noted in table 5, the reforming stocks varied from straight-run naphtha to light gasoline. Yields of reformed gasoline with octane ratings of 57 to 80 ranged from 38 per cent to more than 88 per cent, depending upon the cracking plant operating conditions and the type of stock used.

2. Heavy oils to gasoline

The modern refining of crude oil, when only gasoline is the desired end-product, takes place in combination topping and cracking units. As noted in table 6, in some cases the whole crude was subjected to cracking conditions of heat and pressure to produce the cracked fuel. In other cases either the topped or reduced crude was utilized. The yields of cracked gasoline, based upon the charge, ranged from 44 per cent to over 63 per cent, with ratings from 68 to 77 octane number. It should be mentioned, however, that both the yield and the quality of the gasoline produced are dependent upon the cracking stock and upon such operating conditions as time, temperature, and pressure.

A flow chart of a topping and cracking unit handling 12,500 barrels of California crude oil per day is shown in figure 3. The cracking section is based upon the selective principle, which uses two or more heating coils in order that each fraction of the oil may be converted under its best time, temperature, and pressure conditions.

The crude oil charged to the unit usually contains water as an emulsion, together with dissolved salts, which it is desirable to remove before processing in the unit. To accomplish this, the crude oil is pumped through a heat exchanger under a pressure of approximately 165 lb. per square inch,

TABLE 5

Octane ratings and inspection data for reformed straight-run gasolines and naphtha from various crude oils

CRUDE OIL-PRODUCING FIELDS AND DISTRICTS..	APPALACHIAN-PENNSYLVANIA			MT. PLEASANT, MICHIGAN	MID-CONTINENT		EAST-WEST TEXAS						WEST TEXAS			ROCKY MOUNTAIN: MONTANA	CALIFORNIA	
Type of reforming stock	Light gasoline	Gasoline	Naphtha	Gasoline	Gasoline	Naphtha	Gasoline						Gasoline	Naphtha		Gasoline	Light naphtha	Heavy naphtha
Charging stock:																		
Gravity, °A.P.I.	64.4	58.1	49.8	61.7	59.8	53.6	58.8	Same					58.1	51.5		59.8	46.6	42.4
Sulfur, per cent				0.04			0.14	Same					0.18	0.19		0.11	0.10	0.09
Octane No., C.F.R. motor method	49	38	27	20	42	34	54	Same					60	50		51	50	48
Distillation characteristics:																		
Initial boiling point, °F.	117	152	272	152	115	222	99	Same					95	220		126	303	299
10 per cent	169	215	315	190	177	263	168	Same					160	261		186	311	325
50 per cent	192	280	329	278	277	309	262	Same					374	312		212	320	361
90 per cent	301	354	446	360	347	353	360	Same					364	370		340	340	400
End point, °F.	354	396	479	389	383	385	406	Same					392	410		381	364	427
Operating conditions:																		
Pressure, lb. per square inch	750	500	478	1000	500	500	750	752	750	745	750	750	750	750	750	500	750	750
Furnace discharge, °F.	975	975	975	985	1000	1000	945	960	975	994	995	995	950	950	950	965	975	970
Reaction chamber, °F.	925	926	924	935	950	952	899	909	925	993	995	993	896	898	899	915	925	922
Feed rate, gallons per hour	1.97	0.76	1.04	1.98	1.91	2.03	2.01	1.94	1.98	3.93	3.02	2.06	3.20	2.13	1.58	1.95	1.37	2.02
Cracking results:																		
Gasoline:																		
Yield, per cent of charge	72.2	66.5	64.0	65.5	74.7	74.3	88.7	82.7	76.0	62.8	48.9	37.9	88.1	81.1	77.4	79.5	69.2	70.5
Gravity, °A.P.I.	63.5	57.3	54.5	61.0	59.1	55.5	58.8	58.7	58.2	52.2	49.8	45.7	59.4	54.5	54.2	60.7	48.3	47.5
Octane No., C.F.R. motor method	70	74	74	67	70	70	68	71	72	76	78	80	72	73	75	72	77	77
Distillation characteristics:																		
Initial boiling point, °F.	99	84	88	94	89	91	101	96	96	102	100	106	96	91	100	96	93	88
10 per cent	148	154	145	142	146	164	150	146	146	154	158	158	148	171	168	146	179	178
20 per cent	172	188	192	193	180	204	179	176	174	186	186	184	178	214	203	176	236	236
50 per cent	229	252	289	235	259	280	245	242	238	254	244	234	253	280	277	243	296	316
90 per cent	320	384	397	360	356	358	364	372	354	397	362	359	366	378	368	336	350	380
End point, °F.	363	404	410	396	379	382	403	411	396	436	416	429	400	403	389	386	381	409
Residuum:																		
Yield, per cent of charge	2.5	4.6	7.6	4.3	1.3	2.5	0.0	0.6	3.5	1.1	5.3	5.7	2.1	5.7	4.8	3.8	8.2	12.8
Gravity, °A.P.I.	15.0	2.9	17.2	8.5	−0.7	−4.5		20.8	16.1	7.1	2.8	0.3	12.9	11.7	12.3	14.6	9.1	17.7
Gasoline content, per cent	3.5		0.0	0.5				5.0	2.0	3.0	1.8	2.0	3.5	4.0	3.0	3.0	3.0	2.0
Loss:																		
Liquid volume, per cent	25.3	28.9	28.4	30.2	24.0	23.2	11.3	16.7	20.5	36.1	45.8	56.4	9.8	13.2	17.8	16.7	22.6	16.7
Gas, cu. ft. per barrel of charge	645	946	919	789	611	762	380	499	640	1125	1430	1780	369	535	639	778	695	735

TABLE 6

Octane ratings and inspection data for cracked gasolines from various crude oils

CRUDE OIL-PRODUCING FIELDS AND DISTRICTS	APPALACHIAN	MICHIGAN, INDIANA, ILLINOIS	MID-CONTINENT					GULF COAST			ROCKY MOUNTAIN		CALIFORNIA	
	Corning, Ohio	Mt. Pleasant, Michigan	Kansas	East Texas	West Texas	Smackover, Arkansas	Rodessa, Louisiana	White Castle, Louisiana	Placedo, Texas	Flour Bluff, Texas	Rex Lake, Wyoming	Pondera, Montana	Signal Hill	Los Alamos
Type of cracking stock	Reduced crude	Topped crude	Topped crude	Reduced crude	Heavy naphtha and topped crude	Topped crude	Topped crude	Whole crude	Whole crude	Reduced crude	Topped crude	Topped crude	Topped crude	Whole crude
Cracking stock:														
Yield, per cent of crude	68.0	65.7		52.9	90.0	89.8	63.2	100	100	24.1	70.4	61.9	83.2	100
Gravity, °A.P.I.	28.4	31.0	25.5	26.6	27.4	17.9	35.0	24.0	24.4	27.8	27.4	20.1	20.6	14.1
Cracked gasoline:														
Yield, per cent of cracking stock	61.0	63.5	57.9	54.5	61.0	43.7	61.7	59.0	58.6	57.4	59.8	51.4	48.2	44.1
Gravity, °A.P.I.	59.4	62.3	60.4	59.9	56.0	57.5	63.7	52.7	51.3	59.5	59.0	58.9	56.9	54.0
Octane No., C.F.R. motor method	Approx. 68	64	71	68	69	72	70	Approx. 80	77	70	70	68	71	72
Sulfur, per cent	0.08	0.05	0.06	0.07	0.23	0.26	0.05	0.06	0.06	0.03	0.09	0.29	0.55	1.84
Distillation characteristics:														
Initial boiling point, °F.	90	92	88	90	99	91	96	104	95	97	96	90	99	98
5 per cent	126	125	124	112	132	126	116	132	134	122	123	123	127	133
10 per cent	146	143	136	124	157	140	130	153	154	137	138	144	145	155
20 per cent	182	172	164	156	198		157	190	192		162	180	177	193
50 per cent	268	246	236	244	284	262	226	280	277	243	256	270	364	276
90 per cent	390	342	346	364	384	364	334	376	372	342	355	370	357	366
End point, °F.	404	374	406	404	394	397	393	399	401	412	395	397	396	400
Per cent over	98.0	98.0	98.0	97.0	97.0	97.5	97.5	97.0	95.0	98.0	97.0	95.0	98.0	96.5
Per cent bottoms	1.0	1.0	1.0	1.0	1.5	1.0	1.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0
Per cent loss	1.0	1.0	1.0	2.0	1.5	1.5	1.5	1.5	4.0	1.0	2.0	4.0	1.0	2.5

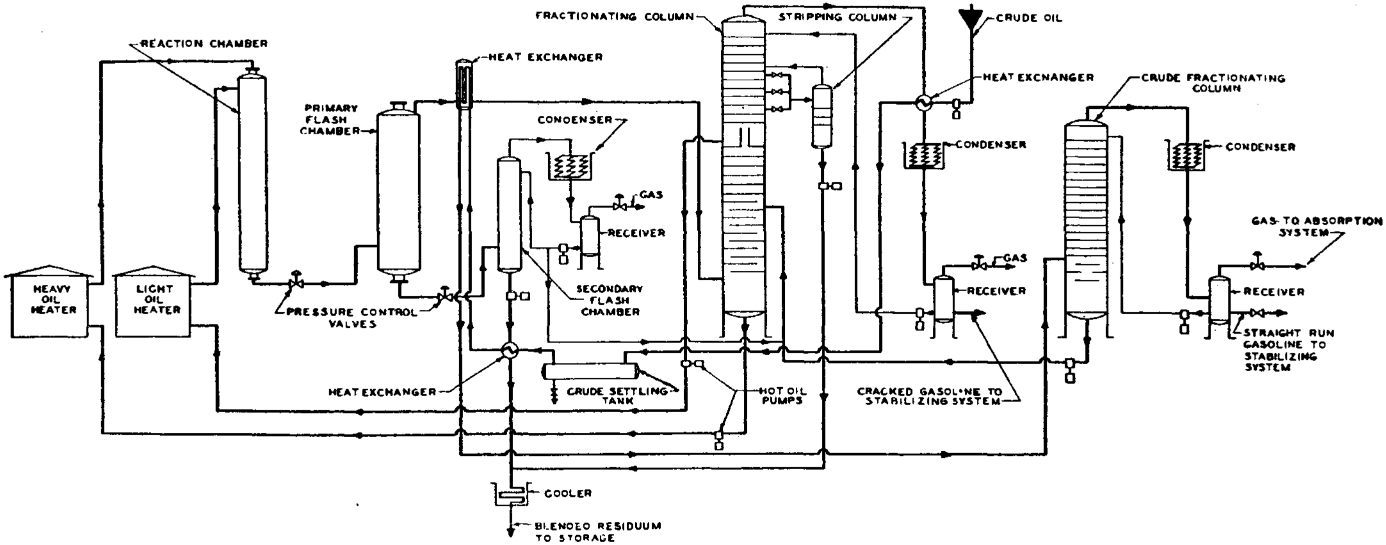


FIG. 3. Flow diagram of modern combination topping and selective cracking unit handling 12,500 barrels of crude oil per day. (Universal Oil Products Company)

where the temperature of the oil is raised to 225°F. It is then passed to a settling chamber. Under these conditions of temperature and pressure the viscosity of the crude oil is reduced, but vaporization of the water is prevented. As a result, the salt water drops out and is removed from the bottom of the settler.

The crude oil then flows from the top of the settling tank through a series of heat exchangers to increase the temperature to approximately 550°F. The preheated oil is passed to the crude oil-fractionating column, where the gasoline is distilled and then condensed, flowing to a storage tank. The fractionating column for this service is 11 ft. in diameter and 49 ft. high. The topped crude from the bottom of the fractionating column is pumped directly to the bubble tower of the cracking unit. The cracking unit fractionating column is 11 ft. in diameter and 74.5 ft. high. The *topped crude passing down through* this column contacts the hot ascending vapors and a partial fractionation takes place. The vapors passing up the column are separated as a liquid sidecut and an overhead consisting of gasoline and gas. The liquid sidecut, called light oil, is pumped from one

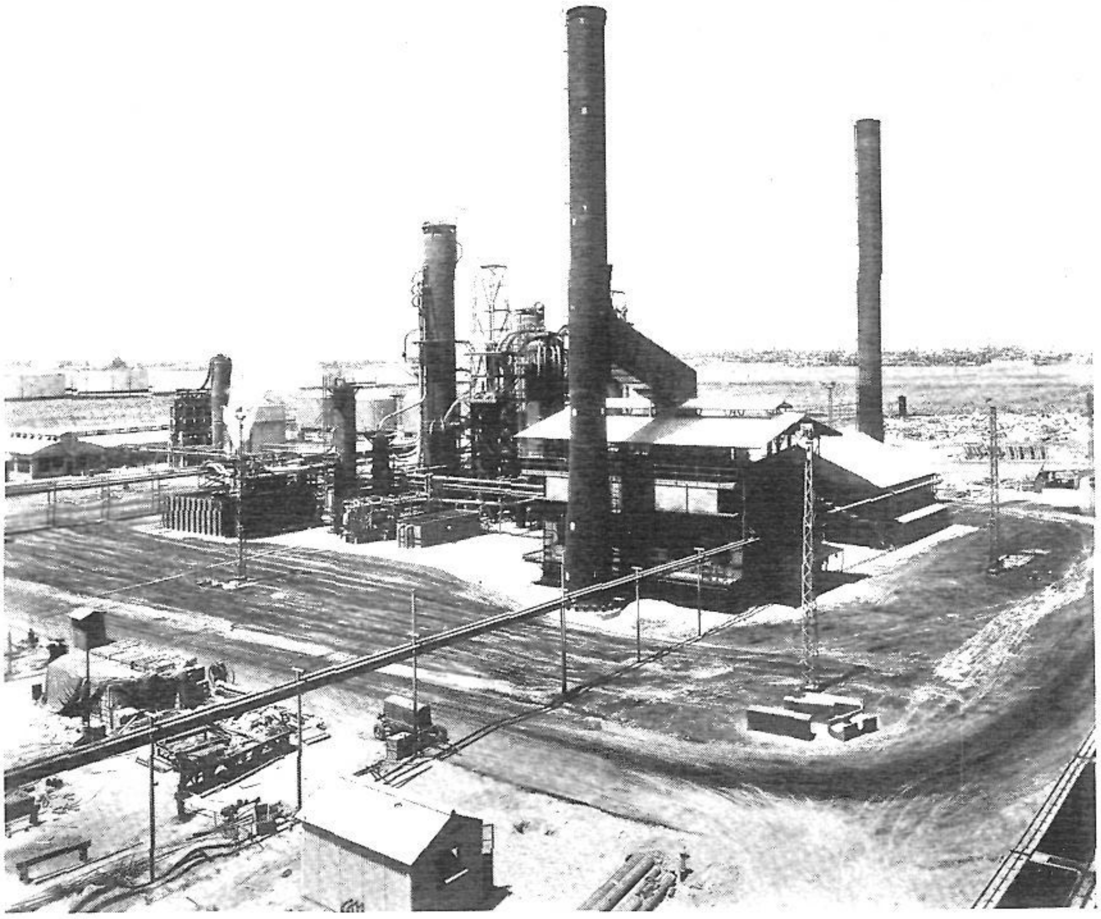


FIG. 4. Topping and cracking unit handling 15,000 barrels per day

of the bubble decks to the light-oil furnace tubes and heated to a temperature of approximately 960°F. The gasoline vapors and gas pass from the top of the fractionating column through a cooling coil to a receiver, where a separation of gasoline and gas is made. The unconverted oil from the bottom of the fractionating column, referred to as heavy combined feed and consisting of the heavy ends of both the charge and the vapors condensed in the tower, is pumped through the heavy-oil furnace tubes, where the temperature is raised to approximately 925°F.

The ratings of the light- and heavy-oil heaters are 53 and 61 million B.t.u. per hour absorbed by the oil. The outlet pressures of the two heaters are 300 and 280 lb. per square inch, respectively. The heated hydrocarbons from both these heaters pass to the top of the reaction chamber, which is 7 ft. in diameter and 50 ft. high and is maintained at a pressure of 275 lb.

The hydrocarbon mixture from the bottom of the reaction chamber passes to the primary flash chamber, which is 11 ft. in diameter and 40 ft. high. The flash chamber and subsequent equipment through the condenser to the receiver are maintained at a pressure of approximately 100 lb. The material entering the flash chamber is separated into bottoms of cracked unflashed residue and overhead vapors of gas, gasoline, and recycle stock. The vapors from the top of the flash chamber pass through a heat exchanger into the fractionating column, where they contact the topped crude oil as previously described. The unflashed residue passes to a secondary flash chamber, which is 6 ft. in diameter and 28.5 ft. high, maintained at about 20 lb. pressure. The material entering this chamber separates into low-gravity cracked residuum bottoms and overhead vapors which are returned to the fractionating column. The residuum is blended with part of the sidecut of the column to produce a blended residue meeting fuel-oil specifications.

The vapors from the top of the fractionating column, at a temperature of 380°F., pass through heat exchangers and a condenser into a receiver, where a separation of the gas and cracked gasoline is made. The cracked gasoline has the required end point and flows to a stabilizer to produce the required vapor pressure, which normally varies from 8 to 12 lb. (Reid at 100°F.) depending upon the season of the year. The cracked gasoline may be water-washed, caustic soda-treated, or sweetened and then fortified against deterioration by antioxidants. It may be colored by a dye, and as such is suitable for marketing.

A typical commercial run of thirty days in the described plant, processing 373,650 barrels of California crude oil at the rate of 12,500 barrels per day, produced an average of 64.03 per cent motor fuel, 28.86 per cent 5.1° A.P.I. gravity cracked fuel oil, and 7.11 per cent gas and loss. A summary of the operating conditions used and of the volumes and properties of the products produced is given in tables 7 and 8.

TABLE 7

Summary of operating conditions used and volumes of products produced when topping and cracking California crude oil

OPERATION AND PRODUCTS	TOTAL NUMBER OF BARRELS	BARRELS PER DAY	PER CENT OF CHARGE
Topping operation:			
Crude oil	373,650	12,455	100.00
Products:			
Straight-run gasoline	119,670	3,989	32.03
Topped crude	250,200	8,340	66.96
Gas and loss	3,780	126	1.01
Totals	373,650	12,455	100.00
Cracking operation:			
Topped crude	250,200	8,340	100.00
Products:			
Cracked gasoline	119,580	3,986	47.79
Cracked residuum	107,820	3,594	43.09
Gas and loss	22,800	760	9.12
Totals	250,200	8,340	100.00
Combination topping and cracking operation:			
Products processed:			
Crude oil	373,650	12,455	100.00
Products:			
Straight-run gasoline	119,670	3,989	32.03
Cracked gasoline	119,580	3,986	32.00
Total gasoline	239,250	7,975	64.03
Cracked residuum	107,820	3,594	28.86
Gas and loss	26,580	886	7.11
Totals	373,650	12,455	100.00

Time on stream = 30 days; total gas produced = 122,400,000 cu. ft.

D. Commercial gasolines and their properties

The average octane ratings and volatility of commercial gasolines as marketed in certain parts of the United States during the last ten years (80) are shown in table 9. It is interesting to note the trend toward higher volatility and increased octane ratings during this period: for the premium grade, an increase of 5 octane numbers resulted during the past six years; for the regular grade, an increase of 10 octane numbers; and for the third grade (largely straight-run gasoline), an increase of 3 octane numbers.

Studies of the properties of motor fuels conducted by the U. S. Bureau of Mines and the Coöperative Fuel Research Committee (74) for the winters of 1935–36 and 1936–37 indicate somewhat higher octane ratings for regular- and premium-price gasolines and somewhat lower for third-grade products during the winter of 1936–37. The average results for eighteen marketing areas in the United States are shown in table 10. Other properties of the three grades of motor fuels are shown in tables 11, 12, and 13.

TABLE 8

Laboratory analyses of straight-run and cracked gasoline produced when topping and cracking California crude oil

PROPERTIES	CRUDE OIL	STRAIGHT-RUN GASOLINE	CRACKED GASOLINE	BLENDED RESIDUE
Gravity, °A.P.I.	30.5	52.1	59.6	5.1
Distillation characteristics:				
Initial boiling point, °F.	156	126	102	
10 per cent	277	199	142	
30 per cent	441	248	184	
50 per cent	583	287	241	
90 per cent	687	389	344	
End point, °F.		425	383	
Per cent distilled at 300°F.	12			
Per cent distilled at 400°F.	26			
Octane No., C.F.R. motor method		56	71	
Reid vapor pressure, lb. per square inch at 100°F.		5.0	9.3	
Sulfur, per cent	0.65	0.06	0.37	
Color		25		
Viscosity, S.F. at 122°F.				240
Flash point, P.M., °F.				194
B. S. & W., per cent				0.1

E. Tractor fuels

Distillates, kerosene, and gasoline are used as tractor fuels. In many cases such fuels are raw or unfinished products. Although a number of tractors are operated on gasoline, the majority still burn kerosene or distillates such as furnace oils, with kerosene gradually being replaced by the lower-grade distillate fuels.

As for the use of gasoline as tractor fuel, it is claimed that consumer demand for high-compression gasoline-burning tractors is increasing at a rapid rate (53). Such engines are now available either as standard or

TABLE 9

Volatility and octane ratings of average commercial gasolines (80)

GASOLINE AND PROPERTIES	YEAR										
	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937
Premium grade:											
Octane No., C.F.R. motor method					72	74	76	75	75	76	77
Distillation characteristics:											
Initial boiling point, °F	117	106	106	94	94	97	96	93	94	91	93
10 per cent	161	153	157	140	141	146	142	136	132	129	126
20 per cent	191	187	185	174	170	171	177	163	157	153	150
50 per cent	257	253	257	256	246	243	237	235	225	223	219
90 per cent	371	370	362	365	361	352	350	344	338	338	332
End point, °F	421	419	404	407	403	363	399	394	392	392	386
Recovery, per cent	98.0	97.7	98.0	97.0	97.6	96.9	96.4	97.1	96.9	96.4	96.5
Reid vapor pressure, lb. per square inch at 100°F					7.5	8.1	9.0	8.8	9.6	10.2	9.2
Regular grade:											
Octane No., C.F.R. motor method					60	61	65	69	69	69	70
Distillation characteristics:											
Initial boiling point, °F	114	99	104	97	97	94	94	92	90	87	89
10 per cent	160	146	150	149	148	143	139	135	127	127	125
20 per cent	192	180	185	182	182	173	166	163	153	155	150
50 per cent	269	267	271	261	255	256	247	242	231	236	240
90 per cent	375	379	381	375	373	377	365	354	352	359	358
End point, °F	426	426	423	416	411	404	406	403	400	406	401
Recovery, per cent	97.8	97.4	97.8	96.5	96.9	96.7	96.5	96.7	96.4	96.2	96.2
Reid vapor pressure, lb. per square inch at 100°F					6.4	9.0	9.5	9.5	10.4	11.1	10.3
Third grade:											
Octane No., C.F.R. motor method						51	53	53	52	51	54
Distillation characteristics:											
Initial boiling point, °F	94	94	95	87		102	96	94	97	99	97
10 per cent	130	146	137	143		152	148	146	148	154	143
20 per cent	162	180	170	177		193	181	180	181	185	173
50 per cent	300	264	265	267		276	264	252	261	257	248
90 per cent	436	386	391	404		380	368	367	373	371	361
End point, °F	456	422	429	437		426	426	425	421	416	411
Recovery, per cent	96.0	96.0	96.5	95.5		97.3	97.3	97.5	97.0	96.7	96.7
Reid vapor pressure, lb. per square inch at 100°F						6.5	7.6	8.4	7.8	8.0	8.0

TABLE 10

Comparative octane ratings for regular-, premium-, and third-grade gasolines (74) for the winters of 1935–36 and 1936–37

FUEL	OCTANE NO.	
	Winter 1935–36	Winter 1936–37
Regular grade:		
Minimum rating	61	64
Maximum rating	72	68.9–71.4
Range of 90 per cent	68–71	74
Premium grade:		
Minimum rating	69.1	74
Maximum rating	81	83
Range of 90 per cent	73.7–80.5	75.4–80.7
Third grade:		
Minimum rating	33.5	44.8
Maximum rating	69.1	69.0
Range of 90 per cent	50–66	50.4–64.0

TABLE 11

Regular-price gasolines (74) for the winters of 1935–36 and 1936–37

PROPERTIES	WINTER OF 1935–36			WINTER OF 1936–37		
	Minimum	Range of 90 per cent	Maximum	Minimum	Range of 90 per cent	Maximum
Gravity at 60°F.:						
Specific	0.763	0.747–0.715	0.707	0.783	0.746–0.717	0.709
°A.P.I	54.0	58.0–66.5	68.6	49.2	58.3–65.9	68.2
Sulfur, per cent	0.014	0.02–0.15	0.30	0.007	0.028–0.14	0.35
Reid vapor pressure, lb. per square inch at 100°F	5.8	7.1–12.4	13.15	7.3	8.4–12.4	12.8
Copper strip test		Negative			Negative	
Octane No., C.F.R. motor method	61	68–71	72	64	68.9–71.4	74
Distillation characteristics:						
Initial boiling point, °F	79	82–98	100	67	83–94	107
10 per cent	108	114–144	155	107	115–144	160
20 per cent	124	132–175	186	130	136–174	192
50 per cent	178	207–255	266	192	235–256	273
90 per cent	245	335–377	388	287	335–370	390
End point, °F	332	385–415	464	342	382–415	443
Per cent loss	0.9	1.0–3.5	5.0	0.8	1.0–3.4	5.0

TABLE 12

Premium-price gasolines (74) for the winters of 1935–36 and 1936–37

PROPERTIES	WINTER OF 1935–36			WINTER OF 1936–37		
	Minimum	Range of 90 per cent	Maximum	Minimum	Range of 90 per cent	Maximum
Gravity at 60°F.:						
Specific	0.779	0.749–0.702	0.684	0.783	0.747–0.710	0.676
°A.P.I	50.1	57.5–70.0	75.4	49.3	57.9–67.9	77.7
Sulfur, per cent	0.006	0.02–0.08	0.179	0.007	0.022–0.19	0.165
Reid vapor pressure, lb. per square inch at 100°F	3.1	5.0–11.5	12.55	5.5	7.3–11.2	12.2
Copper strip test		Negative			Negative	
Octane No., C.F.R. motor method	69.1	73.7–80.5	81	74	75.4–80.7	83
Distillation characteristics:						
Initial boiling point, °F	76	84–107	128	80	86–103	116
10 per cent	110	115–150	178	110	117–150	158
20 per cent	117	134–176	201	117	134–175	187
50 per cent	143	180–252	261	136	185–250	259
90 per cent	264	273–359	378	245	289–364	390
End point, °F	331	343–415	439	335	358–415	426
Per cent loss	0.5	1.0–3.0	3.6	0	0.9–2.8	4.0

TABLE 13

Third-grade gasolines (74) for the winters of 1935–36 and 1936–37

PROPERTIES	WINTER OF 1935–36			WINTER OF 1936–37		
	Minimum	Range of 90 per cent	Maximum	Minimum	Range of 90 per cent	Maximum
Gravity of 60°F.:						
Specific	0.757	0.753–0.724	0.704	0.759	0.751–0.729	0.717
°A.P.I	55.4	56.5–64.0	69.5	55	56.9–62.5	65.8
Sulfur, per cent	0.016	0.02–0.20	0.23	0.005	0.021–0.13	0.27
Reid vapor pressure, lb. per square inch at 100°F	4.2	5.5–10.4	13.4	2.6	5.7–9.8	10.7
Copper strip test		Negative			Negative	
Octane No., C.F.R. motor method	33.5	50–66	69.1	44.8	50.4–64.0	69.0
Distillation characteristics:						
Initial boiling point, °F	78	84–104	128	76	86–104	143
10 per cent	113	127–161	179	119	127–159	198
20 per cent	128	150–196	205	141	160–195	219
50 per cent	184	230–276	282	216	229–278	283
90 per cent	292	330–393	399	312	335–386	391
End point, °F	341	388–430	511	368	388–427	437
Per cent loss	0.5	1.0–3.5	5.5	0	1.0–2.9	5.0

optional equipment on many makes of tractors. It is reported (53) that a tractor designed to operate on 70-octane gasoline will do approximately 33⅓ per cent more work than a similar tractor with low compression using kerosene or a distillate fuel.

No specifications for tractor fuels as such have been issued by the A.S.T.M. Whatever specifications for this product may exist are chiefly those prepared for marketing purposes and by state regulations. For example, the Western Petroleum Refiners Association has adopted the tractor-fuel specifications shown in table 14 to be used as a standard for members of the association (78). The regulations of the State of Illinois (78) are given in table 15.

TABLE 14

Specifications adopted by the Western Petroleum Refiners Association for tractor fuels (78)

Flash point, °F., minimum	110
Distillation characteristics, °F.:	
10 per cent, minimum	347
25 per cent, minimum	392
95 per cent, minimum	464
Color	−16 or darker

TABLE 15

Tractor-fuel specifications (78) of the State of Illinois

Flash point, °F., minimum	100
Distillation characteristics, °F.:	
Initial boiling point, minimum	300
25 per cent, maximum	392
90 per cent, maximum	450

TABLE 16

Tractor-fuel specifications (6) of the State of Minnesota

Distillation characteristics, °F.:	
Initial boiling point, minimum	225
10 per cent, minimum	276
10 per cent, maximum	347
90 per cent, minimum	464
End point, maximum	500
Color	−16 or darker

A bill introduced recently into the Minnesota House of Representatives (6) calls for the specifications shown in table 16. Although the specifications given do not include octane rating, it has been suggested (78) **that** the octane numbers of tractor fuels should be above 30.

Octane ratings and laboratory inspection data on typical Mid-Continent straight-run and cracked fuels (78) are given in table 17.

F. Diesel fuels

Diesel fuels may be derived from petroleum, shale, coal tar, or vegetable oils. For high-speed engines it is generally agreed that fuels of a paraffinic nature give the best results; aromatic fuels are the least suitable. Between these two extremes lie fuels of the naphthenic and olefinic type, which are suitable for the medium-speed and low-speed engines where fuel quality is of less importance.

TABLE 17

Typical Mid-Continent straight-run and cracked products (78)

PROPERTIES	STRAIGHT-RUN PRODUCTS		CRACKED FURNACE OIL	
	Kerosene	Gas oil	No. 1	No. 2
Gravity at 60°F.:				
°A.P.I.	42	32	37	28
Specific	0.82	0.87	0.84	0.89
Distillation characteristics:				
Initial boiling point, °F	350	370	325	375
10 per cent	390	430	380	430
90 per cent	470	640	440	635
End point, °F.	510	700	490	700
Per cent at 392°F	10	2	15	
Flash point, °F.	140	140	120	160
Octane No., C.F.R. motor method	0–10	Below 0	40–50	0–20
Heat content (net):				
B.t.u. per pound	18,600	18,200	18,600	18,300
B.t.u. pound per gallon	126,000	131,500	130,000	135,000

Coal-tar oils, coal dust, and mixtures of coal and oil have been used as Diesel fuels, particularly in Germany (44, 43). They were found to be inferior to petroleum oils.

Vegetable oils such as peanut, cocoanut, soybean, and palm oils have also been used as Diesel fuels. Tests conducted with such fuels resulted in starting difficulties, low power output, and high fuel consumption (44, 43). In the natural state they contain gum-forming materials, but it is reported that they may be cracked to produce usable Diesel fuels.

Shale oils of Diesel boiling range may be mixtures of paraffinic, aromatic, naphthenic, or olefinic hydrocarbons. The shale oils of the paraffinic type have been found to be satisfactory for high-speed Diesel engines (44, 43).

The retorting of oil shale to produce oil, gas, and coke is in commercial operation in a number of foreign countries,—Scotland, France, Spain, Esthonia, Australia, and Manchuria. Oil production from shale is relatively expensive, and, despite a vast amount of research in the United States, to date no process has been found to allow it to compete successfully with petroleum.

It is apparent, therefore, that substantially all Diesel fuel for many years to come (at least in the United States) will be obtained from petroleum chiefly as straight-run and cracked distillates or mixtures thereof.

Distillate fuels are intermediate between gasoline and residual fuel oil. The maximum yield of straight-run distillate fuels would result only when none of the kerosene, gas-oil, and fuel-oil fractions of the crude oil was used as cracking stock, and when all residual fuel was distilled to heavy tars or coke. On the other hand, the available supply of straight-run distillate fuels would be reduced either through an increased demand for cracking stock or through an increased demand for burner and heating fuels. The maximum available yield, if none was used for cracking and if all crude-oil distillation were carried to completion, might be as high as 65 to 70 per cent.

TABLE 18

Average yield of the various products produced from crude petroleum in the United States (73) for the year 1936

PRODUCTS OBTAINED FROM CRUDE PETROLEUM	THOUSAND BARRELS	PER CENT OF CRUDE
Crude petroleum	1,098,516	100.0
Motor fuels	470,907	42.9
Straight-run	231,287	21.1
Cracked	239,620	21.8
Kerosene	56,082	5.1
Gas oil and fuel oil	411,338	37.4
Gas oil and distillates	125,650	11.4
Fuel oil	285,688	26.0
Still gas	54,441	5.0
Lubricants	30,855	2.8
Other products and loss	74,893	6.8

The proportion in which cracked and straight-run distillates are available from average crude by present refinery practice is shown in table 18. From each barrel of crude petroleum processed in 1936, a total of 42.5 per cent of kerosene, gas oil, distillate fuels, and fuel oil was produced (73). Although this total would not have been suitable for the high-speed Diesel, it is reasonable to believe that a percentage of the kerosene and fuel-oil fractions could have been combined with the gas oil and distillate fuels to make available approximately 150 million barrels of suitable high-speed Diesel fuel. Most of the fuel-oil fraction would then be available for use in low-speed engines where fuel quality is of relatively less importance.

The quality of the straight-run and cracked Diesel fuels obtained from the various crude sources in the United States is indicated in table 19. It is apparent from a comparison of the data presented in table 19 and in table 20 that the straight-run fuels from each oil field are suitable for use in the high-speed engine (with the possible exception of the aircraft Diesel). In many cases a considerable amount of cracked fuel may be blended with the straight-run fuel and the mixture will still meet the requirements of the high-speed and medium-speed engines.

TABLE 19

Probable cetane ratings of straight-run and cracked Diesel fuels produced from various crudes in the United States

SOURCE OF CRUDE	1936 PRODUCTION (73)		PROBABLE AVERAGE CETANE RATINGS BY DELAY METHOD (44)	
	Thousand barrels	Per cent of total	Straight-run	Cracked
1. Appalachian:				
Pennsylvania	27,072	2.5	62	29
Kentucky and others	7,245	0.7	52	35
2. Michigan, Lima (Ohio), and Northeastern Indiana	12,586	1.1	68	37
3. Illinois and Southwestern Indiana	5,243	0.5		
4. Mid-Continent:				
East Texas	168,046	15.3	55	40
West Texas and Southeastern New Mexico	88,649	8.1	45	30
Oklahoma, Kansas, and Northern Texas	376,212	34.2	56	35
Arkansas and Northern Louisiana	37,364	3.4		
5. Gulf Coast	139,160	12.7	58	41
6. Rocky Mountain	22,166	2.0	51	38
7. California	214,773	19.5	47	32
Total	1,098,516	100.0		
Average cetane rating based on possible production			54	35

The method each refiner uses to produce the required grades of Diesel fuel will depend upon the economics involved. In most cases it is believed that cracked distillates will constitute the base fuel, with straight-run products added in sufficient quantity to produce the proper ignition

TABLE 20

Manufacturers' recommended fuel specifications and A.S.T.M. Diesel fuel-oil classification for high-, medium-, and low-speed Diesel engines (48)

PROPERTIES	HIGH-SPEED (ABOVE 1000 R.P.M.)			MEDIUM-SPEED (500–1000 R.P.M.)			LOW-SPEED (BELOW 500 R.P.M.)		
	Twenty-five manufacturers		A.S.T.M. No. 1-D	Twenty-six manufacturers		A.S.T.M. No. 3-D	Thirty-three manufacturers		A.S.T.M. No. 4-D
	Spread	Average		Spread	Average		Spread	Average	
Viscosity, S.U. at 100°F.:									
(a) Seconds, minimum	34–40	36	35	34–75	40	35	30–75	40	
(b) Seconds, maximum	40–250	78	50	45–250	87	70	50–250	106	250
Gravity, °A.P.I:									
(a) Minimum	16–30	26		16–31	25		13–30	24	
(b) Maximum	29–45	35		29–45	36		19–45	34	
Sulfur, per cent, maximum	0–2.0	0.9	1.5	0–2.0	1.0	1.5	0–2.0	1.1	2.0
Hard asphalt, per cent, maximum	0.05–1.0	0.51		0.05–1.0	0.62		0.3–0.7	0.43	
Conradson carbon, per cent, maximum	0–3.0	0.6	0.2	0–5.0	1.0	0.5	0–10.0	1.7	3.0
Ash, per cent, maximum	0.01–0.05	0.03	0.02	0–0.1	0.04	0.02	0–0.15	0.04	0.04
Water and sediment, per cent, maximum	0–2.0	0.4	0.05	0–2.0	0.6	0.1	0–4.0	0.8	0.6
Flash point, °F., minimum	135–150	148	Legal	140–195	152	150	140–190	151	150
Pour point, °F., maximum		†	35‡		†	35‡		†	35‡
Distillation characteristics, °F.:									
(a) 10 per cent point maximum	460–475	465		460–510	485				
(b) 90 per cent point maximum	660–700	700		660–750	695		660–750	705	
(c) End point, maximum	650–700	680					700	700	
Ignition quality:*									
(a) Cetene No., C.C.R., minimum	38–45	42		40–50	45		35–50	43	
(b) Cetane No., C.C.R., minimum	45	45		45	45				
(c) Cetane No., delay, minimum	35–45	37	45	35–45	40	35	30–45	37	30
(d) Diesel Index No., minimum	35–40	38	45	40–50	45	30	40	40	20
(e) Viscosity-Gravity No., maximum			0.86			0.89			0.91
(f) Boiling point-Gravity No., maximum			188			195			200

---

* Ignition quality values cannot be considered entirely representative because of the differences in nomenclature used for expressing same.

† 10–15°F. below operating temperature.

‡ Lower pour points may be specified whenever required by local temperature conditions.

quality characteristics. The amount of each will depend upon the cetane ratings of both the straight-run and the cracked materials.

In the production of aircraft Diesel fuels where high ignition quality and low cloud and pour points are required, indications are that other than normal refining methods will be necessary. Refined straight-run fuels of high ignition quality usually have high cloud and pour points, whereas cracked fuels of low ignition quality have low cloud and pour points. It is apparent, therefore, that special methods of refining or treating will be necessary in the production of suitable aircraft fuels or fuels for other purposes where high ignition quality and low pour point are essential. A number of these are as follows: (*1*) hydrogenation; (*2*) polymerization; (*3*) mild cracking; (*4*) dewaxing; (*5*) pour-point depressors; (*6*) acid treating; (*7*) solvent treating; and (*8*) Diesel dopes.

It is reported that hydrogenation produces fuels of high ignition quality and low pour point from either cracked or straight-run petroleum oils. With the proper selection of charging stock, indications are that fuels of 60 to 64 cetane number with pour points as low as −40° to −50°F. may be prepared by this method.[1]

The hydrogenation process may be used also in the production of Diesel oils from coal. A number of coal hydrogenation plants are now in operation in Europe. At present, the principal product of these plants is gasoline, although efforts are being made toward the production of suitable Diesel fuels. In one installation (20) the coal is ground, mixed with oil, and injected into a converter at the high pressure of about 3500 lb. per square inch. It is then heated to about 450°C. (842°F.) and treated with hydrogen at that temperature in the presence of catalysts. The oils produced are separated by distillation. The heavier fractions are used for mixing with the coal as charging stock. The gasoline is ready for use after a slight treatment. The intermediate oil is passed to the vapor-phase converters where it is mixed with hydrogen under pressure and heated to about 500°C. (932°F.). This mixture of hydrogen and oil vapor then passes over a catalyst, where part is converted to gasoline and part to Diesel fuel.

Diesel fuels are produced also from the hydrogenation of carbon monoxide by the Fischer–Tropsch process. It is reported (57) that the gas oil derived from Kogasin oil has a cetene rating of over 100. A mixture of 40 per cent of this gas oil and 60 per cent of a tar oil had a rating of 56 cetene number (probably 54 to 55 cetane number). Additional data on these two fuels are given in table 21.

The production of Diesel fuels by polymerization of olefins or alkylation of olefins and paraffins to produce paraffins can be accomplished when

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[1] Private communication.

the economic needs justify. To date, little thought has been given to the preparation of Diesel fuels by this method, chiefly because of the low price of Diesel fuel as compared to gasoline. From a technical point of view, however, it appears that Diesel fuel of satisfactory quality for high-speed engines can be made by such a process, providing the chemical reactions involved are suitably controlled. It has been found (20), for example, that in the presence of aluminum chloride as a catalyst and at about 50 atm. pressure (735 lb. per square inch) the reactions may be controlled to give products of any desired boiling range and chemical composition. It is claimed also that paraffinic oils may be obtained without the use of a catalyst.

TABLE 21

Cetene rating and physical properties of Kogasin Diesel fuel (57)

PROPERTIES	GAS OIL	MIXED DIESEL FUEL
Cetene No	Over 100	56
Cetane No.*	100	54–55
Distillation characteristics:		
End point, °C. (°F.)		320 (608)
At least 60 per cent, °C. (°F.)	300 (572)	
Specific gravity (d_{20})	0.835–0.91	0.866
Viscosity at 20°C. (Engler)	<2.6	1.28
Flash point, °C. (°F.)	>65 (149)	68 (155)
Solidifying point, °C. (°F.)	<0 (32)	−16 (3)
Soluble alkali, per cent	<4	2
Water	<0.5	Free
Hard asphalt		0.02
Color		Brown

* Estimated by writers.

Another polymerization process has been suggested (75) in which paraffin wax is cracked to give unsaturated hydrocarbons. This material is dewaxed, leaving unsaturated low-boiling liquid hydrocarbons. These hydrocarbons are subjected to a polymerization reaction with a metallic halide catalyst such as zinc chloride, boron fluoride, and ferric chloride, to produce saturated higher-boiling hydrocarbons from which polymerized Diesel fuel of high cetane rating may be obtained by fractional distillation.

The possibility of lowering the pour point of a paraffinic Diesel fuel by mild cracking (79) has been investigated, with results as listed in table 22.

Dewaxing (79) also has an application for producing fuels of high ignition quality and low pour point. Data for naphtha dewaxing of fuel oils are shown in table 23.

Pour-point depressors (79) have been found to be effective on Diesel fuels, particularly those with low pour points. This is illustrated in table 24.

TABLE 22

Effect of cracking on pour point and ignition quality (79)

Cracking temperature, °F		700	700	800	800
Cracking time, hours	0	2	8	2	8
Cracking loss, per cent	0	2	7	7	19
Resultant Diesel fuel:					
Ignition quality:					
Diesel Index No.	63	62	54	57	50
Cetane No. (delay) (45)	56	55	48	51	46
Pour point, °F	35	0	−15	−5	−20

TABLE 23

Effect of dewaxing on ignition quality and pour point (79)

FUEL	POUR POINT	IGNITION QUALITY	
		Diesel Index No.	Cetane No. (45)
	°F.		
Original fuel:	55	73	69
Dewaxed	0	62	55
Dewaxed	−30	58	51
Original fuel:	35	62	55
Dewaxed	0	58	51
Dewaxed	−30	53	48

TABLE 24

Use of Paraflow as a pour-point depressor for Diesel fuels (79)

PARAFLOW ADDED	POUR POINT				
per cent	*°F.*	*°F.*	*°F.*	*°F.*	*°F.*
0.0	50	35	10	−25	−40
0.1	50	30	5	−35	−50
0.5	40	15	5	−40	−60
1.0	40	15	0	−45	−80
3.0	35	5	−15	−75	−85

Acid treating (79) offers possibilities for producing fuels of high ignition quality, as shown in table 25.

Solvent refining (79) offers a method for the production of Diesel fuels. Representative data for extraction of straight-run and cracked fuels with sulfur dioxide are given in table 26. It will be noted that solvent treating is not so effective with straight-run fuels as it is with cracked fuels. This conclusion may not be true for all types of solvents and Diesel oils. Although the "treating loss" (extract) appears large when extracting for the higher ignition qualities, it is not a total loss because the extract, which is aromatic in character, may be blended as tractor fuel or be recracked to produce gasoline of high antiknock value.

TABLE 25

Effect of acid treating on ignition quality and pour point of cracked and straight-run Diesel fuels (79)

	CRACKED FUEL			STRAIGHT-RUN FUEL		
Acid, lb. per barrel	0	10	50	0	10	50
Treating loss, per cent	0	6	27	0	7	25
Diesel Index No.	45	48	55	38	41	48
Cetane No. (45)	42	44	49	39	40	44
Pour point, °F	−25	−25	−10	−50	−45	−30

TABLE 26

Effect of solvent treating on ignition quality and pour point (79)

Cracked fuel:				
Sulfur dioxide, per cent	0	100	300	500
Yield (raffinate), per cent	100	76	59	44
Loss (extract), per cent	0	24	41	56
Diesel Index No.	43	57	68	71
Cetane No. (45)	41	51	62	66
Pour point, °F	−40	−35	−30	−5
Cracked fuel:				
Sulfur dioxide, per cent	0	100	300	500
Yield (raffinate), per cent	100	75	57	41
Loss (extract), per cent	0	25	43	59
Diesel Index No.	38	53	66	70
Cetane No. (45)	39	48	60	65
Pour point, °F	−50	−50	−35	−15*
Straight-run fuel:				
Sulfur dioxide, per cent	0	100	300	500
Diesel Index No.	45	49	57	63
Cetane No. (45)	42	45	51	56
Pour point, °F	−25	−25	−20	0

* With the addition of 0.5 per cent of Paraflow, this −15°F. pour point was lowered to −50°F.

G. Solvent extraction of gasolines

Gasolines derived from the atmospheric distillation of crude oils in general contain paraffin hydrocarbons with straight chains predominating and with naphthenes, aromatics, and sometimes olefins present. Cracked gasolines likewise contain varying percentages of these hydrocarbon groups, as illustrated in table 27.

The solvent extraction of motor fuels to segregate the low-octane fraction (raffinate) from the high (extract) is an effective means for increasing the volume of high-octane gasoline. The residue oil (raffinate) of low octane rating can be cracked into high-octane motor fuel. It is estimated that, if the 500 million barrels of motor fuel produced in the United States in one year (estimated 1937 production) were solvent-extracted, over 100 million barrels of gasoline having an octane number of 90 or over would result.

The Edeleanu process of extraction with sulfur dioxide for the separation of aromatics and olefins from the paraffins and naphthenes is in commercial operation, treating naphtha at the rate of 6000 barrels a day (66). A number of other units are operating, are projected, or are under construction at the present time (September, 1937).

TABLE 27

Chemical analysis of cracked motor fuels

PER CENT OF HYDROCARBONS	NORTHERN KANSAS TOPPED CRUDE OIL	KENTUCKY FUEL OIL	SMACKOVER HEAVY CRUDE OIL	NORTHERN TEXAS FUEL OIL	LOST SOLDIER, WYOMING, CRUDE OIL	SPINDLETOP, TEXAS, CRUDE OIL
Unsaturates	16.1	14.4	14.7	16.0	11.7	14.7
Aromatics	17.8	22.5	27.5	18.6	15.9	17.3
Naphthenes	12.8	10.0	21.2	11.7	14.5	32.6
Paraffins	53.3	53.1	36.6	33.7	57.9	35.4

When extracting a Mid-Continent naphtha of 53° A.P.I. gravity, the yield of high-octane fuel varied from 9.1 to 12.5 per cent, as a function of the temperature of extraction which ranged from 0° to −60°F.; the results are shown in table 28.

A Sumatra naphtha when solvent-treated at 0°F. showed a 30 per cent yield of extract of 81.8 octane number, while at −40°F. the octane rating was 90.3 for a yield of 22 per cent. Detailed data are shown in table 29.

When solvent-extracting a South Texas naphtha of 57.9 octane rating, the yield of 80-octane fuel was 46.5 per cent at 0°F.; at −60°F., a 34 per cent yield of 90.8-octane product was obtained. The results are shown in table 30.

The properties of the raffinates derived from the extraction of Mid-Continent, South Texas, and Sumatra naphthas are shown in table 31.

The South Texas sulfur dioxide extract of 89.9 octane rating was separated into 20 per cent fractions and their properties determined as shown in table 32. The last two fractions, representing 38 per cent of the extract, showed an octane rating of 99.5. When based upon the original South Texas naphtha, a yield of about 13 per cent of a motor fuel having an octane number of 99.5+ was obtained.

TABLE 28

Extraction of straight-run Mid-Continent naphtha with sulfur dioxide (66)

	CHARGING STOCK	HIGH-OCTANE GASOLINE PRODUCED			
Experiment No		1	2	3	4
Sulfur dioxide used, per cent by volume		40	40	40	40
Extraction temperature, °F		0	−20	−40	−60
Yields, per cent by volume		12.5	10.6	9.6	9.1
Gravity, °A.P.I	53.1	36.7	34.7	33.5	32.2
Octane No., C.F.R. motor method	Below 41	82.6	86.2	89.0	91.0
Unsaturates and aromatics, per cent by volume	9.5	70.7	78.6	84.3	89.1
Naphthenes, per cent by volume	15.6	7.3	5.9	4.8	3.4
Paraffins, per cent by volume	74.9	22.0	15.5	10.9	7.5
Sulfur, per cent by volume	0.03				0.10
Distillation characteristics:					
Initial boiling point, °F	225	243	251	251	255
10 per cent	256	271	276	275	279
50 per cent	301	309	313	313	314
90 per cent	359	362	362	361	364
End point, °F	397	412	413	414	414

TABLE 29

Extraction of straight-run Sumatra naphtha with sulfur dioxide (66)

	CHARGING STOCK	HIGH-OCTANE GASOLINE PRODUCED	
Experiment No		5	6
Sulfur dioxide used, per cent by volume		85	55
Extraction temperature, °F		0	−40
Yields, per cent by volume		30.0	22.0
Gravity, °A.P.I	53.6	40.8	36.2
Octane No., C.F.R. motor method		81.8	90.3
Unsaturates and aromatics, per cent by volume	19.8	61.6	78.7
Distillation characteristics:			
Initial boiling point, °F	190	202	207
10 per cent	211	226	233
50 per cent	241	253	261
90 per cent	288	293	296
End point, °F	321	318	324

The comparative blending characteristics of a 91- and a 98-octane extract and isoöctane (2,2,4-trimethylpentane), in concentrations of 25, 50, and 75 per cent, are shown in table 33. The 91-octane number extract was obtained by treating the South Texas stock with 70 per cent sulfur dioxide at −60°F., as shown in table 30 under experiment 10. The 98-octane number blending stock was produced by fractionation of another South Texas extract obtained at −60°F. A Mid-Continent straight-run naphtha, with an octane rating of 63.4 and boiling between 102° and 266°F., was used for the blending tests. Table 33 and figure 5 show the octane numbers of the respective blends in relation to the amounts of extract or isoöctane present. It will be noted that the blending value of

TABLE 30

Extraction of straight-run South Texas naphtha with sulfur dioxide (*66*)

	CHARGING STOCK	HIGH-OCTANE GASOLINE PRODUCED				
Experiment No.		7	8	9	10	11
Sulfur dioxide used, per cent by volume		70	70	70	70	70
Extraction temperature, °F.		0	−20	−40	−60	0 to −60
Yields, per cent by volume		46.5	39.5	35.9	34.0	34.0
Octane No., C.F.R. motor method	57.9	80.0	84.4	88.2	91.1	90.8
Gravity, °A.P.I.	46.8	38.9	36.5	35.0	33.7	33.6
Unsaturates and aromatics, per cent by volume	31.2	63.1	73.5	80.2	84.0	84.7
Naphthenes, per cent by volume	19.8	13.2	10.1	8.0	6.2	5.8
Paraffins, per cent by volume	49.0	23.7	16.4	11.8	9.8	9.5
Aniline point, °C.		−12.8	−17.7	−19.3	−19.3	−19.5
Sulfur, per cent by weight	Below 0.01	0.01			0.01	0.01
Freezing point, °F.					Below −60	
Distillation characteristics:						
Initial boiling point, °F.	232	239	237	241	247	247
10 per cent	256	258	259	261	267	267
50 per cent	292	290	288	289	292	292
90 per cent	344	338	336	336	337	336
End point, °F.	382	398	390	390	394	391

TABLE 31

Properties of raffinates produced by extracting straight-run naphthas with sulfur dioxide (66)

	ORIGIN OF NAPHTHA					
	Mid-Continent		Sumatra		South Texas	
Experiment No.	1	4	5	6	7	11
Extraction temperature, °F	0	−60		−40	0	−60
Raffinates produced:						
Yields, per cent by volume	87.5	90.9	70.0	78.0	53.5	66.0
Gravity, °A.P.I.	54.8	55.3	59.2	59.1	53.7	54.0
Octane No., C.F.R. motor method		Below 41	51.2	50	Below 41	Below 41
Unsaturates and aromatics, per cent by volume		1.5	2.0	1.2	3.5	1.3
Naphthenes, per cent by volume		16			24.5	25.1
Paraffins, per cent by volume		82.5			72.0	73.6
Distillation characteristics:						
Initial boiling point, °F	223		190		236	
10 per cent	255		211		259	
50 per cent	303		240		298	
90 per cent	362		292		350	
End point, °F	399		320		394	

TABLE 32

Fractionation of South Texas sulfur dioxide extract (66)

PROPERTIES	SULFUR DIOXIDE EXTRACT—VARIOUS CUTS					
	0–100 per cent	0–20 per cent	20–40 per cent	40–60 per cent	60–80 per cent	80–98 per cent
Gravity, °A.P.I.	35.6	41.8	35.8	35.6	32.9	32.5
Doctor test	Sweet	Sweet	Sweet	Sweet	Sweet	Sweet
Unsaturates and aromatics, per cent by volume	78.2	53.2	81.3	82.0	92.7	92.0
Octane No., C.F.R. motor method	89.9	81.1	92.2	94.1	99.5+	99.5+
Distillation characteristics:						
Initial boiling point, °F	222	194	224	246	273	284
10 per cent	239	201	227	252	276	289
50 per cent	258	211	228	262	278	295
90 per cent	291	224	231	275	280	312
End point, °F	333	244	254	290	296	335

the 98-octane number extract compares favorably with isoöctane, and that the blending values of these extracts are about the same as their octane numbers.

Additional information on the subject of solvent extraction is given by F. W. Sullivan and O. FitzSimons. Sullivan (70) reports the use of a mixture of liquid carbon dioxide and sulfur dioxide as solvent upon a cracked naphtha boiling between 250° and 400°F. When solvent-extracted at -115°F., the cracked naphtha, containing 52 per cent of olefins, 47 per cent of paraffins and naphthenes, and 1 per cent of aromatics, produced a fraction of 109 octane number (C.F.R. research method). FitzSimons (33) reports the use of a mixture of heterocyclic nitrogen bases, such as pyridine, quinoline, quinaldine, the picolines, the lutidines, etc. in conjunction with sulfur dioxide, for separation of the antiknocking from the knocking hydrocarbons in cracked naphthas rich in olefin hydrocarbons. When using a solvent mixture of 23 per cent pyridine and 77 per cent liquid sulfur dioxide, a yield of 28 per cent of extract of 103 octane number (C.F.R. research method) was obtained from vaporphase cracked naphtha.

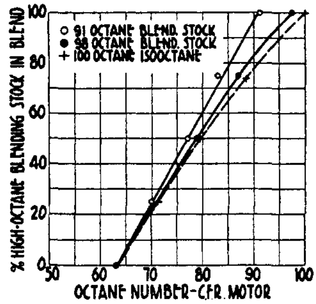

Fig. 5. Blending values of solvent-refined gasolines

TABLE 33

Octane numbers of various blends of extract and isoöctane with 63.4-octane straight-run gasoline (66)

PER CENT BLENDED WITH 63.4-OCTANE STRAIGHT-RUN GASOLINE	OCTANE NO. OF BLENDS		
	Sulfur dioxide extracts		Isoöctane
100	91.1	98.0	100
75	83.1	86.5	88.5
50	77.5	79.0	79.7
25	70.0	71.5	71.0
0	63.4	63.4	63.4

III. MOTOR FUELS FROM NATURAL GAS

A. Natural gas as source

1. Methane, ethane, propane, and butanes: direct use as a motor fuel

Hydrocarbon gases are being used to an ever-increasing extent for motor fuel in the form of liquefied methane–ethane mixtures, propane–butane mixtures, or as butanes. Methane–ethane mixtures are used to a limited extent, chiefly as fuel (not liquefied) for large stationary and "gas Diesel" engines. In Germany and France a number of service stations are now selling liquefied methane–ethane as fuel for trucks and busses. In the United States, liquefied propane–butane mixtures and butanes are used for tractors, trucks, busses, trains, construction and mine locomotives, power shovels, road graders, ditch diggers, industrial plant jitneys, oil well drilling, and in many other installations.

The volume of methane and ethane available during the year 1936 from natural and refinery gas was 2,475 billion cubic feet, of which 2,175 billion came from natural gas.[2] This volume suggests a potential source of over 55 billion gallons of liquefied methane–ethane motor fuel. The volume of propane and butanes available in the United States during 1936 from natural gases was approximately 8 billion gallons, from the distillation of crude oil about 1.5 billion, and from cracked gases about 4.5 billion gallons, or a total of over 14 billion gallons (34). Thus the total volume of motor fuel potentially available from hydrocarbon gases in the United States during 1936 was over 69 billion gallons, or over three times as much gasoline as was consumed during that year.

Propane–butane mixtures, like methane–ethane mixtures, have advantages when used in the spark-ignition internal-combustion engine. It is reported that compression ratios may be increased and higher thermal efficiencies obtained; better carburetion, not possible with a liquid fuel such as gasoline, is attained; dilution of lubricating oils is eliminated; very little carbon deposit results; the engine runs more smoothly and cooler with greater power output and better acceleration and idling; engine wear is reduced; spark plug life is lengthened; and obnoxious exhaust odors are eliminated (34). Compression ratios with propane–butane or methane–ethane as fuel may be increased to as high as 9 to 1, depending upon combustion chamber design, size and speed of engine, and type of service. This increase in compression ratio is made possible by the high antiknock values of these gases, which range from 91 to over 125 octane number as shown in table 34.

The heating values of propane–butane and methane–ethane mixtures are considerably lower than those of regular motor gasoline on a B.t.u.

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[2] Estimated by Gustav Egloff from references 2 and 58.

per gallon basis. However, because of the higher compression ratios possible with these gases, thermal efficiencies are higher, with the result that fuel consumption is about the same as with gasoline. The heating values for a number of liquid and gaseous fuels are shown in table 35. For comparative purposes, additional properties are included.

TABLE 34

Octane ratings of various hydrocarbon gases (23)

HYDROCARBON	OCTANE NO. C.F.R. MOTOR METHOD
Methane	125*
Ethane	125*
Propane	125*
Isobutane	99
n-Butane	91
Mixture: 30 per cent propane and 70 per cent butanes	105*

* Approximate ratings.

TABLE 35

Heating values and physical properties of various hydrocarbon fuels (liquid)

FUEL	BOILING POINT		GRAVITY AT 60°F.		VAPOR PRESSURE IN LB. PER SQUARE INCH AT 100°F.	HEATING VALUE (GROSS)	
	°C.	°F.	Specific	°A.P.I.		B.t.u. per pound	B.t.u. per gallon
Methane*	−161.5	−258.7	0.247	440		23,910	49,250
Ethane*	−89.4	−129.0	0.410	213		22,040	75,380
Propane*	−42.2	−44.1	0.511	145	190	21,690	92,400
Isobutane*	−12.2	10.0	0.576	114	76	21,290	102,390
n-Butane*	−0.5	31.0	0.585	111	52	21,330	104,080
Aviation gasoline (34)			0.702	70		21,400	125,000
U. S. motor gasoline (34)			0.739	60		21,050	129,000
Kerosene (34)			0.816	42		20,000	135,000
Diesel fuel (34)			0.904	25		19,000	142,000

* Calculated from results of F. D. Rossini and G. B. Kistiakowsky, in Bureau of Standards Publications.

Methane–ethane and propane–butane mixtures, with their high volatility, do not present the problems of incomplete vaporization and unequal distribution which are commonly encountered with gasoline or other less volatile liquid fuels. Since these fuels are gases when they enter the carburetor and manifold, uniform distribution to all cylinders is assured and the difficulties occasioned by the wetting of the walls of the intake manifold through condensation are eliminated. These characteristics add materially to the life of both the engine and the lubricants, since dilution of the oil in the crank case cannot occur from unvaporized fuel dropping from the pistons.

One of the most interesting applications of methane–ethane fuel is in the gas Diesel engine (59) which the city of Lubbock, Texas, installed in its lighting plant in 1936. The engine is substantially a standard Nordberg two-cycle air-injection Diesel. The gas, under pressure, enters the spray-valve cage exactly as does the injection air. When the spray-valve needle is lifted, the gas at 1100 lb. per square inch pressure (contrasted to the 500 lb. compression pressure in the engine cylinder) blows through the atomizer into the cylinder. Its high velocity, due to the pressure drop, insures proper diffusion and proper mixing with the air in the cylinder. According to reports (68), the operation of this gas Diesel engine has been excellent. The unit has carried its rated load without difficulty and handles variations in load with satisfaction. Cylinder wear has been about half the amount usually found in Diesel engines of the same size. The performance of this engine has prompted the Lubbock Light Department to order another Nordberg gas Diesel engine and to arrange for the conversion of another Diesel engine to the use of natural gas. There appear to be unusual possibilities in this new type of Diesel engine, particularly since it may be switched readily from gas to oil or from oil to gas as occasion dictates.

Liquid propane–butane applications are more numerous. Late in 1934, the city of Spokane, Washington, as a trial, converted ten busses of a fleet of one hundred thirty from gasoline operation to a mixture of propane and butane (16). This mixture consisted of 35 per cent of propane and 65 per cent of butanes. The experiment was found successful enough to warrant changing the entire fleet from gasoline to liquefied propane–butane. Over a two-year period a saving of 30 per cent in engine maintenance was reported (16).

The cost of converting a truck or bus to use liquefied propane–butane (5) varies from $75 to $200, depending upon the number and size of the fuel tanks installed and whether a change in compression is desired. In preparing this fuel for the engine, four distinct stages are required: namely, initial regulation, application of heat, final regulation, and carburetion. Because of the fact that the pressure of the propane–butane mixture might vary as much as 150 lb., initial regulation is necessary to reduce this variable pressure to a practically constant pressure of about 10 lb. per square inch. Heat is applied by means of an exchanger which utilizes the heat in the cooling-water system. Fuel is delivered from the heat exchanger as a gas under 10 lb. pressure to the final regulator. In many

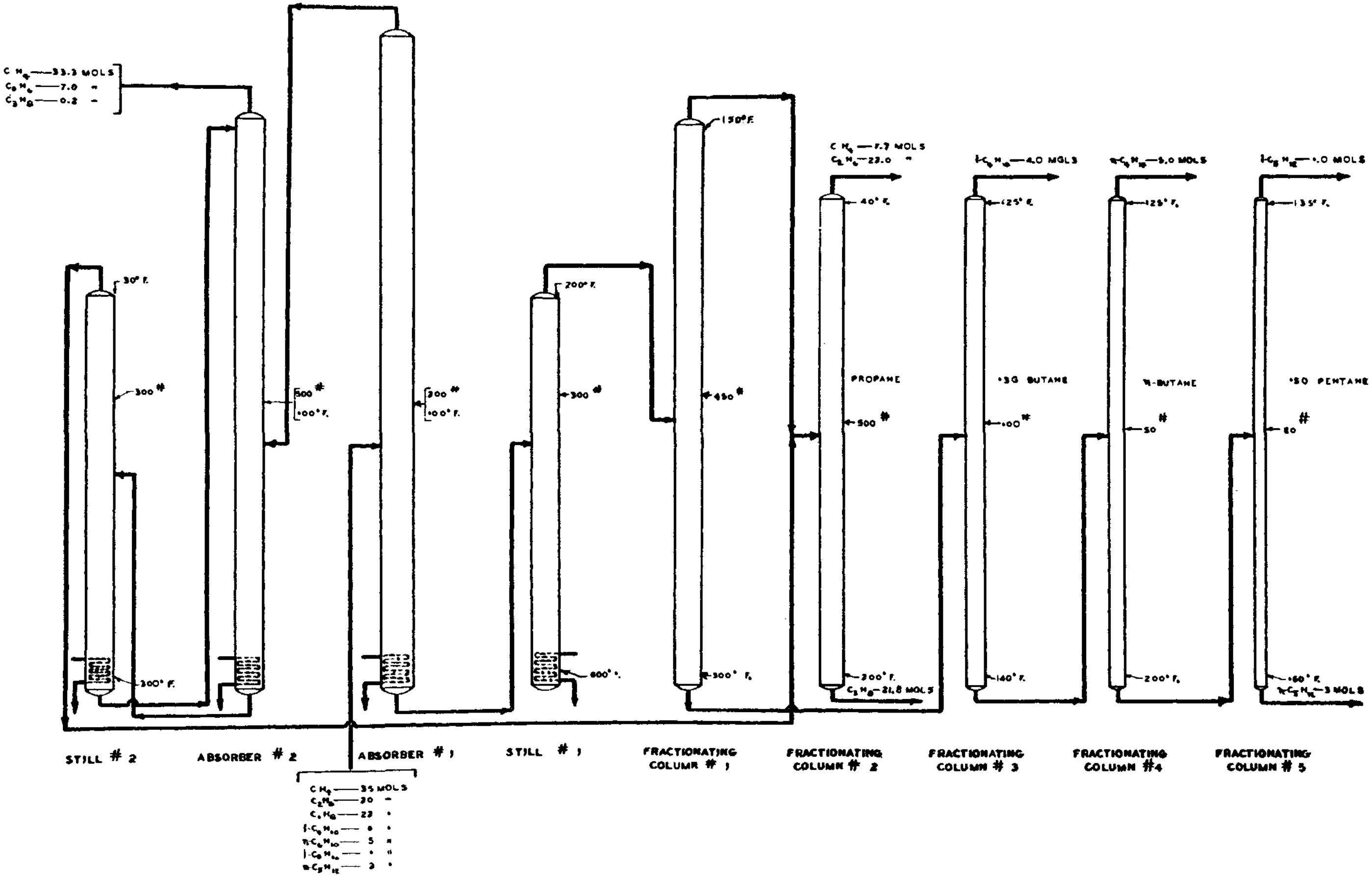

FIG. 6. Flow diagram of commercial process for separating hydrocarbon gases

cases, particularly in truck operation, it is often found desirable to provide for the use of gasoline as a stand-by fuel. In such cases, combination gasoline and propane–butane carburetors are installed.

Hydrocarbon gases, whether derived from oil wells, gas wells, the distillation of crude oil, or the cracking process, may be separated into their components,—methane, ethane, propane, butanes, and pentanes,—by compression, absorption, distillation, and stabilization. A schematic outline of a commercial process used for this separation (76) is shown in figure 6. In this process, a natural gas having the composition shown in table 36 is separated into its components in the following manner. The gas is compressed at a pressure of 200 lb. while in contact with an absorption oil, such as mineral seal, at a temperature of 100°F. (absorber 1). The undissolved gas from the top of absorber 1 is compressed to a pressure of 500 lb. as it enters absorber 2. The gas leaving the top of absorber 2 consists of 33.3 moles of methane, 7.0 moles of ethane, and 0.2 mole of propane. The oil from absorber 2 is discharged into still 2 at a pressure of 300 lb. and temperatures of 300°F. at the bottom and 30°F. at the top. The oil from absorber 1, containing dissolved gases, is pumped to still 1 at 300 lb. pressure where temperatures are maintained at 600°F. at the bottom and 200°F. at the top. The gaseous hydrocarbons from still 2 are compressed to a pressure of 500 lb. in fractionating column 2, where a top temperature of 40°F. and a bottom temperature of 200°F. are maintained. The gases from the top of fractionating column 1, which consist of a mixture of methane, ethane, and propane, are discharged into fractionating column 2 along with the gases from still 2 for the separation of the methane and ethane from the propane. The propane fraction from the bottom of column 2 is discharged to a storage tank after cooling. The gas recovered from column 2 contains 1.7 moles of methane and 23 moles of ethane. The purity of the propane fraction leaving the bottom of column 2 is 99.0

TABLE 36

Composition of sample of natural gas (76)

HYDROCARBON	MOLES
Methane	35
Ethane	30
Propane	22
n-Butane	5
Isobutane	4
n-Pentane	3
Isopentane	1

per cent, representing 21.8 moles of the 22 moles present in the original gas.

The butanes and pentanes discharge from the bottom of fractionating column 1 into column 3, where the isobutane is separated under 100 lb. pressure at 125°F. The normal butane and the pentanes discharge from the bottom of column 3 into column 4, where the normal butane is separated from the pentanes at a pressure of 50 lb. and a top temperature of 125°F. The normal pentane and isopentane are discharged to storage tanks from the bottom of column 4 into column 5 at a pressure of 20 lb.

TABLE 37

Plant operating conditions for separation of hydrocarbon gases (76)

	PRESSURE	TEMPERATURE	
		Top	Bottom
	lb. per square inch	*°F.*	*°F.*
Absorber:			
No. 1	200	100	
No. 2	500	100	
Still:			
No. 1	300	200	600
No. 2	300	30	300
Fractionating column:			
No. 1	450	150	300
No. 2	500	40	200
No. 3	100	125	140
No. 4	50	125	200
No. 5	20	135	160

TABLE 38

Separation of hydrocarbon gases (76)

COMPONENT	ORIGINAL GAS	RECOVERY		FRACTIONATING COLUMN NO.
		Per cent	Moles	
	moles			
Methane	35	4.8	1.7	2
Ethane	30	76.7	23.0	2
Propane	22	99.0	21.8	2
Isobutane	4	100.0	4.0	3
n-Butane	5	100.0	5.0	4
Isopentane	1	100.0	1.0	5
n-Pentane	3	100.0	3.0	5

and a top temperature of 135°F., at which point the isopentane is separated from the normal pentane.

The operating conditions are summarized in table 37. The recovery of the various components in the gas under consideration is shown in table 38.

Typical analyses of a number of commercial hydrocarbon gases are shown in table 39.

TABLE 39

Typical analyses of natural (casinghead and gas-well) gases

DISTRICT	SAMPLE	PER CENT BY VOLUME OF						
		Carbon dioxide	Methane	Ethane	Propane	Isobutane	Normal butane	Pentanes and heavier
California (70):								
Kettleman Hills	Gas from field	0	81.60	8.47	5.29	0.78	2.03	1.83
North Belridge	Gas from field	1.1	92.21	3.05	1.77	0.28	0.92	0.67
Ventura Avenue	Gas from field	0	89.49	3.34	3.64	0.78	1.32	1.43
Mountain View	Gas from field	0.9	75.84	5.45	7.82	2.0	3.83	4.16
Santa Fe Springs	Gas from field	1.3	68.69	12.16	10.42	1.65	3.35	2.43
Taft-Maricopa	Gas from field	14.2	64.97	5.14	5.72	1.72	3.10	5.15
Kettleman Hills	Absorption plant discharge gas (based on extraction of 21.9 lb. Reid vapor pressure gasoline)	0	83.59	8.68	5.42	0.80	1.48	0.03
North Belridge		1.1	93.49	3.09	1.79	0.28	0.67	0.01
Ventura Avenue		0	91.20	3.40	3.71	0.79	0.88	0.02
Mountain View		0.9	80.43	5.71	8.19	2.09	2.62	0.06
Santa Fe Springs		1.3	71.09	12.58	10.78	1.71	2.51	0.03
Taft-Maricopa		15.1	69.15	5.47	6.10	1.83	2.28	0.07
Texas (14):								
East Texas	Casinghead gas	0	41.40	15.80	24.20	2.80	9.70	6.10
Panhandle	Gas-well gas	0	87.13	5.83	4.25	0.55		2.22
Louisiana (14):								
Northern Louisiana	Combined casinghead and gas-well gas	0	92.53	3.85	1.57	1.57	1.09	0.96

2. Natural gasoline

Natural gasoline is an important part of our motor fuel supply, chiefly because of its high volatility, blending properties, and antiknock value, which ranges from 70 to 85 octane number. It is obtained from casinghead gas, which flows from oil wells along with the crude oil, and from gas-well gas. These gases contain hydrocarbons, such as methane, ethane, propane, butanes, pentanes, hexanes, heptanes, and octanes, from which natural gasoline may be fractionated.

The presence of natural gasoline was first discovered (14) in the early 1880's, when many operators of natural-gas transportation systems experienced trouble with condensation in the lines. It was soon determined that this condensate was gasoline, and draw-off drips were installed in low places along the lines. At that time the facilities for collecting this so-called drip gasoline consisted in utilizing the normal gas line pressure with the addition of a few cooling coils.

Today, there are about eight hundred and fifty natural-gasoline plants in operation in the United States, with an estimated total daily capacity of over 10 million gallons (14). The greatest natural gasoline-producing area of the United States lies in the Mid-Continent and Gulf Coast fields. The actual production in the United States during 1936 amounted to 1,766 million gallons, or more than 8 per cent of the total U. S. motor fuel production (73). In 1916 the volume was 103 million gallons, or about 5 per cent of the total (14). Production for the intermediate years is shown in table 40.

TABLE 40

Production of natural gasoline in the United States (73, 14) for the years 1916–1936

YEAR	MILLION GALLONS	PER CENT OF TOTAL MOTOR FUEL PRODUCTION
1916	103	5
1920	385	7
1925	1,127	10
1930	2,210	12
1935	1,632	8
1936	1,766	8

When natural gasoline is the primary product desired from casinghead or gas-well gas, its separation from methane, ethane, and propane is much simpler than when individual components are the desired products. This separation may be accomplished by: (*1*) simple compression and stabilization; (*2*) compression followed by absorption and fractionation, or absorption, distillation, and fractionation; (*3*) absorption in activated carbon followed by distillation and stabilization. This process is now largely superseded by the other processes mentioned.

The simplest method is shown in the flow diagram of figure 7, which utilizes compression of the gases followed by stabilization of the gasoline produced to the desired vapor pressure (15). The gas is compressed to 250 lb. per square inch, after which it is cooled to 75°F., run to a surge tank for intermediate storage, and then to the stabilizer shown. The bottom portion of the stabilizer or fractionator is maintained at a temperature of 250°F., while the top temperature is held at 110°F. by recirculation of the liquid in the accumulator tank. The pressure is maintained at 225 lb.

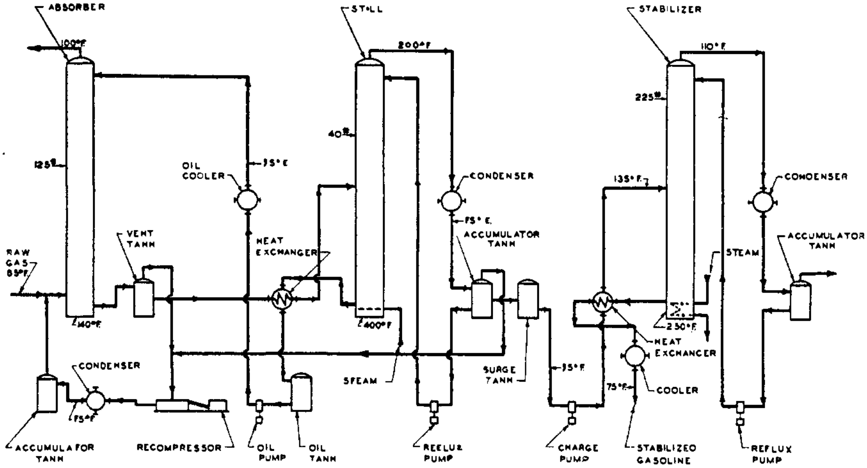

FIG. 7. Flow diagram of method (compression, followed by stabilization) for extracting gasoline from hydrocarbon gases.

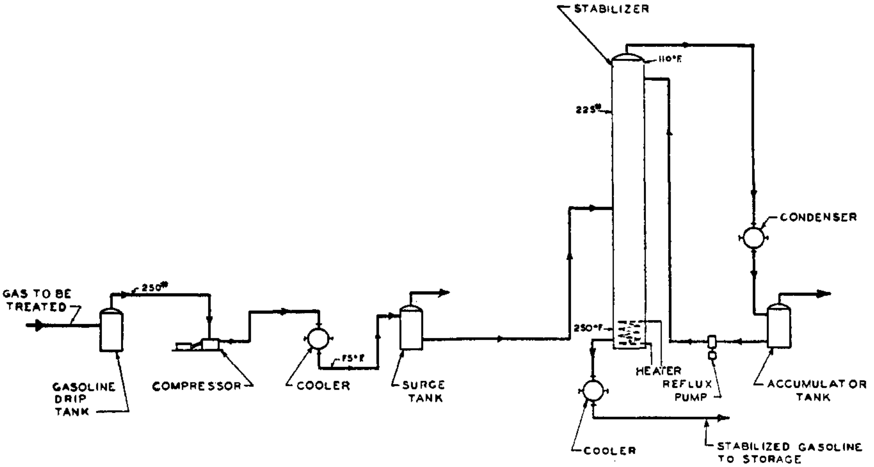

FIG. 8. Flow diagram of method (compression, followed by absorption and fractionation) for extracting natural gasoline from hydrocarbon gases.

Another method for producing natural gasoline is shown in figure 8. The gas is first compressed; this is followed by absorption in a solvent such as mineral seal oil; the gasoline is then distilled and finally stabilized to the desired vapor pressure (15).

For commercial purposes natural gasoline is defined by the following specifications:

Reid vapor pressure at 100°F	10–34 lb. per square inch
Per cent evaporated at 140°F	25–85
Per cent evaporated at 275°F	Not less than 90
End point	Not higher than 375°F.
Corrosion	Non-corrosive
Doctor test	Negative (sweet)
Color	Not less than +25 (Saybolt)

Typical analyses of natural gasoline as produced in the Mid-Continent and Gulf Coast fields are given in tables 41 and 42.

When reducing natural gasoline from the various sources to three groups, it is obvious that considerable leeway must be allowed in octane rating and specific hydrocarbons present. It will be noted that as front-end volatility increases so does the octane rating. However there are a few plants, principally in the Gulf Coast area, which produce a product of relatively low volatility but of high octane rating. Examination shows this to be due to the presence of aromatics, naphthenes, and certain branched-chain paraffins (14).

TABLE 41

Typical analyses of Mid-Continent and Gulf Coast natural gasoline (14)

PROPERTIES AND COMPOSITION OF GASOLINE	SOURCE OF GASOLINE			
	East Texas		North Texas	
Reid vapor pressure, lb. per square inch at 100°F.	26	18	26	18
Gravity, °A.P.I	91.0	86.4	87.5	82.5
Distillation characteristics:				
Per cent evaporated at 100°F	55.0	33.0	40.0	27.5
Per cent evaporated at 140°F	85.0	77.5	72.5	65.0
Per cent evaporated at 212°F	96.0	95.5	92.5	91.5
End point, °F	304	309	315	320
Octane No., C.F.R. motor method	84	78	82	75
Hydrocarbon composition, volume per cent:				
Propane			0.08	
Isobutane	1.23		1.54	1.04
n-Butane	35.26	14.42	30.95	14.05
Isopentane	24.15	31.66	10.59	13.25
n-Pentane	20.37	28.06	20.25	25.45
Hexane	10.22	13.97		
Hexane plus	8.77	11.89	36.59	46.21

TABLE 42

Typical analyses of Mid-Continent natural gasoline of low, medium, and high volatility (14)

PROPERTIES AND COMPOSITION OF GASOLINE	VOLATILITY			VOLATILITY		
	Low	Medium	High	Low	Medium	High
Reid vapor pressure, lb. per square inch at 100°F	26	26	26	18	18	18
Gravity, °A.P.I.	78–82	82–85	84–90	77–81	80–84	84–88
Distillation characteristics:						
Per cent evaporated at 100°F	5–10	20–30	30–45	5–10	15–25	30–40
Per cent evaporated at 140°F	35–45	55–70	70–85	30–40	50–65	68–80
Per cent evaporated at 212°F	70–80	85–92	93–97	70–80	82–90	91–96
End point, °F	365	347	329	365	347	329
Octane No., C.F.R. motor method	Up to 72	74–78	80–85	65–70	71–74	75–78
Hydrocarbon composition, volume per cent:						
Butanes				18–20	16	15
Pentanes				25–30	35–40	55–60
Hexanes plus				50–57	44–49	25–30

TABLE 43

Octane ratings and physical properties of various straight-chain and branched-chain paraffin hydrocarbons contained in natural gasoline

HYDROCARBON	OCTANE NO. BY C.F.R. MOTOR METHOD	GRAVITY AT 60°F.		BOILING POINT	
		Specific	°A.P.I.	°C.	°F.
Butanes:					
Isobutane	99	0.5665	119.3	−10.2	13.6
n-Butane	91	0.5824	110.7	0.6	33.8
Pentanes:					
2,2-Dimethylpropane	83	0.631 D		9.5	49.1
Isopentane	90	0.621 $D^{19.1^\circ}$	94.9	28.0	82.3
n-Pentane	64	0.631 D^{20°		36.2	97.2
Hexanes:					
2,3-Dimethylbutane	95	0.6612 D^{20°		58.1	136.6
n-Hexane	59	0.66 D^{20°		69.0	156.2
Heptanes:					
2,2-Dimethylpentane	93	0.674 D^{20°		78.6	173.5
2,3-Dimethylpentane	85	0.6950		89.4	192.9
2,4-Dimethylpentane	90	0.681 D^{20°		83.9	183.0
2-Methylhexane	64	0.707 D^{20°		90.4	194.7
n-Heptane	0	0.684 D^{20°		98.4	209.1
Octanes:					
n-Octane	−28	0.707 D^{15°		124.6	256.3
2,2,3-Trimethylpentane	101	0.722 D^{15°		110.8	231.4
2,2,4-Trimethylpentane	100	0.704 D^{15°		99.3	210.7

As indicated in tables 41 and 42, the hydrocarbons present in natural gasoline are predominantly straight-chain and branched-chain paraffins.

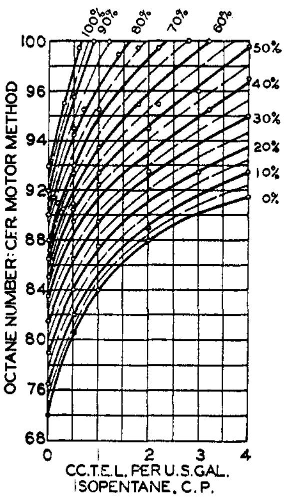

Fig. 9. Isopentane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

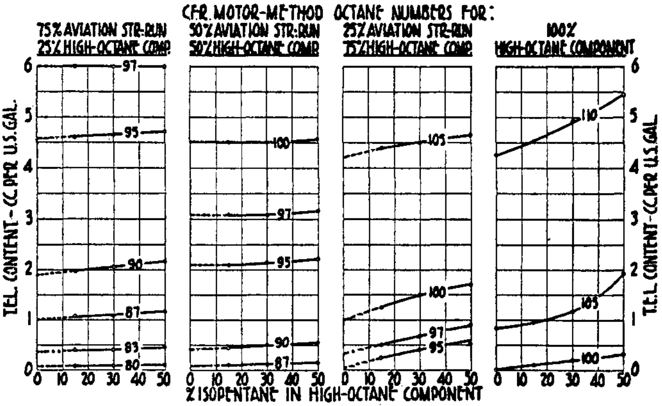

Fig. 10. Isopentane blended with isoöctane and aviation straight-run gasoline, with and without addition of tetraethyl lead.

The octane ratings and physical properties of a number of these individual hydrocarbons are shown in table 43.

One of the principal constituents of natural gasoline is isopentane. It is estimated that by simple fractionation 190 million gallons of isopentane could be produced annually in the United States (62). Its high antiknock value (90 octane number), good susceptibility to tetraethyl lead, and low boiling point (82.3°F.) make it an excellent blending agent for high-octane aircraft fuels. These properties are illustrated in figures 9 and 10.

In the production of 100-octane aircraft fuel, isopentane is generally blended with the main components, isoöctane and straight-run gasoline, for the purpose of supplying the required front-end volatility. The amount of isopentane added is usually restricted to about 15 per cent, because of its relatively high vapor pressure. This is illustrated in table 44, wherein 100-octane isoöctane, 74-octane aviation straight-run gasoline of 7 lb. Reid vapor pressure, and isopentane are blended to produce 100-octane fuel with 3 cc. of tetraethyl lead per gallon.

TABLE 44

Composition of 100-octane fuel containing 3 cc. of tetraethyl lead per gallon (62)

ISOPENTANE	AVIATION GASOLINE	ISOÖCTANE	REID VAPOR PRESSURE
per cent	*per cent*	*per cent*	*lb. per square inch at 100°F.*
0	38.0	62.0	4.0
10	37.2	52.8	5.8
17	36.7	46.3	7.0
20	36.4	43.6	7.7
30	35.7	34.3	9.5
40	34.9	25.1	11.4
50	34.1	15.9	13.3

IV. MOTOR FUELS FROM CRACKED GASES

A. General

Hydrocarbon gases, such as propane, propene, butanes, and butenes, derived from natural gas and petroleum, present a potential yearly output of 9 billion gallons of motor fuel ranging from 76 to 100 octane number (24).

The methods used for converting these gases into high-octane motor fuels are thermal and catalytic polymerization (24). The thermal method produces aromatic and olefinic types of motor fuels at high temperatures and high and low pressures, whereas the catalytic method operates at comparatively low temperatures and pressures and produces an olefinic type gasoline. If desired, the catalytic method can be controlled so that when the butenes are polymerized and hydrogenated an isoöctane gasoline of 90 to 100 octane number results.

The octane ratings of a number of pure olefin hydrocarbons are shown in table 45.

Thermal and catalytic polymerization methods are now in commercial use,—namely, the "unitary" and "multiple-coil" thermal methods and the UOP catalytic method. The daily production of polymer gasoline, including those units under construction (August 1, 1937), is over 1,300,000 gallons of gasoline ranging in octane number from 76 to 100.

B. Thermal polymerization

The unitary thermal process (24, 49) converts hydrocarbon gases at high temperatures and pressures into liquids ranging in properties from gasoline to gas oil. In this process, which is owned by the Polymerization Process Corporation, gaseous olefins and paraffins are treated at temperatures between 800°F. and 1100°F. and pressures ranging from 800 to 1200 lb. per square inch. The gasoline derived from this process has an octane rating of 76 to 79, depending upon the charging stock and operating conditions of the plant. The use of feed stocks high in unsaturates (65 to 70 per cent) results in a product in which aromatics and monoölefins appear to be predominant. The products obtained from feed stocks lower in unsaturates (30 to 38 per cent) are more paraffinic than aromatic or olefinic, and a considerable portion of the paraffins is isoparaffins. Production by this method is at the rate of 10,000 barrels of gasoline per day.

A flow chart of the unitary process is shown in figure 11.

The results obtained by processing a stabilizer reflux on a recycling basis are given in table 46.

Inspection data on typical products from processing various representative feed stocks by the unitary polymerization process are given in table 47.

In the multiple-coil process (24, 18) the operation consists of first treating cracking plant gas at temperatures of 900–1000°F. and pressures of 600–800 lb. per square inch. The liquids derived from this operation are withdrawn and the gaseous portion, which consists of the residue paraffins, is subjected to further cracking at 1300°F. for production of olefins. The olefinic gas from this operation is treated at temperatures of 1150–1300°F. and pressures of 50–75 lb., producing gasoline, fuel oil, and tar. In the high-temperature operation, a gasoline of 85 to 105 octane rating is obtained. At the lower temperatures the octane rating of the polymer gasoline is between 78 and 80.

The process is owned by the Pure Oil and Alco Products Companies. Daily production amounts to 2800 barrels. A flow chart of the process is shown in figure 12.

The results obtained from three types of hydrocarbon gases by the multiple-coil process are shown in tables 48 to 52 inclusive.

C. Catalytic polymerization

The UOP catalytic polymerization process (24, 22), which is owned by the Universal Oil Products Company, operates on olefin-containing gases.

TABLE 45

Octane ratings and physical properties of pure olefins

OLEFIN	BOILING POINT		GRAVITY AT 60°F.		OCTANE NO., C.F.R. MOTOR METHOD	OCTANE NO., C.F.R. RESEARCH METHOD BLENDING* (35)
	°C.	°F.	Specific	°A.P.I.		
Ethylene	−103.9	−156.0	0.410	213.0		86
Propene	−47.7	−54.0	0.526	138.0		102
1-Butene (23)	−6.1	21.0	0.600	104.0	80	112
2-Butene (23)	+1.5	33.9	0.613	99.0	83	
Isobutene (23)	−6.6	20.0	0.597	105.0	87	
Diisobutene					84	
Triisobutene					87	
Diisopentene					75	
2,2,4-Trimethyl-3-pentene (9)	102.6	216.68	0.715		89	144
2,2,4-Trimethyl-4-pentene (9)	101.2	214.16			86	150
α-Isononene (9)	141.5–143.0	286.7 –289.4			75	
β-Isononene (9)	143.0–145.0	289.4 –293.0			84	
1-Pentene	40.0	104.0	0.652	85.4		99
2-Pentene	38.39	101.1	0.667	80.8		
α-Isoamylene	25.0	77.0	0.653	85.3		
β-Isoamylene	36.39	97.5	0.656	84.3		125
2-Methyl-2-butene	38.4	101.12	0.668			157
2,3-Dimethylbutadiene	68.8– 68.9	155.84–156.02	0.7264 $D^{68°}$			212
3-Methyl-2-pentene	65.7	150.26	0.722			109
2,4-Hexadiene	82.0	179.6	0.718			174
1,5-Hexadiene	60.0	140.0	0.688			79
1-Hexene	64.1	147.38	0.683			85
2-Hexene	67.9	154.22	0.6813 $D^{68°}$			100
1-Heptene	99.0	93.7–93.8 at 771 mm.	0.6993 $D^{68°}$			55

3-Heptene	95.8	204.44	0.7016 D^{68°			95
3-Ethyl-2-pentene	98.0	208.4	0.725			124
2,2-Dimethyl-4-pentene	76.0– 76.1	168.8 –168.98	0.6881 D^{68°			147
2,3-Dimethyl-2-pentene	95.1	203.18	0.719			127
2,4-Dimethyl-2-pentene	84.0	183.2	0.699			122
2-Methyl-5-hexene	84.7	184.46	0.6936 D^{68°			83
3-Methyl-5-hexene	87.2– 87.5	188.96–189.5	0.6969 D^{68°			86
2,2,3-Trimethyl-3-butene	77.8– 77.2	170.96–172.04	0.7023 D^{68°			132
1-Octene	121.85 at 765 mm.	251.24	0.7158 D^{68°			25
2-Octene	123.2–123.7	253.76–254.66	0.722 D^{68°			55
3-Octene	122.7–122.9	252.86–253.22	0.7185 D^{68°			73
4-Octene	122.0–122.3	251.6 –252.14	0.7184 D^{68°			91

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* Calculated blending value = 25 per cent in 50-octane straight-run reference fuel.

The sources of these gases may be either the cracking process or the catalytic dehydrogenation or cracking of propane and butanes to their corresponding olefins.

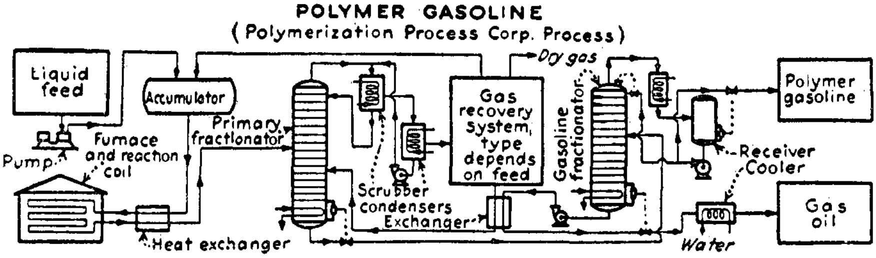

FIG. 11. Flow diagram of "unitary" polymerization process

TABLE 46

Stabilizer reflux (recycling operation) (24, 49)

Pressure, lb. per square inch	800	1200	1200	1200
Temperature, °F	1000	1000	1100	1030
Net yield, per cent by weight	67.9	69.0	69.6	64.5
Saturates in feed (net), per cent by weight	57.0	54.0	60.7	59.9
Unsaturates in feed (net), per cent by weight	43.0	46.0	39.3	40.1
Net yield, per cent unsaturates in fresh feed	158	150	177	161
Gallons liquid per 1000 cu. ft.:				
Net gaseous feed	12.78	13.10	14.40	13.5
Gross feed, per cent by volume:				
Ethylene	3.4	1.9	2.4	2.0
Ethane	12.2	6.8	9.0	6.5
Propene	29.6	30.5	21.3	21.0
Propane	46.3	49.8	38.8	39.6
Butene	4.3	4.8	11.0	13.6
Butane	4.2	6.2	16.9	17.3
Net feed, per cent by weight:				
Propene	43.0	41.1	23.1	20.3
Propane	57.0	54.0	36.4	37.1
Butene		4.9	16.1	19.8
Butane			24.3	22.8
Octane No., C.F.R. motor method:				
Blending value, 50 per cent in fuel A-3*	92	90	83	88

* Octane No. = 43.6.

The distinctive property of cracked gas is its content of unsaturated hydrocarbons. By regulation of the cracking process (time, temperature, and pressure) the percentages of the different hydrocarbons may be varied considerably. The quality of cracked gases is shown in table 53.

TABLE 47

Pilot plant and commercial plant operation (24, 49)

PROPERTIES	PRODUCT FROM PILOT PLANT OPERATION WITH STABILIZER REFLUX		PRODUCT FROM COMMERCIAL PLANT ON BUTANE FEED
	Raw product†	Clay-treated	Clay-treated
Gravity, °A.P.I.	65.1	66.5	61.4
Distillation characteristics:			
Initial boiling point, °F.	100	105	95
10 per cent	123	126	120
20 per cent	134	134	133
50 per cent	164	161	180
90 per cent	296	258	361
End point, °F.	414	314	449
Octane No., C.F.R. motor method:			
Straight			79
Blending value, 50 per cent in reference fuel A-3*	92	90	
Reid vapor pressure, lb. per square inch at 100°F.	10.7		
Color		30+	30+
Color after 8 hr. in sun		30+	
Copper-dish gum, mg		10.4	
Induction period, min.			120

* Octane No. = 43.6.

† Cut to 329°F. end point before clay-treating; treating loss, 1 per cent.

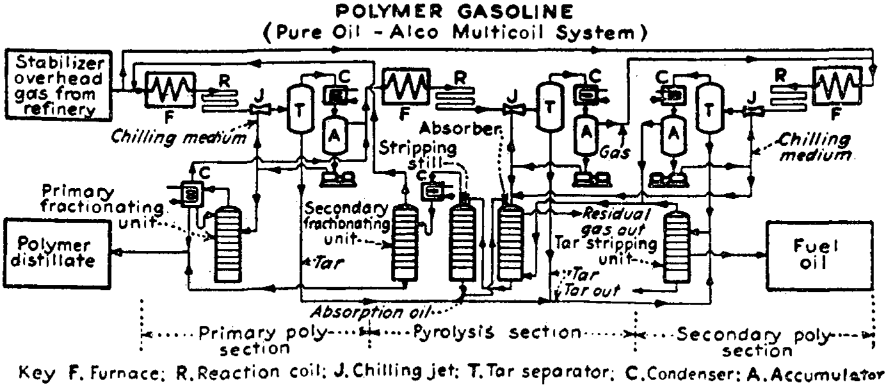

FIG. 12. Flow diagram of "multiple-coil" polymerization process

In this process the gases are heated to about 450°F., under 200 lb. pressure, in a pipe-coil heater from which they flow to catalyst chambers containing solid phosphoric acid. The reaction is exothermic, a temperature rise of about 150°F. taking place in the catalyst bed. The polymer gasoline vapors pass through a cooling coil and thence to a receiver. The gasoline is pumped to a stabilizer in order to produce a product of the desired vapor pressure. The polymer product as produced has an octane rating of 80 to 83.

TABLE 48

Typical analysis of Gyro vapor phase residue and stabilizer overhead gases (24, 18)

CONSTITUENT	RESIDUE GAS	STABILIZER OVERHEAD
	mole per cent	*mole per cent*
Methane and hydrogen	32.5	0.5
Ethylene	23.9	9.2
Ethane	13.4	8.3
Propene	16.8	40.3
Propane	4.9	10.4
Butene	6.1	28.4
Butane and heavier	2.4	2.9

TABLE 49

Typical operation with residue gas (24, 18)

Charging stock:	
Specific gravity	1.06
Unsaturates, per cent	47.2
Yields of products:	
Treated gas:	
Cu. ft. per cubic foot of charge	0.80
Specific gravity	0.87
Unsaturates, per cent	18.4
Liquid:	
Gal. per 1000 cu. ft. of charge	4.4
End-point gasoline:	
Gal. per 1000 cu. ft. of charge	3.7
Gravity, °A.P.I.	52.4
Total liquid, per cent	84
Distillation characteristics:	
Initial boiling point, °F.	96
10 per cent	134
50 per cent	220
80 per cent	320
End point, °F.	420

The residue gas from the stabilizer is made up substantially of propane and butanes. These paraffin hydrocarbons may be dehydrogenated

TABLE 50

Typical operation with stabilizer overhead gas (*24*, *18*)

Once-through operating conditions:	
Temperature of coil outlet, °F	1175
Pressure of coil outlet, lb. per square inch gage	55
Conversion, per cent	80
Charging stock:	
Specific gravity	1.352
Unsaturates, per cent	79.6
Yields of products:	
Treated gas:	
Cu. ft. per cubic foot of gas charged	0.46
Specific gravity	0.86
Unsaturates, per cent	34.5
Liquid:	
Gal. per 1000 cu. ft	98
End-point gasoline:	
Per cent boiling up to 350°F	68
Gravity, °A.P.I	26.4
Octane No., C.F.R. motor method	86
Distillation characteristics:	
Initial boiling point, °F	120
10 per cent	172
30 per cent	190
50 per cent	204
90 per cent	267
End point, °F	352

TABLE 51

Typical operation with absorber gas (*24*, *18*)

Once-through operating conditions:	
Temperature of coil outlet, °F	1275
Pressure of coil outlet, lb. per square inch gage	60
Conversion, per cent	37.4
Charging stock:	
Specific gravity	0.79
Unsaturates, per cent	39.4
Yields of products:	
Treated gas:	
Cu. ft. per cubic foot of gas charged	0.85
Specific gravity	0.72
Unsaturates, per cent	0.29
Liquid:	
Gal. per 1000 cu. ft	1.75
Gravity, °A.P.I	21.6
End-point gasoline:	
Per cent boiling up to 350°F	76
Octane No., C.F.R. motor method	102

TABLE 52

Typical operation with liquid feed (using higher molecular weight constituents only) (24, 18)

Commercial plant handling 4,050,000 cu. ft. per day; average operation, September 1 to 20, 1934

Charging stock (including recycle):	
Specific gravity	1.51
Unsaturates, per cent	49.4
Conversion of unsaturates, per cent	86.7
Recycle ratio	1.75
Yields of products:	
Fuel oil:	
Gal. per 1000 cu. ft. of fresh charge	3.0
Gravity, °A.P.I.	8.0
Treated gas:	
Specific gravity	1.01
Unsaturates, per cent	22.0
End-point gasoline:	
Gal. per 1000 cu. ft. of fresh charge	8.8
Gravity, °A.P.I.	55.0
Octane No., C.F.R. motor method	76.0
Distillation characteristics:	
Initial boiling point, °F.	90
10 per cent	105
30 per cent	145
50 per cent	182
90 per cent	323
End point, °F.	398

TABLE 53

Typical analyses of cracked gases

DISTRICT	PER CENT BY VOLUME									
	Methane	Ethane	Propane	Butanes	Pentanes	Ethylene	Propene	Butenes	Hydrogen	Carbon dioxide, etc.
Mid-Continent (23):										
Receiver gas	22.2	17.3	26.8	5.6	0.2	6.0	11.2	4.0	4.3	2.4
Stabilizer reflux	0.1	3.2	16.8	40.5	1.2	0.6	16.6	20.2	0.1	0.7
Stabilizer gas	3.4	17.8	22.2	2.0	0.2	16.0	29.0	4.9	0.6	3.9
Lean gas		20.2	18.0	7.1		4.7	7.5	4.2	35.4	2.9
"BB" fraction				51.9				44.0	2.5	1.6
Michigan (5):										
Stabilizer reflux	0	3.2	18.5	23.4		0.3	11.9	42.7	0	0
Stabilizer gas	0	3.4	26.6	17.9	0.3	1.9	16.4	33.5	0	0
Lean absorber gas	20.4	25.4	16.3	5.3	1.2	6.2	13.6	6.1	4.1	1.4
Receiver gas	16.2	22.8	15.8	5.7	6.4	6.0	13.4	9.2	3.4	1.1
Total gas	14.5	18.0	15.7	9.6	0.7	5.1	20.7	6.0	3.8	5.9

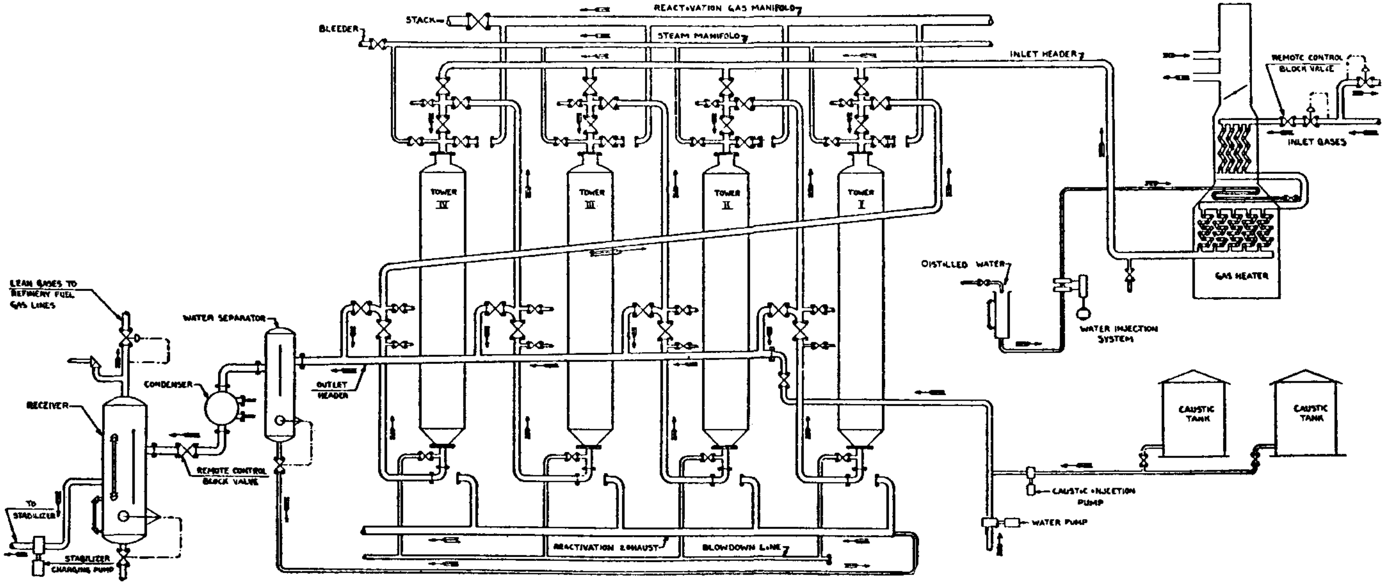

FIG. 13. Flow diagram of "UOP Catalytic" polymerization process

catalytically to olefins, or cracked to olefinic gases, and then pumped to the catalytic polymerization unit and processed exactly the same as the original gases.

A flow diagram of the UOP catalytic polymerization process is shown in figure 13.

Experimental data, using stabilizer gas from typical vapor-phase and liquid-vapor-phase cracking as charging stock, are shown in table 54. With this particular gas, the yield of polymer gasoline having a Reid vapor pressure of 10 lb. per square inch was 6.5 gallons per 1000 cu. ft. By catalytic dehydrogenation of the gas leaving the polymerization plant, followed by catalytic polymerization, an additional yield of 2.2 gallons per 1000 cu. ft. was obtained, making a total yield of 8.7 gallons of polymer gasoline. This is equivalent to 19.7 gallons per 1000 cu. ft. based on the C_3–C_4 (propane–propene and butanes–butenes) fraction.

TABLE 54

Operation of catalytic polymerization process (24, 22)

CHARGING STOCK AND YIELD OF GASOLINE	VAPOR-PHASE CRACKED GAS	LIQUID-VAPOR-PHASE CRACKED GAS
	mole per cent	*mole per cent*
Charging stock:		
Methane	26.5	8.6
Ethane–ethylene	29.5	13.0
Propene	18.6	14.0
Propane	8.2	34.4
Butenes	9.4	10.2
Butanes	2.4	18.2
Pentenes	4.0	1.6
Yields of gasoline,* gallons per 1000 cu. ft.:		
Catalytic polymerization only	6.5	4.6
Catalytic dehydrogenation and polymerization of polymer unit residue gas	2.2	10.7
Polymerization and dehydrogenation operation:		
Base on total gas charged	8.7	15.3
Based on C_3–C_4 fraction	19.7	19.5

* Reid vapor pressure = 10 lb. per square inch.

The catalytic polymerization process may also be carried out to polymerize selectively the normal butene and isobutene present in the gases to isoöctenes which, on hydrogenation, yield isoöctane gasoline of 90 to 100 octane number. It is estimated that there are over a billion gallons of this isoöctane fuel potentially available yearly from the hydrocarbon gases in the United States. This is assuming that the butanes in natural and refinery gases are catalytically dehydrogenated to butenes, then polymerized to isoöctenes, and finally hydrogenated to isoöctanes. Production by the UOP catalytic polymerization process, when all units are in operation, is at the rate of 16,500 barrels per day, of which 6000 barrels are isoöctane gasoline.

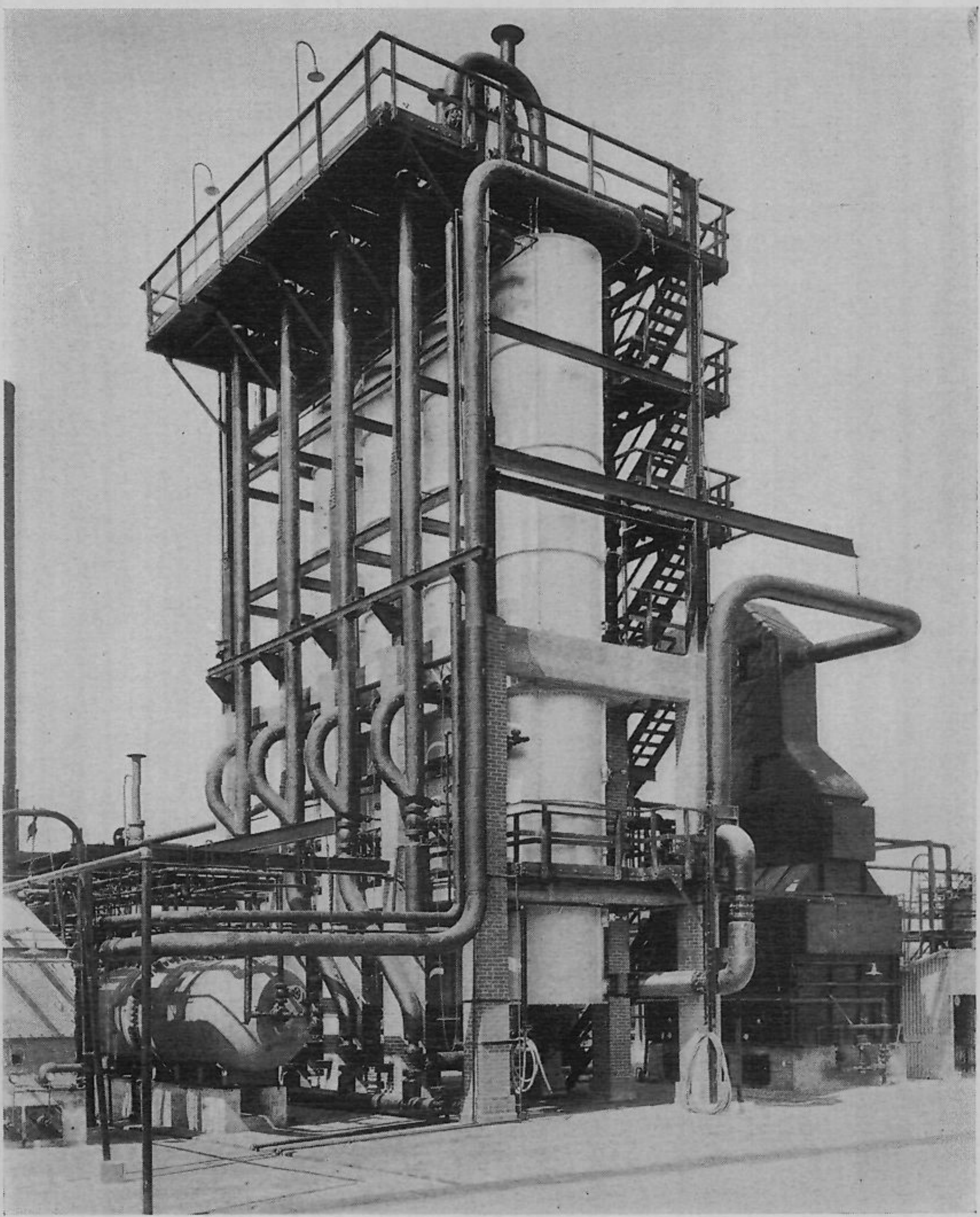

Fig. 14. Catalytic gas polymerization unit of the Universal Oil Products Company, handling eight million cubic feet of gas per day.

Laboratory data, octane ratings, and octane blending values of gasolines produced commercially by the three polymerization processes described

TABLE 55

Laboratory inspection data and octane blending values of various polymer gasolines, isoöctanes, and benzene

GASOLINE	GRAVITY, °A.P.I.	DISTILLATION CHARACTERISTICS, °F.						OCTANE NO. OF BLENDS OF HIGH-OCTANE FUEL IN REFERENCE FUEL A-3*								OCTANE BLENDING VALUE OF BLENDS OF HIGH-OCTANE FUEL IN REFERENCE FUEL A-3†							
		Initial boiling point	10%	20%	50%	90%	End point	5%	10%	15%	20%	25%	50%	75%	100%	5%	10%	15%	20%	25%	50%	75%	100%
Polymer gasoline:																							
Unitary polymer (49)......								47.0	49.5	52.0	54.5	56.5	66.0	74.0	82	112	105	101	97	95	88	85	82
Multiple-coil (18):																							
High-pressure polymer†..	54.7	101	146	163	208	339	402	47.0	49.5	52.0	54.0	56.5	66.0	71.0	73	112	103	99	96	95	88	80	73
High-octane polymer†...	31.5	169	195	202	225	324	392	46.5	49.5	52.0	55.5	58.0	70.0	82.5	94	102	103	99	103	101	96	96	94
Catalytic:																							
Regular polymer.........	67.0	101	156	178	212	314	408	48.0	52.0	55.5	59.5	62.5	73.5	79.0	82	132	128	123	123	119	103	91	82
Selective polymer.......	61.4	190	221	225	228	238	280	48.0	52.5	56.5	60.0	64.0	77.0	82.0	84	132	133	130	126	124	110	95	84
Diisobutene............	64.5	212	213	214	215	216	238	49.0	54.5	58.5	62.5	66.0	77.5	82.0	84	152	153	143	138	133	111	95	84
Isoöctane gasoline:																							
Hydrogenated selective polymer................	66.6	188	218	222	226	238	273	46.0	48.5	51.0	53.0	55.5	69.5	83.0	95	92	93	93	91	91	91	95	95
Hydrogenated diisobutene..	71.0	206	208	209	210	213	244	46.0	48.5	51.5	53.5	56.5	70.5	84.5	99	92	92	96	93	95	97	98	99
Benzene (commercial).......	29.3	173	174	174	175	175	212	45.0	47.0	49.0	51.0	53.0	66.5	85.0	100+	72	78	80	81	81	89	89	100+

* Straight-run reference fuel, 43.6 octane number.

† Samples submitted by C. R. Wagner, Pure Oil Company, Chicago.

above,—namely, unitary, multiple coil, and catalytic,—are given in table 55. Similar data for commercial benzene are included. These results are shown graphically in figure 15. It will be noted that a straight-run gasoline of 43.6 octane number (reference fuel A-3) was used for the comparative blending tests.

The blending characteristics of UOP catalytic polymer gasoline are illustrated more completely in figure 16, in which "regular" low-sulfur polymer gasoline (see table 55 for inspection data) is blended with straight-run and cracked gasolines from various crudes. It will be noted that the blending value is lower in cracked than in straight-run gasolines. The reason is obvious.

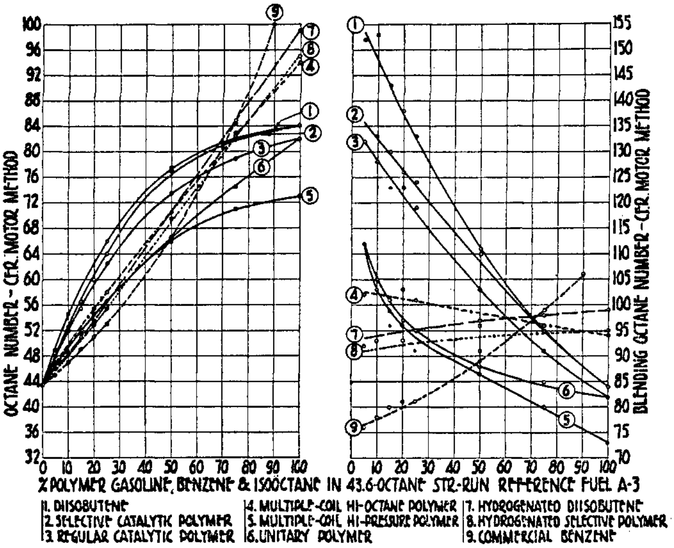

FIG. 15. Comparison of octane blending values of products produced by three polymerization methods.

D. Isoöctanes

In the production of isoöctane gasoline by the selective catalytic polymerization method, it may be found more economical to produce isoöctanes of 90 to 95 octane number than those approaching 100 octane. This is due, in part, to the much higher yields obtained for the lower octane products and to the good lead susceptibility of the various isoöctanes. For example, from a given quantity of gas containing both normal butene and isobutene, it is possible to produce considerably more 90–95 isoöctane than 99–100 isoöctane. The lead susceptibilities are such that the 90 and

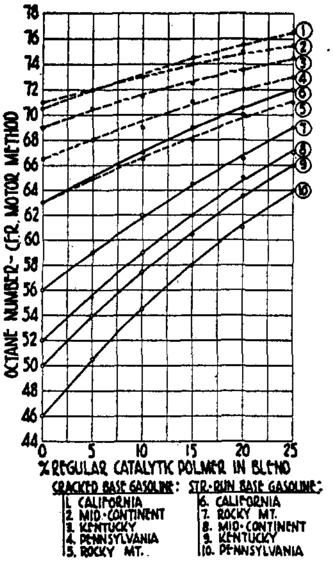

FIG. 16. UOP catalytic polymer gasoline blended with straight-run and cracked gasolines from various crudes.

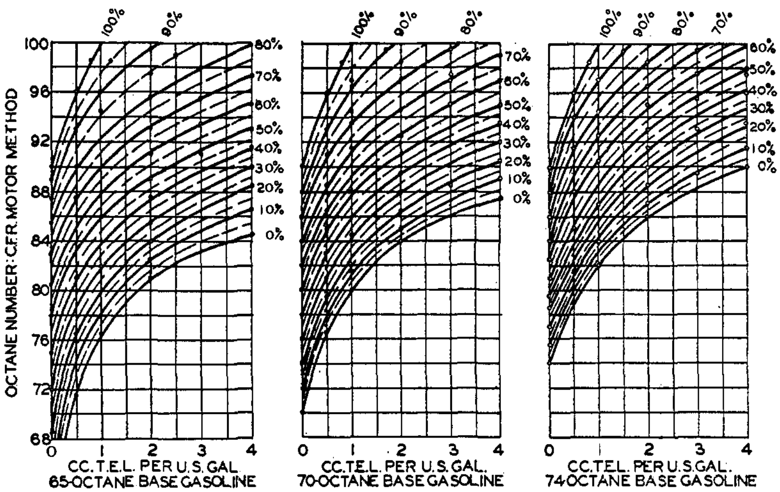

FIG. 17. 90-octane isoöctane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

95 isoöctanes can be increased to 100 octane (determined by the motor method) by the addition of 1.0 and 0.4 cc. of tetraethyl lead per U. S. gallon, respectively.

This difference in antiknock rating is due entirely to the varying proportions of different isomers which are present in the various isoöctane

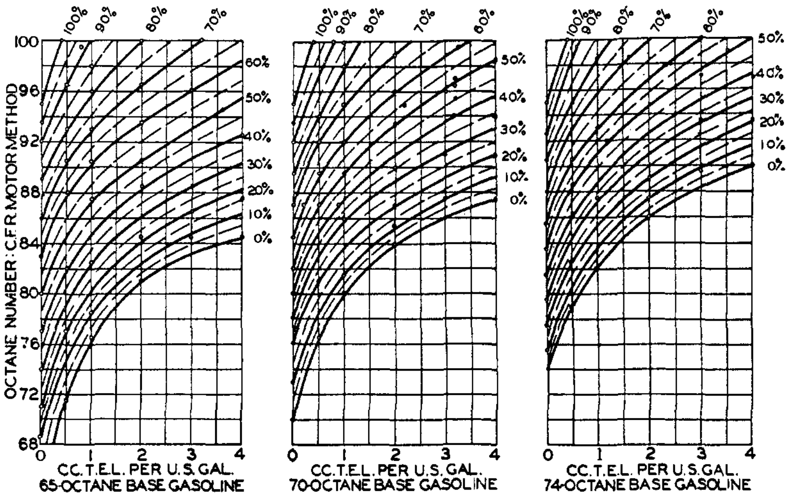

FIG. 18. 95-octane isoöctane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

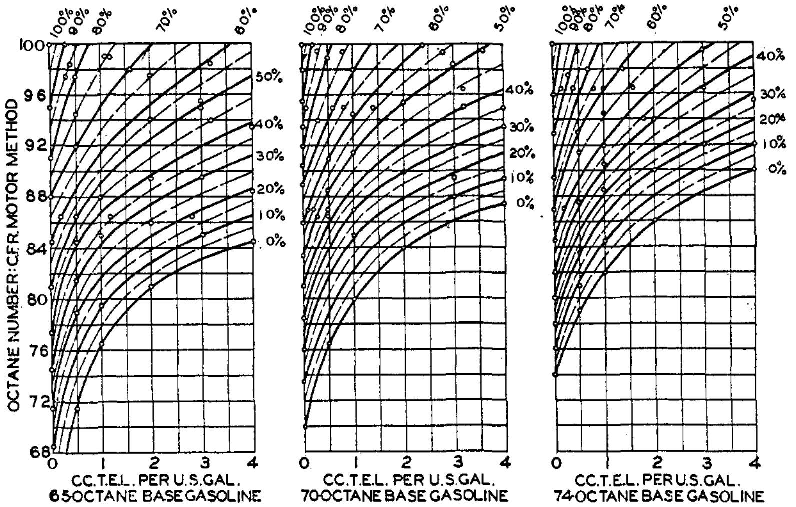

FIG. 19. 100-octane isoöctane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

products. For example, the isoöctane used as a standard in knock testing consists exclusively of one isomer, 2,2,4-trimethylpentane, and by definition rates 100 octane number. The 90 and 95 isoöctanes have lower octane ratings because they consist of mixtures of different isoöctanes (isomers), some of which have a lower octane rating than 2,2,4-trimethylpentane.

During the past few years isoöctane has become the principal blending agent in the manufacture of high-octane aircraft fuels. This is due to its ability to "stand up" best under the most divergent engine operating conditions, its high heat value, and its high stability without the use of inhibitors.

An interesting set of data is illustrated in figures 17, 18, and 19, in which commercial isoöctanes of 90, 95, and 100 octane rating are shown blended with 65-, 70-, and 74-octane straight-run gasolines, with and without the addition of tetraethyl lead.

E. Alcohols, ethers, and ketones from cracked gases

1. General

With the demand for motor fuels of higher octane number increasing, a number of liquids have been developed for motor fuels. These alcohol, ether, and ketone fuels are produced from hydrocarbon gases, and their octane ratings are of the order of 100 and higher. Generally speaking, the alcohols, ethers, and ketones are lower in fuel efficiency, owing to the lowered heat content of the oxygenated fuel, and while the octane rating is high the general efficiency is considerably lower than that of hydrocarbon fuels on a weight basis.

2. Alcohols

Ethyl alcohol is prepared from cracked gases by synthesis, although fermentation of agricultural products is the main source.

In commercial practice tertiary alcohols are generally manufactured by absorbing cracked petroleum gases which contain isobutene and other isoölefins. Sulfuric acid of 76 per cent concentration is used as the absorbing agent. Dilution with water hydrolyzes the mixture and the final step is steam distillation.

Further discussion of alcohols as motor fuel is given in section VII.

3. Ethers and ketones

Contrary to the behavior of ethyl ether, which is a violent knock inducer, some ethers, notably isopropyl ether, have high antiknock value and in general good susceptibility to tetraethyl lead.

Isopropyl ether is produced by chemical treatment of propene, which is present in refinery cracking plant gases or which may be produced by dehydrogenating or cracking the propane contained in both natural and refinery gases. It is estimated that there is now sufficient propene available in the United States, exclusive of all normal demands for other purposes, to produce approximately 340 million gallons of technical

TABLE 56

Octane blending value and tetraethyl lead susceptibility of isopropyl ether

ISOPROPYL ETHER	OCTANE NO.
C.F.R. motor method:	
Straight	98.0
Blended 50 per cent with 70-octane straight-run gasoline*	85.5
+ 1 cc. TEL per gallon	93.0
+ 2 cc. TEL per gallon	96.0
+ 3 cc. TEL per gallon	98.0
+ 4 cc. TEL per gallon	99.0
Army method:	
Straight	98.0
Blended 50 per cent with 70-octane straight-run gasoline*	87.5
+ 1 cc. TEL per gallon	94.0
+ 2 cc. TEL per gallon	97.0
+ 3 cc. TEL per gallon	98.5
+ 4 cc. TEL per gallon	100.0

* California straight-run gasoline.

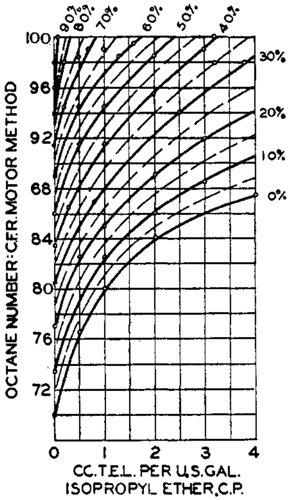

FIG. 20. Isopropyl ether blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

isopropyl ether per year. This quantity of isopropyl ether, when blended 40 per cent with gasoline and "leaded" with 3 cc. of tetraethyl lead per gallon, will equal 850 million gallons yearly of 100-octane gasoline (13, 42).

The volume of antiknock ethers could be greatly increased if mixed ethers, such as methyl isopropyl or methyl isobutyl ether, are produced. In addition, if all the propane available in the United States were dehydrogenated to propene and converted to isopropyl ether, the potential volume of 100-octane gasoline would be increased still further.

The use of isopropyl ether as a blending agent in the production of aircraft fuels of high octane number has been described in the literature (13, 42). Its value as a blending agent is illustrated in table 56 and figure 20, in which octane ratings are given for various blends of chemically pure isopropyl ether with a 70-octane straight-run gasoline, with and without the addition of tetraethyl lead (46). In figure 20 the straight-run base gasoline was a blend of reference fuels C-9 and A-4, whereas the base gasoline in table 56 was a California straight-run product.

TABLE 57

Octane ratings of blends of isopropyl ether and isoöctane in straight-run gasoline (13)

PER CENT IN BLEND			OCTANE NO. BY ARMY METHOD		BLENDING VALUE OF ISOPROPYL ETHER
Straight-run	Isopropyl ether	Isoöctane	Clear	With 3 cc. of TEL per U. S. gallon	
100	0	0	74.8	93.0	
70	30	0	85.7	98.4	111
70	0	30	82.0	97.0	99
70	15	15	84.1	97.6	106
60	40	0	88.3	Equals isoöctane + 0.18 cc. TEL per gallon	109
60	0	40	84.4	98.7	99
60	20	20	86.7	99.2	105
				Equals isoöctane	
50	50	0	90.6	+ 0.44 cc. TEL per gallon	106
50	0	50	86.5	+ 0.05 cc. TEL per gallon	98
50	25	25	88.8	+ 0.08 cc. TEL per gallon	103

Isopropyl ether might be used as a supplement to isoöctane fuel, the ether supplying the necessary front-end volatility which isoöctane lacks. Antiknock data for blends of the two products are given in table 57. Comparative data on physical properties are shown in table 58.

The octane ratings and physical properties of a number of mixed ethers (42) are given in table 59.

Ketones have also been found to have high antiknock value and good susceptibility to tetraethyl lead. The two discussed here are acetone and methyl ethyl ketone.

Acetone may be prepared catalytically from ethanol or by special fermentation of corn or molasses. In the latter case, both acetone and *n*-butyl alcohol are formed. Acetone is also being produced commercially,

TABLE 58

Physical properties of C.P. isopropyl ether and isoöctane (2,2,4-trimethylpentane) (13)

PROPERTIES	ISOPROPYL ETHER	ISOÖCTANE
Boiling point, °F	153–158	211
Density at 68°F	0.725	0.691
Refractive index at 68°F	1.3680	1.3921
Freezing point, °F	−125	−162
Viscosity, centipoise at 68°F	0.322	0.543
Latent heat of vaporization, B.t.u. per pound	123	130
Heat of combustion:		
High value, B.t.u. per pound	16,900	20,580
Low value, B.t.u. per pound	15,600	19,200
Low value of heat of combustion, plus latent heat of vaporization, B.t.u. per gallon	95,100	111,400
Reid vapor pressure, lb. per square inch at 100°F	5.3	2.2

TABLE 59

Physical properties, octane blending values, and tetraethyl lead susceptibilities of various branched-chain and mixed ethers (42)

ETHER	BOILING POINT		GRAVITY AT 60°F.		OCTANE (C.F.R. MOTOR METHOD) BLENDING VALUES.* 25 PER CENT BLEND IN 74-OCTANE AVIATION GASOLINE	
	°C.	°F.	Specific	°A.P.I.	Non-leaded	With 1 cc. of tetraethyl lead per gallon
Diisopropyl ("isopropyl")	68.4	155.1	0.722	64.5	101	105
Methyl isopropyl	31.5	88.7	0.735†	61.0	73	90
Methyl *tert*-butyl	55.3	131.5	0.735	61.0	111	106
Methyl *tert*-amyl	86.0	186.8	0.754†	56.2	108	108
Ethyl isopropyl	54.0	129.2	0.720	65.0	75	87
Ethyl *sec*-butyl	81.3	178.3	0.738	60.2	63	73
Ethyl *tert*-butyl	72.3	162.1	0.736	60.7	115	114
Ethyl *tert*-amyl	101.5	214.7	0.759†	54.9	112	106
Isopropyl *tert*-butyl	87.6	189.7	0.736	60.7	112	118
n-Propyl *tert*-butyl	98.0	208.4	0.747	57.9	103	106
Di-*sec*-butyl	114.0	237.2	0.756†	55.7	95	
Sec-butyl *tert*-butyl	114.0	237.2			106	105
Tert-butyl *n*-butyl	123.0	253.4	0.758	55.2	81	92
Tert-butyl *n*-amyl	143.0	289.4	0.770	52.3	63	80

* Calculated blending value.

† Other reference sources.

starting with the propene present in cracked gases. Methyl ethyl ketone is manufactured by catalytic dehydrogenation of butanol-2, which may be obtained from the butenes contained in cracked gases (77).

Octane ratings and physical properties of these ketones are given in table 60.

TABLE 60

Octane ratings and physical properties of several ketones

PROPERTIES AND OCTANE RATINGS	ACETONE	METHYL ETHYL KETONE
Boiling point:		
°C	56.1	79.6
°F	133.0	175.3
Gravity at 60°F.:		
Specific	0.795	0.808
°A.P.I	46.6	43.6
Refractive index at 68°F	1.359	1.379
Freezing point:		
°C	−94.3	−86.4
°F	−137.7	−123.5
Latent heat of vaporization, B.t.u. per pound	237.4	190.7
Heat of combustion:		
Low value, B.t.u. per pound	12,179	13,464
High value, B.t.u. per pound	13,163	14,519
Low value of heat of combustion plus latent heat of vaporization, B.t.u. per gallon	82,196	91,889
Octane No.:		
C.F.R. motor method:		
Straight	100.0	98.5
Blended 50 per cent with 70-octane straight-run gasoline:*	84.5	86.5
+ 1 cc. TEL per gallon	92.5	93.0
+ 2 cc. TEL per gallon	95.5	95.0
+ 3 cc. TEL per gallon	97.5	96.0
+ 4 cc. TEL per gallon	98.5	96.5
Army method:		
Straight	100.0	99.0
Blended 50 per cent with 70-octane straight-run gasoline:*	86.5	86.5
+ 1 cc. TEL per gallon	94.5	93.5
+ 2 cc. TEL per gallon	98.0	96.5
+ 3 cc. TEL per gallon	100.0	98.0
+ 4 cc. TEL per gallon	100.0+	99.0

* California straight-run gasoline.

V. MOTOR FUEL FROM COAL

A. General

Coal as a source of motor fuel is available in any quantity desired. It is estimated that the earth contains over 7,400 billion tons of coal, which can be converted into 1,850 billion tons of gasoline by hydrogenation. The coal can be converted into motor fuel by carbonization and hydrogenation. The carbonization process produces hydrocarbon gases, benzene, toluene, and xylenes, which are used as motor fuel. Coal is also being converted into liquid fuel by the hydrogenation process. Water gas produced from coal is being converted catalytically into gasoline. Coal or coke briquets are converted into gaseous fuels directly connected with automotive trucks and busses.

B. Benzene and other aromatics

For many years aromatic hydrocarbons, particularly benzene, have been added to motor fuels to improve their antiknock qualities. The volume of benzene used for this purpose in the United States during 1936 was 106,554,000 gallons or 0.5 per cent of the total gasoline produced (73).

Benzene is used also as a blending agent for aircraft fuel. However, owing to its relatively high freezing point (42°F.), usually less than 20 per cent may be used. Toluene, the xylenes, and ethylbenzene have lower freezing points than benzene and consequently offer greater possibilities as suitable blending agents for aircraft fuels. Toluene appears to offer the best possibilities, but has been discounted because of its high cost and its potential use as war material. It may be prepared in large quantities from coal, petroleum oils, and refinery and natural gases[2] (62).

Benzene, toluene, and xylenes are produced primarily from the high-temperature carbonization of coal and the cracking of gas oil to produce illuminating gas. The products derived from these processes are gases, liquids, and solids. The gas either is scrubbed with oil, such as creosote or gas oil, or is contacted with activated carbon to recover the benzene, toluene, and xylenes present, while the tar is distilled for its light-oil content. The impurities present in the light oil, such as free sulfur, hydrogen sulfide, carbon disulfide, thiophene, phenols, and nitrogen bases, are removed before the oil is used as motor fuel. The "crude benzol" fraction is treated with caustic soda and sulfuric acid and then distilled to the desired product.

It must be recognized that benzene, toluene, and xylenes are not used as motor fuel in the pure state, but as mixtures with olefins, paraffins, and naphthenes. Lichte (54) reports a "benzole" product as having a boiling range of 78°–165°C. (172°–329°F.) and containing 71.8 per cent of aromatic hydrocarbons, 15.5 per cent of unsaturates, 6.6 per cent of naphthenes, and 6.6 per cent of paraffins.

An American specification for "benzol" motor fuel is as follows: initial boiling point, 76°–82°C. (169°–180°F.); less than 60 per cent distilled

TABLE 61

Octane ratings and physical properties of various pure aromatic hydrocarbons

PROPERTIES	BENZENE	TOLUENE	XYLENES			ETHYL-BENZENE
			Ortho	Meta	Para	
Boiling point (81):						
°C	80.2	110.8	144.2	139.3	138.4	136.2
°F	176.4	231.4	291.6	282.7	281.1	277.1
Gravity at 60°F. (81):						
Specific	0.884	0.872	0.880	0.868	0.865	0.871
°A.P.I.	28.5	30.8	29.3	31.5	32.1	31.0
Refractive index at 60°F. (81)	1.5044	1.4999	1.5071	1.4956	1.4986	1.496
Freezing point (81):						
°C	5.5	−95.0	−25.0	−47.4	13.4	−94.9
°F	41.9	−139.0	−13.0	−53.3	57.1	−138.8
Latent heat of vaporization, B.t.u. per pound	166.5	155.9		149.2		146.0
Heat of combustion:						
Low value, B.t.u. per pound	17,428	17,480		17,599		18,497
High value, B.t.u. per pound	18,160	18,307		18,497		18,497
Low value heat of combustion plus latent heat of vaporization, B.t.u. per gallon	128,967	127,684		129,739		128,474
Octane No.:						
C.F.R. motor method:						
Straight	100+ (Isoöctane + 0.5 cc. TEL per gallon)	100+ (Isoöctane + 0.2 cc. TEL per gallon)		100+ (Isoöctane + 0.2 cc. TEL per gallon)		96.0
Blended 50 per cent with 70-octane straight-run gasoline:*	80.0	81.5		84.0		85.5
+ 1 cc. TEL per gallon	85.0	87.0		88.0		89.5
+ 2 cc. TEL per gallon	87.5	90.0		90.5		92.0
+ 3 cc. TEL per gallon	89.0	92.0		92.0		93.0
+ 4 cc. TEL per gallon	89.5	93.5		93.5		94.0

Army method:						
Straight	88.0	100+ (Isoöctane + 0.5 cc. TEL per gallon)		100+ (Isoöctane + 2.8 cc. TEL per gallon)		96.0
Blended 50 per cent with 70-octane straight-run gasoline:*	80.5	83.5		85.5		85.5
+ 1 cc. TEL per gallon	85.5	90.0		91.5		90.0
+ 2 cc. TEL per gallon	88.0	93.0		94.0		92.5
+ 3 cc. TEL per gallon	89.5	95.0		96.0		94.0
+ 4 cc. TEL per gallon	90.0	96.0		97.5		95.0

* California straight-run gasoline.

at 100°C. (212°F.); less than 90 per cent distilled at 120°C. (248°F.); end point, 170°C. (338°F.).

The octane ratings and properties of pure benzene, toluene, xylene (ortho, meta, para), and ethylbenzene are given in table 61. Figure 21 shows these hydrocarbons blended with a 70-octane straight-run gasoline, with and without the addition of tetraethyl lead. The blending value of benzene as compared with UOP catalytic polymer gasoline, when blended in various proportions with a 44-octane straight-run gasoline, has already been illustrated in figure 15.

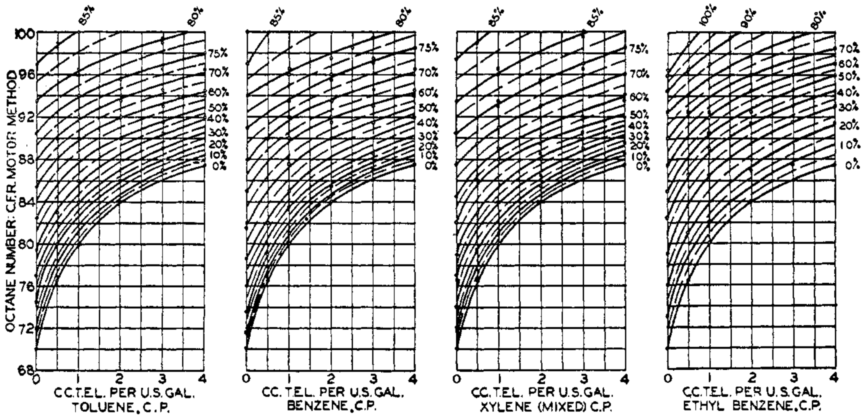

FIG. 21. Benzene, toluene, xylene, and ethylbenzene blended with 70-octane straight-run gasoline and tetraethyl lead.

TABLE 62

Octane ratings of several aromatic hydrocarbons (46)

HYDROCARBONS	OCTANE NO. BY C.F.R. MOTOR METHOD BLENDED WITH 70-OCTANE STRAIGHT-RUN GASOLINE* PLUS TEL PER GALLON			
	Straight	0 cc.	1 cc.	3 cc.
o-Xylene	100+	79	82	84
m-Xylene	100+	83	89	92
p-Xylene	100+	83	89	92
Isopropylbenzene		87		98
n-Butylbenzene		82		91
tert-Butylbenzene		88		97
sec-Butylbenzene		78		90

* Blend of reference fuels C-9 and A-4.

Antiknock data for a number of other aromatic hydrocarbons are given in table 62.

C. Hydrogenation

The hydrogenation of coal, oil, and carbon monoxide to produce motor fuel is in commercial operation in, or is projected for, Germany, England, France, Italy, Japan, and Australia. In the United States two hydrogenation units are in operation using oil, primarily to produce oil products other than gasoline. It is estimated that a total of about 2,775,000 tons of oil will be produced yearly when all the operating hydrogenation units and those under design and construction are completed (65). A list of hydrogenation units is given in table 63.

TABLE 63

Hydrogenation units in various parts of the world (65)

COUNTRY AND PLANT	RAW MATERIALS USED	THOUSAND TONS OIL PER YEAR
Germany:		
Luena	Brown coal	350–400
Bohlen-Magdeburg	Brown coal tar	300
Scholven	Bituminous coal	150
Plants not specified	Carbon monoxide (water gas from coke)	750
Great Britain:		
Billingham	Bituminous coal	112
Italy:		
Bari	Heavy oils	120–150
Livorno, Leghorn	Raw materials not given	120–150
Florence	Raw materials not given	120
France:		
Société des Produits Chimiques Courierres	Carbon monoxide	25
Japan:		
South Manchurian Railway	Coal	20
Chosen Coal Industry Co.	Coal	50
Several plants	Carbon monoxide (water gas from coke)	80
United States:		4000–6000 barrels per day capacity
Baton Rouge, Louisiana	Petroleum oils	600
Bayway, New Jersey	Petroleum oils	600

1. Coal

In the hydrogenation of coal (38), the yield of motor fuel is about 60 per cent by weight, with octane ratings ranging from 71 to 73; additional properties of the fuel are given in table 64.

In the hydrogenation of coal to motor fuel the first beneficial stage is to clean the coal of mineral matter, which is accomplished as shown in figure 22, by floating the raw coal upon a suspension of sand and water (38, 40).

It has been found that injection of hydrogen chloride or hydrogen chloride-forming compounds during the hydrogenation of coal improves the reaction itself and the operating results by neutralizing the residual coal ash. Although hydrogen chloride is highly corrosive, this factor is overcome by pumping in an alkaline paste.

The hydrogen used in the commercial unit at Billingham, England, is produced from coke and steam and hydrocarbon gases produced from the hydrogenation process. A flow chart of this stage of operation is shown in figure 23.

TABLE 64

Properties of hydrogenated motor fuel from coal (38)

Gravity at 60°F.:		
Specific	0.740–0.745	
°A.P.I	59.5–58.6	
Distillation characteristics:	*°C.*	*°F.*
Initial boiling point	35	95
20 per cent	70	158
40 per cent	100	212
75 per cent	140	284
90 per cent	158	316
End point	170	338
Residue, per cent	1.0	
Loss, per cent	1.0	
Reid vapor pressure, lb. per square inch at 100°F	9	
Octane No., C.F.R. motor method	71–73	
Color, °Saybolt	+25	
Odor	Marketable	
Sulfur, per cent	0.05	
Doctor test	Negative	
Corrosion	Non-corrosive	
Gum, Pyrex dish without air jet, mg. per 100 cc.	2.0	

In the flow diagrams shown in figures 24 and 25, the process of hydrogenation may be applied to coal and oil mixtures, low- and high-temperature coal-tar mixtures, or to heavy oils from low- and high-temperature carbonization of coal, for the production of motor fuel. When coal is used, it is first mixed with heavy oils to form a paste which is pumped into the apparatus. Oil is produced when coal is in contact with hydrogen gas, at a pressure of about 250 atm. and a temperature of 450°C. (842°F.), in the presence of organic tin catalysts. The hydrogenation process takes place in three stages. The first stage hydrogenates the coal paste, producing

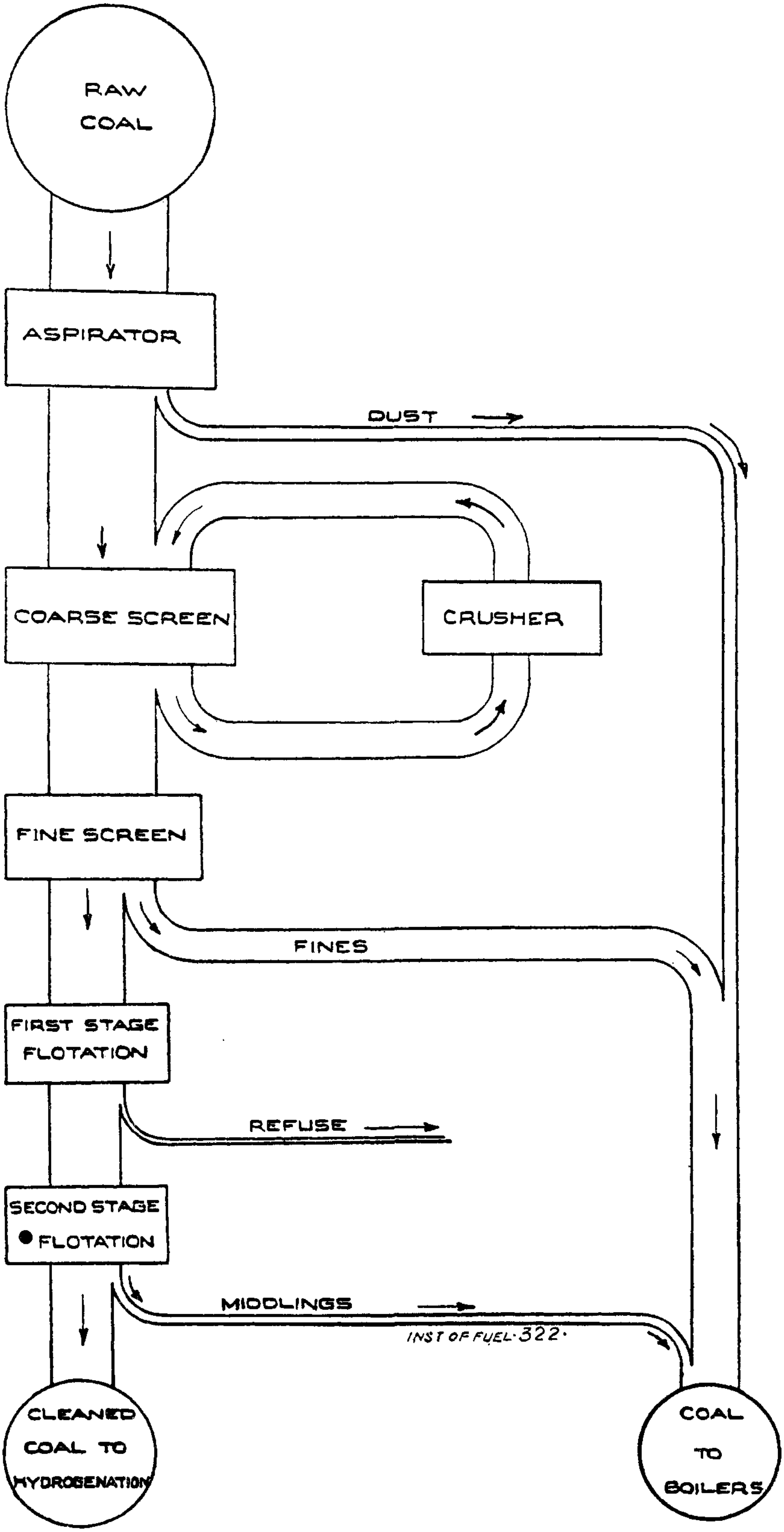

Fig. 22. Diagram of method used for cleaning coal prior to hydrogenation

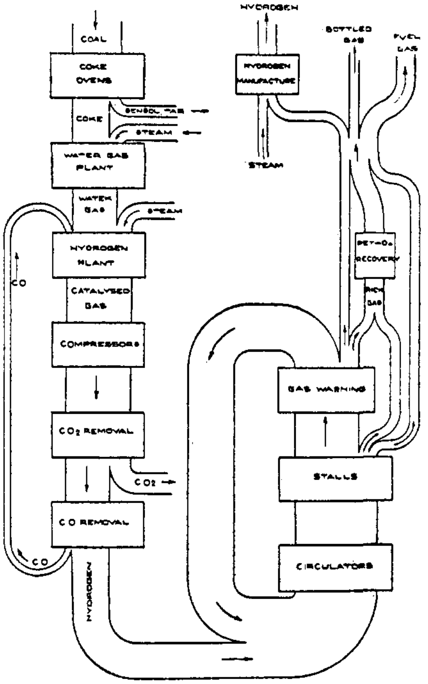

Fig. 23. Flow diagram of hydrogen production and treatment of hydrogenation plant gases

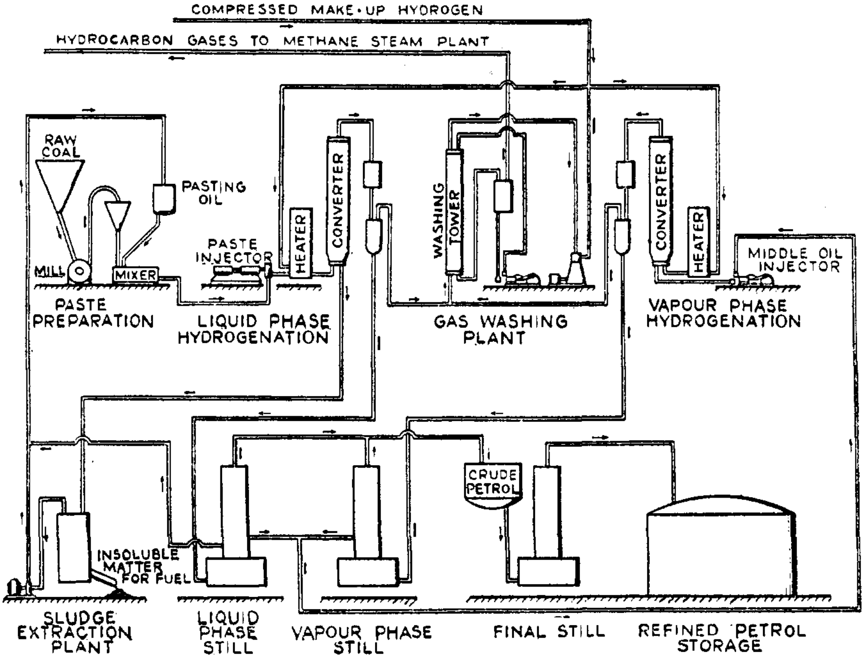

Fig. 24. Flow diagram for hydrogenation of coal

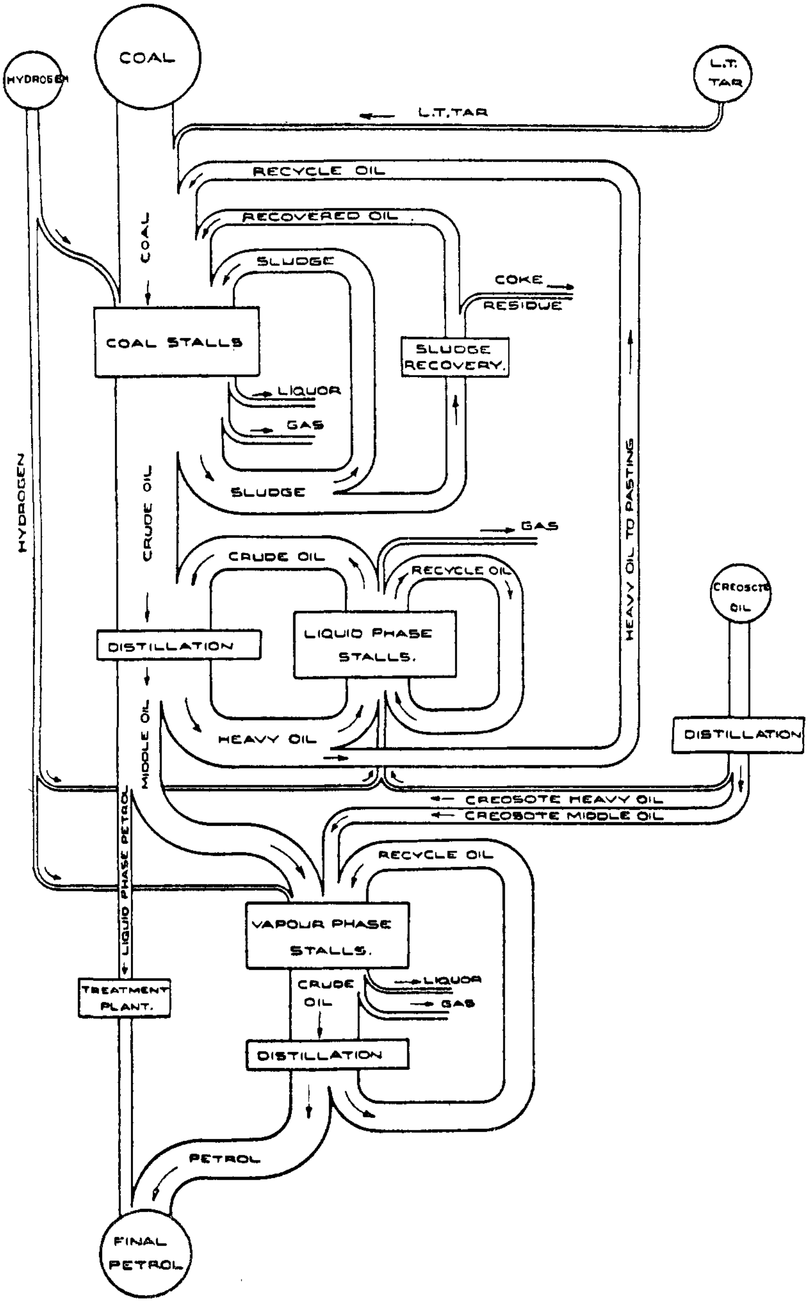

FIG. 25. Flow diagram of Billingham plant for hydrogenation of coal, creosote oil, and low-temperature tar.

an oil, which is fractionated into motor fuel and middle and heavy oils. The heavy oil is hydrogenated in the liquid phase to motor fuel, while the middle oil is hydrogenated in the vapor phase to gasoline. The motor fuel produced is then refined to a finished product of 71 to 73 octane number. In this process, four tons of coal are required to produce one ton of gasoline.

The Billingham coal–oil hydrogenation plant (38) to produce 150,000 tons or 1,070,000 barrels of gasoline a year cost 5,500,000 pounds or about $27,000,000. It is stated that this is substantially more than would be required for an entirely new plant of similar output (38). Nearly 4000 tons of coal per day, as shown below, are required to operate this plant:

	Tons of coal per year
Coal consumption for the manufacture of 100,000 tons per year of gasoline from coal and 50,000 tons a year of gasoline from creosote oil and low-temperature tar (including coal actually hydrogenated together with all that is used for hydrogen manufacture and power production)	600,000
For purposes other than the manufacture of gasoline	750,000
Total	1,350,000

The ratio of four tons of coal to one ton of gasoline produced can be maintained in a new plant (even if coal is used without creosote or low-temperature tar), owing to the improved methods of hydrogen manufacture which would be employed (38).

When petroleum oils are hydrogenated, the principles involved are similar to those of the coal–oil mixture operation. The two oil hydrogenation units in operation in the United States are not used primarily to produce motor fuel, but to produce special oils such as solvents and lubricants.

An interesting comparison of the results obtained by cracking and by hydrogenation are shown in tables 65 and 66.

2. Carbon monoxide from coal or coke

The Fischer–Tropsch process for converting water gas into hydrocarbon oil, called Kogasin (named from *kohle* + *gas* + *benzine*), is in commercial use in Germany and France.

This process utilizes a mixture of hydrogen and carbon monoxide with cobalt, iron, or nickel as catalysts (without alkali) at a temperature of 200°C. (392°F.) and atmospheric pressure (30). In the presence of strong alkali the polymerization continues until solid paraffins rather than liquids are produced (32). The theoretical yield of liquid hydrocarbons (31) is 185 g. per cubic meter of gas containing 29.5 per cent carbon monoxide and 60 per cent hydrogen. A conversion of this water-gas mixture into

TABLE 65

Comparison of gasolines obtained by cracking and hydrogenation (40)

Hydrogenation results given are typical of low-temperature operations

	NAPHTHA BOTTOMS		MID-CONTINENT GAS OIL	
Feed stock:				
Gravity, °A.P.I.	30.8		33.4	
Aniline point, °F.	110		156	
50 per cent distillation point, °F.	447		540	
Hydrogen content, per cent	12.0		13.8	
	CRACKING	HYDROGENATION	CRACKING	HYDROGENATION
Products:				
Gasoline yield, per cent	41.0	109.5	57.0	108.5
Tar yield, per cent	49.5	None	29.5	None
Gasoline octane No.*	78.5	64.0	69.6	54.0

* Series 30 engine; research method.

TABLE 66

Comparison of gasolines obtained by cracking and hydrogenation (40)

	WEST TEXAS CYCLE GAS OIL				
Feed stock:					
Gravity, °A.P.I.	30.3				
Distillation characteristics:					
Initial boiling point, °F.	400				
Per cent at 460°F.	56.0				
End point, °F.	612				
Sulfur, per cent	0.192				
Aniline point, °F.	102				
	CRACKING	HYDROGENATION			
Products:					
Gasoline yield, per cent	40.2	94.5	89.6	94.8	92.0
Gravity, °A.P.I.	51.0	39.8	38.6	47.8	58.4
Distillation characteristics:					
Initial boiling point, °F.	104	110	98	98	96
Per cent at 212°F.	25.0	13.5	16.0	25.0	33.5
Per cent at 284°F.	46.0	25.0	28.5	42.0	72.0
Per cent at 356°F.			45.0	67.0	
Per cent at 374°F.		76.0	50.5	53.0	76.0
Per cent at 400°F.		88.0	70.5	71.0	
End point, °F.	436	436	436	403	330
Octane No.*	79.0	82.2	85.0	82.76	
Gas formation, per cent	13.0	19.0	20.4	18.8	19.5
Sulfur, per cent		0.005	0.005	0.006	0.022
For formation, per cent	21.9	0.0	0.0	0.0	0.0
Cycle gas oil, per cent	24.9	0.0	0.0	0.0	0.0

* Series 30 engine; research method.

81.6 per cent of hydrocarbons may be obtained from a two-stage operation at 184°–190°C. (363°–374°F.) using a cobalt–copper–thorium–kieselguhr catalyst. Water gas, containing 42 per cent carbon monoxide and 48 per cent hydrogen, gave a yield of 160 cc. of oil per cubic meter of water gas, using a nickel–manganese–aluminum oxide catalyst (1). On the basis of 40 lb. of coke required to produce 1000 cu. ft. of water gas (4), this is equivalent to 56 U. S. gallons of liquid hydrocarbons per short ton of coke.

Kogasin is principally a mixture of straight-chain or slightly branched-chain saturated and unsaturated hydrocarbons (51) containing: gasoline, 30°–220°C. (86°–428°F.); Diesel oil, 220°–350°C. (428°–662°F.); and wax. The gasoline fraction is water-white and sulfur-free. Fatty acids are present in small quantities (52) and olefins to over 50 per cent (72).

The nature of the hydrocarbons in Kogasin depends upon the catalyst and water-gas mixture used, cobalt producing more unsaturated oils than nickel (29). The olefin content of Kogasin from various sources is as follows:

SOURCE OF GASES	OLEFINS IN KOGASIN GASOLINE PER CENT BY VOLUME	
	Nickel catalyst	Cobalt catalyst
Water gas ($CO:H_2 = 1:1$)	35	55
Mixed gas ($CO:H_2 = 1:2$)	16	35
Cracked gas ($CO:H_2 = 1:3$)	5	12

The water gas used for catalytic conversion to hydrocarbons is derived commercially from the reaction of steam upon coke or gases such as methane. A relatively high degree of purity of water gas is required, owing to the poisoning effect upon the catalyst of hydrogen sulfide and organic sulfur compounds. A water gas derived from coke and steam, having the composition of 6 per cent carbon dioxide, 40 per cent carbon monoxide, 50 per cent hydrogen, and 4 per cent nitrogen, methane, and oxygen, was reported by Martin as a commercial gas for catalytic conversion to hydrocarbons (57).

The flow chart of the process is shown in figure 26, where the water gas from coke and steam passes to a gas holder and then to purifiers to remove hydrogen sulfide, carbon disulfide, mercaptans, etc. The purified water gas passes on to the catalytic reaction chamber where conversion to gaseous, liquid, and solid hydrocarbons takes place at a temperature of about 190°C. (374°F.) and atmospheric pressure. The reaction is exothermic and heat must be abstracted. The heat of reaction is 600 cal. per cubic meter of water gas. The control of the temperature may be carried out according to Studien and Verwertungs (69) by circulating water, steam, or oil under pressure through a nest of tubes surrounded by the catalyst bed. The hydrocarbon products leaving the catalytic chamber pass into a tower counterflow to a stream of cooling water. The liquefied hydrocarbons and water are separated in a tank. The hydrocarbon gases from the water cooling system are absorbed in activated carbon, steam distilled, and the gasoline recovered. The propane and butane produced are condensed to liquids. The Kogasin oil is then passed to a pipe still and fractionating unit, where it is separated into gasoline, kerosene, Diesel oil, and paraffin oil. The gasoline recovered from the activated carbon passes to a distillation unit to be separated into a light and heavy fraction.

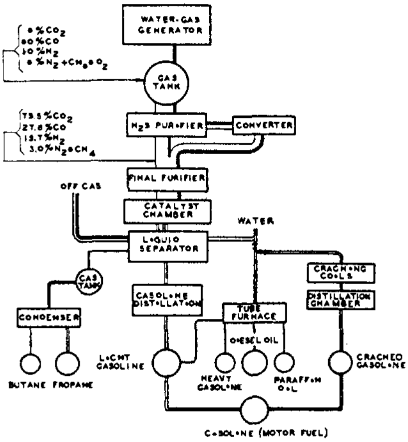

FIG. 26. Flow diagram of catalytic water-gas reaction

TABLE 67

Primary products of catalytic water-gas reaction (*57*)

PRODUCTS	YIELD	OLEFINS PRESENT
	per cent	*per cent*
Propane, propene, butane, and butene	8	50–55
Gasoline distilling to 392°F	60	30–35
Gas oil	22	5–6
Paraffin wax, melting point, 68°–212°F	10	

The Kogasin oil or fractions thereof may be pumped to a cracking unit where it is converted to motor fuel of high octane rating and blended with the gasoline produced from the distillation of the primary oil.

The process of converting water gas catalytically into hydrocarbons at atmospheric pressure yields primary products (57) such as given in table 67.

TABLE 68

Properties of gasolines produced by the catalytic water-gas reaction (57)

Light primary products:

BOILING POINT OF FRACTIONS	OCTANE NO.	GRAVITY AT 60°F.	
		Specific	°A.P.I.
°F.			
262	66	0.670	79.7
270	64	0.670	79.7
284	62	0.673	78.7
297	58	0.675	78.1

Gasoline produced:

BOILING RANGE OF RAW MATERIALS	BOILING RANGE OF GASOLINE PRODUCED	OCTANE NO.	GRAVITY AT 60°F.	
			Specific	°A.P.I.
°F.	*°F.*			
297–662	Up to 383	65–70	0.730	62.3
132–662	Up to 383	65–70	0.725	63.7

TABLE 69

Yields and quality of light gasoline fractions from Kogasin oil

Yields, volume per cent of Kogasin oil:										
Gasoline	20.0		33.8		43.5		56.3		68.4	
Bottoms	79.8		66.0		56.0		43.5		31.4	
Recovery	99.8		99.8		99.7		99.8		99.8	
Loss	0.2		0.2		0.3		0.2		0.2	
Properties of light gasolines:										
Gravity at 60°F.:										
°A.P.I	84.1		79.3		75.8		72.4		69.6	
Specific	0.6563		0.6713		0.6826		0.6940		0.7036	
Octane No., C.F.R. motor method	73		66		58		49		40	
	°F.	*°C.*	*°F.*	*°C.*	*°F.*	*°C.*	*°F.*	*°C.*	*°F.*	*°C.*
Distillation characteristics:										
Initial boiling point	84	29	104	40	110	43	97	36	107	42
10 per cent	108	42	124	51	138	59	140	60	155	68
20 per cent	114	46	134	57	150	66	160	71	176	80
50 per cent	129	54	162	72	190	88	214	101	247	119
90 per cent	172	78	210	99	252	122	298	148	359	182
End point	209	98	250	121	299	148	350	177	396	202
Per cent over	96.5		98.0		98.0		98.0		98.0	
Per cent bottoms	1.0		1.5		1.0		1.5		1.0	
Per cent loss	2.5		0.5		1.0		0.5		1.0	

The gasolines of varying boiling ranges have the properties (57) shown in table 68.

TABLE 70

Properties of Kogasin oil

Gravity at 60°F.:		
°A.P.I.	63.0	
Specific	0.7275	
Sulfur, per cent	0.01	
Octane No., C.F.R. motor method	20	
	°F.	*°C.*
100-cc. Engler distillation:		
Initial boiling point	113	45
5 per cent	148	64
10 per cent	170	77
20 per cent	205	96
30 per cent	245	118
40 per cent	286	141
50 per cent	323	162
60 per cent	368	187
70 per cent	420	216
80 per cent	487	253
90 per cent	657	347
End point	702	372
Per cent over	97.5	
Per cent bottoms	1.0	
Per cent loss	1.5	

TABLE 71

Properties of gas oil from Kogasin

PROPERTIES	GAS OIL	DIESEL OIL MIXTURE
Color		Brown
Specific gravity, d^{20°	0.835–0.91	0.866
Cold test, °C	0°	
Viscosity (Engler)	2.6	1.28
Flash point	65°	68°
Boiling point	Lowest 60 per cent at 300°C.	320° (End)
Alkali-soluble	4 per cent	2 per cent
Water-soluble	0.5 per cent	0
Cetane No.	Over 100	56

The data relating to gasolines (28) from Kogasin oil and their properties are shown in table 69.

A distillate analysis of the Kogasin as produced is shown in table 70.

Diesel oils are also produced from the hydrogenation of carbon monoxide by the Fischer–Tropsch process. It is reported (73) that a gas oil derived from Kogasin oil has a cetane number of over 100. The data concerning this gas oil and a mixture with a low cetane number are shown in table 71.

The motor fuel derivable from Kogasin by means of distilling a light fraction therefrom, reforming the naphtha cut, cracking the residue (bottoms), and catalytically polymerizing the olefins present in the cracked gases and blending the four fractions, will yield 84.3 per cent of a 66-octane product. The results (28) are shown in table 72.

TABLE 72

Products produced from Kogasin oil (28)

YIELD OF PRODUCTS FROM KOGASIN OIL	PER CENT BY VOLUME
Light gasoline	29.1
Reformed gasoline from naphtha	26.8
Cracked gasoline from bottoms	22.6
Polymer gasoline	5.8
Total gasoline	84.3
Octane No. of blends of all gasolines	66

3. Gas from coal carbonization

Hydrocarbon gas produced by the carbonization of coal in coke ovens is used not only for household and industrial heating, but also as motor fuel in trucks and busses in Germany.

There are now over forty filling stations (68) in Germany where city gas (methane–ethane) is available in high-pressure holders, at pressures up to 5000 lb., for recharging containers on trucks and busses just as gasoline tanks are filled at ordinary gasoline stations. Special types of containers have been developed for this use. Weights and dimensions of two sizes to withstand approximately 3000 lb. pressure most generally used are as follows:

CAPACITY	DIAMETER	LENGTH	WEIGHT
gallons	*inches*		*lb.*
14.0	9	5 ft. 0.25 in.	138
20.9	13	5 ft. 8 in.	300

A schematic drawing of a typical truck installation is shown in figure 27. In this case, the cost of converting a medium-sized truck to operate on city gas is stated to be from $40 to $60.

4. Gasified coal and coke directly in motor vehicle

There are two types of gas-driven motors used in Germany at the present time (39). The simplest type is that using the compressed city gas (methane–ethane) in high-pressure holders. The second type is that which carries its own gas generator as an integral part of the motor vehicle. The use of this gas generator is less expensive than the liquid fuels produced in the country and its continued use is expected, since wood, brown coal, coal, and coke are native fuels.

Coal or coke is used for producing fuel gases for motors the principle of which is Diesel operation. With a few alterations the Diesel engine may be converted into a high-compression gas-burning machine which is suitable because of heavy construction. Gas conduits and carburetors on the modern installations, as well as improved mixing equipment, have raised the power economy. Some of the problems necessary to work out in connection with these motors have been the removal of dust from the gas generator and an adequate gas-cooling system which removes as much water as possible from the gas before it passes to the combustion chamber. These problems have been met by the use of centrifuges and filters. A flow diagram of the mechanism is shown in figure 28.

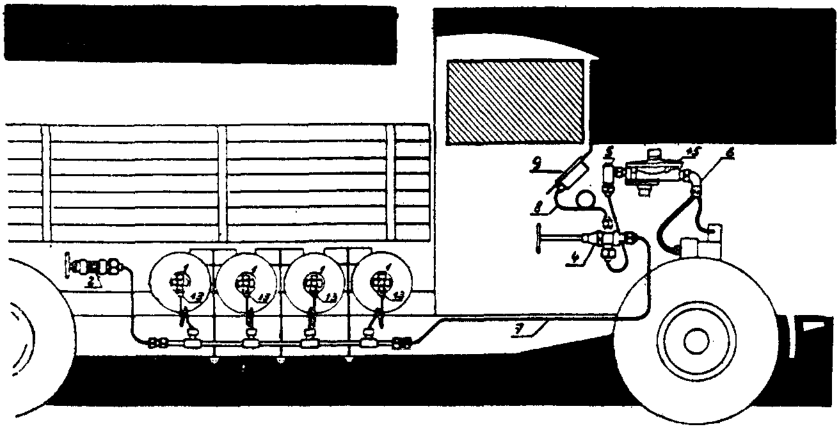

Fig. 27. Schematic drawing of typical truck installation for burning methane–ethane gas mixture

The fuels used in the gas generator have presented difficulties in operation, owing to the types of fuels themselves which are available for use. Peat and brown coal must be coked, owing to their high water content. These fuels have been used in France, England, and Belgium. Peat coke was found to be an especially suitable fuel, owing to its hardness, high energy content and low ash, with very little sulfur present. It is nearly like charcoal in its characteristics and may be used in charcoal generators.

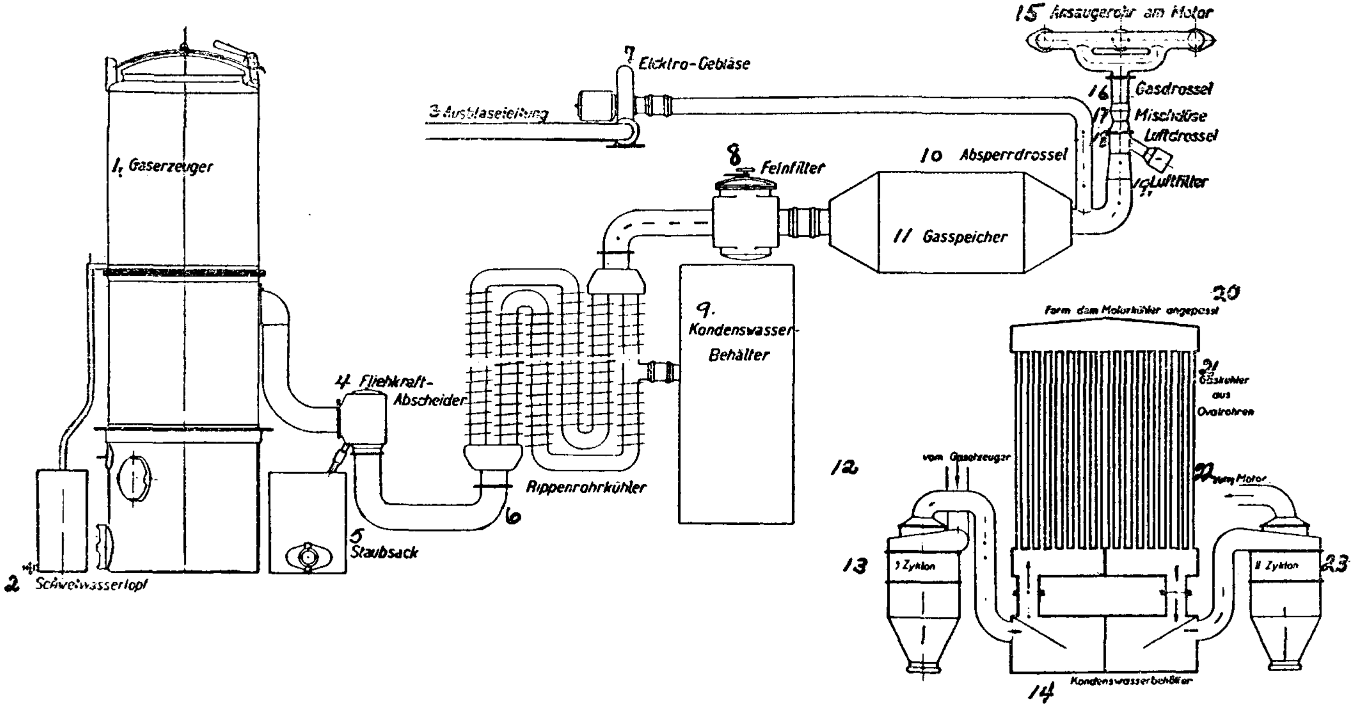

FIG. 28. Flow diagram of a Diesel engine converted into a high-compression gas-burning machine

1. Gas generator
2. Cold-water tank
3. Exhaust pipe
4. Centrifugal separator
5. Dust filter
6. Radiator cooler
7. Electric bellows
8. Fine filter
9. Condensed-water tank
10. Cut-off throttle
11. Gas accumulator
12. From gas generator
13. Cyclone separator I
14. Condensed-water tank
15. Suction tube from motor
16. Gas throttle
17. Mixing nozzle
18. Air throttle
19. Air filter
20. Form of motor cooler, fitted oval tube
21. Gas cooler
22. To motor
23. Cyclone separator II

The limitations found in using coal for gaseous motor fuel are due to its low reactivity. As a comparison, the gasification temperatures of each of the solid fuels are given:

Charcoal	900°-1000°C.
Brown coal	1100°-1200°C.
Coal	Above 1400°C.

The tendency in France, Belgium, and England has been to raise the temperature in the firebox as high as possible. In Germany, lower temperatures and gas velocities have been used and the resulting poorer gas quality is improved by adding steam.

The particular field of gas-producing vehicles has been heavy trucking, but they are not limited to that field alone. Italy has required all omnibusses to be operated on generator or compressor gases by the end of 1936; this type of installation has also been used in small river boats on the Rhine. Possibilities of producer gas automobiles have also been studied.

VI. MOTOR FUEL FROM OIL SHALE

The oil shale resources of the world are enormous. The shales vary widely in their oil content from a few gallons per ton to over one hundred. Commercial plants to produce oil from shale are in operation in Scotland, France, Esthonia, and Manchuria. The oil shales are subjected to high-temperature treatment in retorts. The vapors evolved are condensed and refined to marketable products such as gasoline, kerosene, gas oil, heavy oils, and waxes.

The heavy oils, which may or may not contain the kerosene and gas-oil fractions, have been cracked into gasoline. Typical oils derived from shales of France, Manchuria, Australia, Esthonia, Spain, South Africa, and Sweden were subjected to high temperatures and pressure in order to convert them into high-octane gasoline. The yield of gasoline ranged from 38 to 65 per cent, depending upon the quality of the charging stock and mode of operation. The yields, quality of products, and operating conditions are shown in table 73.

VII. MOTOR FUEL FROM PLANTS AND WOOD

A. Alcohol

1. Fermentation process

Alcohol, chiefly ethyl and methyl, is used in many countries for blending with gasoline as motor fuel. Ethyl alcohol is used in greater volume than methyl. Both may be prepared by synthesis. However, most of the

TABLE 73

Shale oils

SOURCE OF CHARGING STOCK	MANCHURIAN SHALE OIL		AUSTRALIAN SHALE OIL			ESTHONIA		SPAIN BLENDED CRACKING STOCK		SOUTH AFRICA			SWEDISH SHALE OILS			FRENCH SHALE OIL	
			Bunker C	Pitch						Tor-banite	Shale oil	2 parts Torbanite and 1 part shale oil					
Charging stock analysis:																	
Gravity, °A.P.I.	26.6		26.2			18.2		21.7		26.0	21.6	24.6	14.6			25.4	
Engler distillation:																	
Initial boiling point, °F	430		308			164		384		212	225	202	230			292	
10 per cent	508		415			293		448		322	339	325	339			389	
20 per cent	556		502			366		485		410	410	400	413			456	
50 per cent	669		660			548		579		613	607	606	625			610	
90 per cent	756		758			746		734			743					738	
End point	760+							744								760	
Per cent at 400°F	0.0		8.5			24.0		1.0		19.0	18.5	20.0				11.5	
Per cent at 572°F	24.5		30.0			47.0		24.0		43.0	43.0	44.5	41.0			43.0	
Sulfur, per cent by weight	0.60		0.59			0.63		0.5				0.65	1.81			0.60	
B. S. &. W., per cent	2.0 Wax		Trace			0.4		0.3					0.1				
Cold test, °F	95					Below zero							Below zero			55	
Viscosity (S.F.) sec. at 122°F	10		16 at 77°F.			15		14					15 at 77°F.			13 at 77°F.	
	Resid-uum	*Non-residuum*						*Resid-uum*	*Coke*		356° End point *Gasoline*	392° End point *Gasoline*				*Resid-uum*	*Coking*
Throughput and yields:																	
Per cent of charge:																	
Gasoline	38.2	64.8	44.2	52.2	47.5	43.7	37.5	41.4	60.0		47.8	43.8	42.8	42.1	41.8	49.3	69.1
Residuum	56.0	0.0	37.9	34.8	34.5	49.9	60.1	45.5			47.8	55.5	55.2	51.0	45.9	45.6	None
Coke	5.8	35.2	1.2								4.4	0.7					
Gas and loss			17.9	13.0	18.0	6.4	2.4						2.0	6.9	12.3	5.1	30.9
Barrels per day on stream:																	
Coke, lb. per barrel of charging stock		84.0							95.3								
Gas, cu. ft. per barrel of charge	290	697	605	655	613	290	176	544	932		304	134	196	269	399	374	638

Analysis of products:																	
Gasoline:																	
Gravity, °A.P.I.	59.2	57.9	63.9	62.5	61.9	52.7	53.0	60.0	60.2				46.4	45.9	46.9	55.2	56.1
A.S.T.M. distillation:											58.7	53.3					
Initial boiling point, °F	95	96	99	90	98	102	103	98	105		108	108	106	110	108	94	99
10 per cent	143	147	136	135	137	165	171	148	147		162	182	218	215	201	157	163
20 per cent	178	184	162	166	167	198	205	178	171		198	219	252	258	245	201	205
50 per cent	270	279	220	230	231	270	270	240	236		257	290	307	307	299	294	292
90 per cent	362	377	320	328	326	361	352	330	330		321	372	364	366	362	368	367
End point, °F	391	393	368	377	370	393	389	388	388		355	393	402	403	392	391	381
Octane No., A.S.T.M., motor method	61	60	75	75	74	73	73	67	66		63	61				66	67
Octane No., research method	64	63	68					74	74		71	68	89	89	90	72	72
Gum, copper dish, mg. per 100 cc.	452	604			47	1163	503				205	192	276	182	256	217	844
Residuum:																	
Gravity, °A.P.I.	13.7		5.4	2.1	0.3	0.5	4.2	6.4			6.9	9.7	2.4	−0.1	−2.7	7.1	
Viscosity (S.F.) sec. at 122°F	32		242	842	1984	274	78	112			62	37	95	197	2400+	40	
B. S. & W., per cent	2.0 Wax		0.6	0.6	1.2	0.4	0.4	3.9			6.2	3.0	0.1	0.2	0.3	0.2	
Sediment by extraction, per cent	0.33																
Flash, Cleveland open cup, °F	270		290		280	210	225	250			260	240	235	200	220	280	
Flash, Pensky-Martens, °F	170		150		180	190	205	182			210	205	195	190	200	185	
Cold test, °F	85		40		70	+65	30	60			50	40	25	60	70	15	
Operating conditions:																	
Heater outlet, temperature, °F	925					920	910				875	875	900	900	900		
Light-oil heater outlet, temperature, °F			900(A) Furnace														
Heavy-oil heater outlet, temperature, °F			950(B) Furnace														
Reaction chamber, pressure, lb. per square inch	250		200			350	348				200	200	200	200	200		

ethyl alcohol is derived from the fermentation of agricultural products such as beet sugar, molasses, potatoes, and corn.

TABLE 74

Alcohol consumed as motor fuel in foreign countries (27, 71) for the year 1934

COUNTRY	METRIC TONS CONSUMED
Austria	4,400
Czechoslovakia	42,477
France	293,600
Germany	180,000
Hungary	8,731
Italy	5,000
Jugoslavia	6,592
Latvia	6,457
Poland	5,941
Spain	12,000
Sweden	12,250
Total	577,448

TABLE 75

Octane blending value of ethyl alcohol (27, 61)

FUEL	OCTANE NO., C.F.R. MOTOR METHOD		
	Of blend	Increase due to alcohol	Blending value of alcohol
Gasoline No. 1:			
Straight	63.0		
5 per cent alcohol	67.5	4.5	152
10 per cent alcohol	72.0	9.0	153
15 per cent alcohol	76.5	13.5	153
Gasoline No. 2:			
Straight	61.0		
5 per cent alcohol	66.4	5.4	168
10 per cent alcohol	70.4	9.4	155
15 per cent alcohol	75.0	14.0	154

In the United States during 1936 the production of ethyl alcohol amounted to about 100 million gallons, of which 10 per cent was produced from cracked gases.

The volumes of alcohol consumed in eleven foreign countries (27, 71) for the year 1934 are shown in table 74.

The advantages of ethyl and methyl alcohol when compared to most gasolines are high octane rating and blending value and high latent heat of vaporization. The octane blending value of alcohol depends upon the percentage of alcohol in the blend and upon the octane rating and chemical composition of the base fuel. Typical data (27, 61) are given in table 75.

The high latent heat of vaporization of alcohol is particularly valuable in reducing manifold temperature. This permits a greater weight of charge to be taken into the cylinders, thereby increasing the power output of the engine.

TABLE 76

Physical properties of various alcohols

PROPERTIES	ALCOHOLS							
	Methyl	Ethyl	Butyl	*sec*-Butyl	Isobutyl	*tert*-Butyl	*n*-Amyl	*tert*-Amyl
Boiling point:								
°C	64.5	78.5	117.7	99.5	107.3	82.8	137.9	101.8
°F	148.1	173.3	243.9	211.1	225.1	181.0	280.2	215.2
Gravity at 60°F.:								
Specific	0.795	0.792	0.813	0.811	0.805	0.792	0.820	0.812
°A.P.I	46.4	47.1	42.5	43.0	44.3	47.1	41.1	42.7
Refractive index at 68°F	1.329	1.361	1.399	1.397	1.396	1.387	1.414	1.406
Freezing point:								
°F	−144.0	−179.1	−129.6	−128.2	−162.4	+77.9	−109.3	10.6
°C	−97.8	−117.3	−89.8	−89.0	−108.0	+25.5	−78.5	−11.9
Latent heat of vaporization, B.t.u. per pound	511.7	367.7	254.3	241.9	248.5	234.8	216.3	190.5
Heat of combustion:								
Low value, B.t.u. per pound	8,352	11,523	14,269	14,269	14,269	14,037	14,969	14,775
High value, B.t.u. per pound	9,542	12,765	15,555	15,555	15,555	15,323	16,267	16,073
Low value of heat of combustion plus latent heat of vaporization, B.t.u. per gallon	58,678	78,260	98,323	97,948	97,268	94,194	103,716	101,167

Even with these advantages, ethyl and methyl alcohol show a marked decrease in efficiency as measured by fuel consumption. This is due to the relatively low heating value of these low molecular weight alcohols (27, 55). Compared to gasoline as 100 per cent (21,140 B.t.u. per pound, gross heating value), the values of methyl and ethyl alcohol are 45 and 66 per cent, respectively. The heating values of the higher alcohols are somewhat higher; tertiary butyl and tertiary amyl alcohols are about 73 and

76 per cent, respectively, with normal butyl and amyl alcohols at 74 and 77 per cent, respectively. Thus the tertiary alcohols, or alcohols containing at least four carbon atoms, have a heat value approximately 75 per cent that of gasoline (see table 76).

In addition to the heating value advantage of the tertiary alcohols, they have greater susceptibility to tetraethyl lead than the lower alcohols (67), as indicated in tables 77 and 78.

It will be noted that, although a number of alcohols effect an appreciable increase in octane number, their tetraethyl lead susceptibilities vary over a wide range. The tertiary butyl and tertiary amyl alcohols show a lead susceptibility equal to or better than that of the straight-run base fuel.

TABLE 77

Octane blending values and tetraethyl lead susceptibilities of various alcohols (67)

FUEL	OCTANE NO.*		OCTANE NO. INCREASE DUE TO	
	Nonleaded	With 1 cc. of TEL per gallon	Alcohol	Tetraethyl lead†
Straight-run base gasoline	68.2	77.7		9.5
30 per cent alcohol in base gasoline:				
Ethyl	77.5	82.1	9.3	4.6
Butyl	69.9	71.0	1.7	1.1
sec-Butyl	76.0	79.8	7.8	3.8
Isobutyl	75.2	77.1	7.0	1.9
tert-Butyl	77.5	87.2	9.3	9.7
n-Amyl	66.0	68.8	2.2	2.8
tert-Amyl	75.2	86.6	7.0	11.4

* Determined on series 30 engine at 900 R.P.M. and 375°F. jacket temperature. This is substantially equivalent to the C.F.R. motor method.

† Tetraethyl lead susceptibility, i.e., increase in octane rating due to the addition of 1 cc. of TEL per gallon.

Road and laboratory tests conducted with a 10 per cent ethyl alcohol–gasoline blend have indicated a fuel consumption at least 4 per cent higher than with gasoline alone. The results of "official" road tests (27, 63) conducted by the American Automobile Association, the National Bureau of Standards, the National Automobile Chamber of Commerce, the American Petroleum Institute, and others are shown in table 79.

C.F.R. dynamometer tests (27) with gasoline and a 10 per cent alcohol–gasoline blend of equal octane rating gave results as shown in table 80.

Aside from this increased fuel consumption with alcohol–gasoline blends, the use of alcohol introduces certain operating difficulties such as starting, acceleration, and vapor lock (27, 12). The lower or water-soluble alcohols

TABLE 78

FUEL	OCTANE NOS. OF FUELS CONTAINING VARIOUS ALCOHOLS							
	Methyl†	Ethyl	*n*-Butyl	Isobutyl	*sec*-Butyl	*tert*-Butyl	Amyl	*tert*-Amyl
C.F.R. motor method:								
Straight	98.0	99.5	87.5	87.5		100+ (isoöctane + 3 cc. TEL per gallon)	77.5	100+ (isoöctane + 0.2 cc. TEL per gallon)
Blended 50 per cent with 70-octane straight-run gasoline	89.0	88.5	81.5	82.0	85.0	83.5	72.5	84.5
+ 1 cc. TEL per gallon	91.5	89.0	84.5	84.5	87.0	91.0	79.0	89.5
+ 2 cc. TEL per gallon	93.5	89.0	86.5	86.0	88.5	95.0	82.0	92.0
+ 3 cc. TEL per gallon	95.0	89.5	87.5	87.0	89.0	97.0	83.5	92.5
+ 4 cc. TEL per gallon	96.0	89.5	88.5	87.0	89.5	99.5	84.5	93.0
Army method:								
Straight						100+ (isoöctane + 3 cc. TEL per gallon)		100+ (isoöctane + 0.5 cc. TEL per gallon)
Blended 50 per cent with 70-octane straight-run gasoline*	85.5	86.5	80.5	84.5		85.5	72.5	85.0
+ 1 cc. TEL per gallon	87.5	87.0	83.5	86.0		93.0	78.0	91.0
+ 2 cc. TEL per gallon	88.0	87.0	85.0	87.5		97.0	80.5	93.5
+ 3 cc. TEL per gallon	88.0	87.5	85.5	88.5		99.0	82.5	94.0
+ 4 cc. TEL per gallon	88.0	87.5	85.5	89.0		100.0+	84.0	

* California straight-run gasoline.

† Blend contained 40 per cent of methyl and 10 per cent of ethyl alcohol.

are difficult to blend with gasoline unless they are substantially anhydrous or unless a binder such as benzene, toluene, or one of the higher alcohols (*n*-propyl, isopropyl, *n*-butyl, isobutyl, or *tert*-butyl) is used.

Alcohol blends can also cause considerable corrosion and solvent troubles with certain materials commonly used in the construction of motor car and aircraft engines, such as aluminum alloys used in fuel tanks, carburetor float-bowl castings, etc.

As to the future use of alcohol-gasoline blends as aircraft fuel, opinions differ. According to F. R. Banks (7): "Alcohol fuels have not justified themselves as constituents of aviation gasoline, even in those countries where the respective governments have fully supported their use by subsidy or monopoly.

TABLE 79

Increase in fuel consumption over gasoline when using a 10 per cent alcohol-gasoline blend (27, 63)

MAKE OF CAR	PER CENT INCREASE IN FUEL CONSUMPTION WITH A 10 PER CENT ALCOHOL-GASOLINE BLEND	
	By weight	By volume
1933 Chrysler "6" sedan	4.87	4.13
1933 Oldsmobile "6" sedan	3.81	3.07
1932 Ford "V-8" coupe	10.20	9.51
1932 Rockne "8" convertible sedan	3.75	3.06
Average	5.66	4.94

TABLE 80

Comparative C.F.R. dynamometer tests with 10 per cent alcohol-gasoline blend and gasoline alone (27)

FUEL	BRAKE HORSEPOWER	POUNDS OF FUEL PER BRAKE HORSEPOWER HOUR	PER CENT INCREASE IN CONSUMPTION
Gasoline	2.19	0.75	
10 per cent alcohol-gasoline blend	2.19	0.78	4.0

"It is a feature that they do not deteriorate in the ordinary sense of the word, but they can and do preignite violently when subjected to certain operating conditions of the engine.

"The principal advantage of the alcohols, ethyl and methyl, is that they have a high latent heat of vaporization. Even when blended with gasoline in amounts up to about 20 per cent, this feature is particularly valuable in reducing the "boost" or supercharge temperature; thus allowing a greater charge weight to enter the cylinders of the engine, thereby improving its power output.

"Therefore, although it would be unsafe to dogmatize regarding the use of these alcohols as constituents of aviation fuel, they appear to be very critical to operating conditions, and their employment is uneconomical.

"The higher alcohols, such as isopropyl, have been investigated, but do not at the moment appear to offer any particular advantage."

According to A. R. Ogston (64): "Certain of the higher alcohols, such as isopropyl, are likely to prove very valuable anti-detonants.

"The utility of alcohol as an anti-detonant arises from both its very high spontaneous ignition temperature and its exceptionally high latent heat of vaporization; the latter property would largely overcome the difficulties which arise from the high boost temperatures created by superchargers and may even obviate the necessity for intercoolers. Certain alcohols are also very efficient de-icers of the induction system (in aircraft engines).

"One of the most suitable methods of utilizing the properties of alcohol will be by supplying it to the carburetor from a separate tank installed in the aircraft, rather than use of a ready mixed blend fed from the main fuel tank. The separate alcohol feed could be controlled by the pilot, and probably need be used only when the engine has to be operated in excess of say 70 per cent maximum power or during icing conditions."

B. Gasified wood

Wood, as far as history advises us, was the first source of heat and power that man used. The early settlers of North America over 300 years ago began using wood from the 900 million acres of forest land for their energy supplies. Wood is still an important source of energy, as it represents over 7 per cent of the total which was used in the United States during the year 1934 (25). The consumption of wood for the production of energy is far greater in the rest of the world than in the United States. It is interesting to note that in some countries which have relatively large sources of oil the steam locomotives are still being fired with wood. In the case of Rumania this is due to the desire of the government to keep the wood choppers employed. Countries which have no oil deposits are utilizing other fuel resources to some extent, such as coal, oil shale, and wood.

In Germany, Italy, and France wood or the product of its carbonization is converted into gas which is used as fuel in motor busses and trucks. Italy has several hundred such motor vehicles in operation. Many motor busses or trucks propelled by the gasification of wood cannot be distinguished in outward appearance from cars using gasoline or Diesel engines. Gasoline itself can be produced from the tar obtained from the distillation of wood, the yield being about 40 gallons per ton. By cracking, 26 per cent of motor fuel, 21 per cent of Diesel oil, and the balance fuel gas and coke can be produced. Illustrations of the application of wood-burning motors (39) are shown in figures 29, 30, and 31.

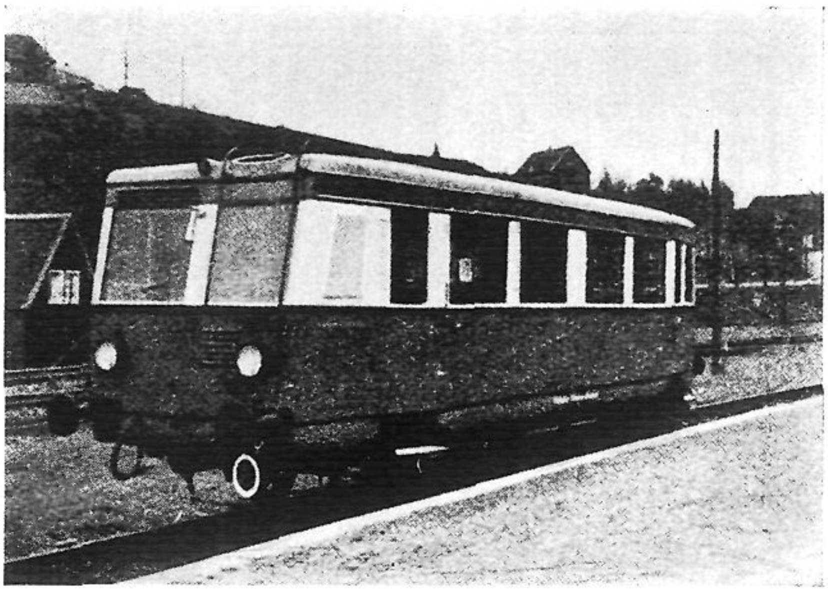

FIG. 29. The wood-gas generator set up in a motor bus

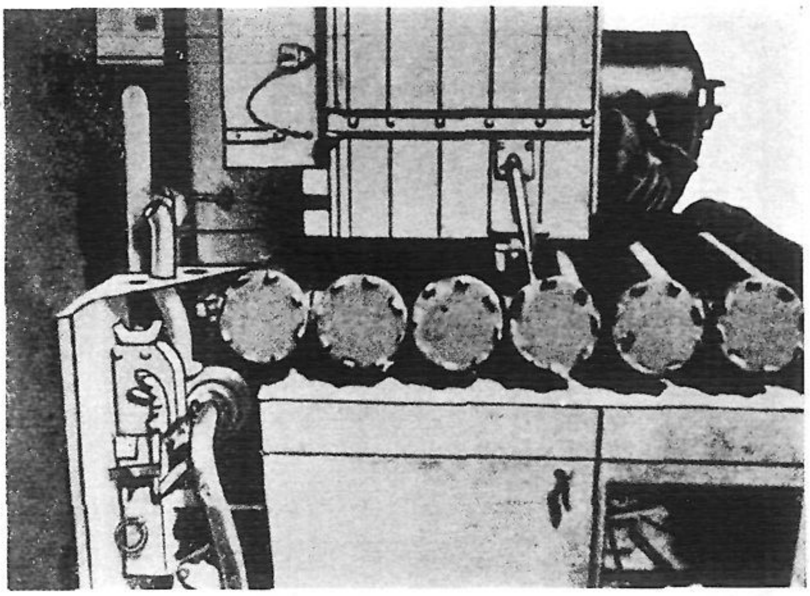

FIG. 30. Gas purifiers of the wood burner with baffle plates

VIII. COMPOUNDS ADDED TO IMPROVE OCTANE AND CETANE NUMBERS OF FUELS

A. Tetraethyl lead for gasoline

An effective method for improving the antiknock quality of motor fuels is the use of tetraethyl lead. For Q-grade and premium-grade Ethyl gasolines, it is added in the form of "Q" Ethyl fluid; for leaded aircraft fuels, in the form of "IT" Ethyl fluid. The composition of each varies from time to time as researches prove certain mixtures more desirable. At present (21), the respective compositions are shown in table 81.

The antiknock ingredient of Ethyl fluid is tetraethyl lead. It is important, therefore, that when reference is made to the addition of Ethyl fluid to a gasoline, the quantity of tetraethyl lead only should be specified, as for example, 1 cc. TEL per gallon.

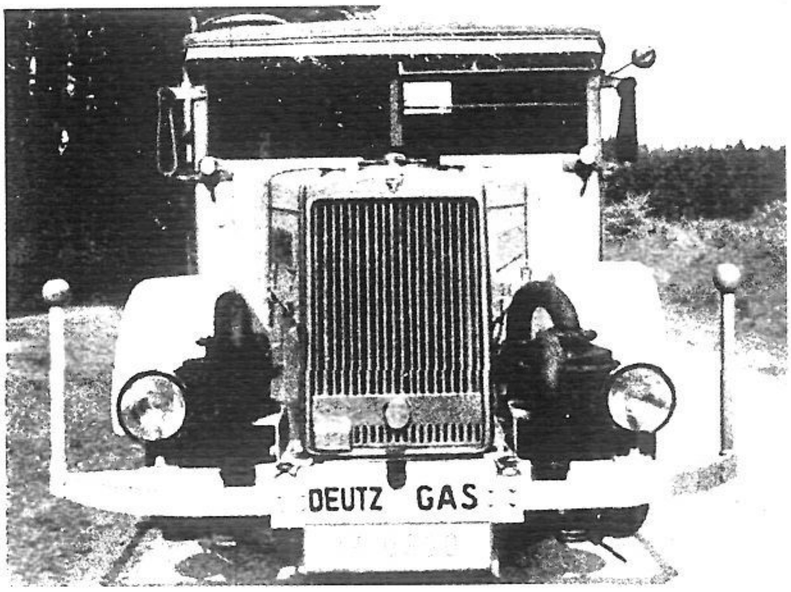

FIG. 31. Wood-gas purifier on a Humboldt-Dietz motor

TABLE 81

Composition of Ethyl fluid (21)

COMPOSITION, PER CENT BY VOLUME	"Q" FLUID	"IT" FLUID
Tetraethyl lead	63.30	61.42
Ethylene dibromide	25.75	35.68
Ethylene dichloride	8.78	
Kerosene	1.10	1.75
Dye	0.13	0.25
Impurities	0.94	0.90
Total	100.00	100.00

The response of a fuel to the addition of tetraethyl lead varies according to the chemical composition of the fuel and to the amount of impurities, such as free sulfur or sulfur compounds, present in the fuel. The variation in tetraethyl lead response for commercial base gasolines is illustrated in figure 32. The effect of chemical composition on lead response is shown in tables 82 and 83.

TABLE 82

Effect of chemical composition on tetraethyl lead susceptibility (46)

C.P. FUELS BLENDED 50 PER CENT WITH 70-OCTANE STRAIGHT-RUN GASOLINE*	OCTANE NO., C.F.R. MOTOR METHOD			
	Of blend	With TEL per gallon		
		1 cc.	2 cc.	3 cc.
Isoöctane (2,2,4-trimethylpentane)	84	92	96	98
Isopropyl ether	86	94	99	100+
Isopentane	81	90	93	96
Benzene	82	88	90	92
Toluene	82	88	90	92
o-Xylene	79	82		84
m-Xylene	83	89		92
p-Xylene	83	89		92
Ethylbenzene	85	90	93	95
n-Butylbenzene	82			91
tert-Butylbenzene	88			97
sec-Butylbenzene	78			90
Isopropylbenzene	87			98
Mesitylene	85			96
Cyclohexane (not blended)	77	78	79	80
Hexane (not blended)	62	74	79	81

* Blend of reference fuels C-10 and A-4.

TABLE 83

Tetraethyl lead susceptibility of solvent-extracted gasolines (extracts) (66)

BLENDS OF 63.4-OCTANE MID-CONTINENT STRAIGHT-RUN GASOLINE WITH:	OCTANE NO., C.F.R. MOTOR METHOD		
	Of blend	With TEL per gallon	
		1 cc.	2 cc.
25 per cent of 91-octane extract	70.0	77.0	80.1
50 per cent of 91-octane extract	77.5	81.7	83.6
50 per cent of 98-octane extract	79.0	82.8	84.7
50 per cent of 100-octane isoöctane	79.7	84.9	

Interesting data on lead susceptibility for a number of gasolines from different sources (41) are given in table 84.

A number of years ago it was discovered that the tetraethyl lead susceptibility of certain distillates was substantially reduced after treatment with acid or plumbite (41). This is illustrated in figure 33 for a West

Texas straight-run gasoline tested under the following conditions: A, untreated; B, Doctor-treated; C, acid-treated, plant scale; D, acid-treated, laboratory scale; E, sample D, redistilled; F, sample D, neutralized before removing sludge.

It will be noted that, in all except the untreated sample (sample A), there was a lag in the action of the tetraethyl lead. This lag amounted to over 5 cc. per gallon in the case of the laboratory treated sample (D), showing "that apparently some compound had been formed in the gasoline which probably combined with the tetraethyl lead in the gasoline, rendering it inactive. However, in all cases except F, the action of the tetraethyl lead was apparently normal after a certain concentration had been reached" (41). The increase in lead susceptibility after redistillation is "not be-

TABLE 84

Tetraethyl lead susceptibility of various gasolines (41)

GASOLINE	OCTANE NO. C.F.R. MOTOR METHOD	TEL SUSCEPTIBILITY*
Straight-run gasolines:		
Mid-Continent	46.1	1.28
West Texas	54.1	0.77
Hendricks	59.8	0.73
Yates	58.8	0.77
Texas Panhandle (3)	60.7	0.85
Okmulgee (Okla.) (3)	45.2	0.97
California	69.5	1.31
Pennsylvania (3)	50.0	0.95
Kansas (3)	44.7	0.77
Cracked gasolines:		
Okmulgee (Okla.) (3)	67.0	1.33
Mid-Continent and Texas, Doctor-treated	70.5	0.78
Kansas (3)	62.6	1.00
Texas Panhandle (3)	58.5	0.76
Natural and aviation gasolines:		
Special-cut natural, 9.7-lb. Reid vapor pressure (3)	64.1	2.00
Stabilized natural	69.3	1.81
Stabilized natural, 13.0-lb. Reid vapor pressure (3)	67.2	1.46
Natural, 10.0-lb. Reid vapor pressure (3)	60.5	1.38
Black Bayou-White Castle aviation	79.0	1.59
Smackover aviation	70.0	1.55
Gulf Coast aviation (3)	62.1	1.55
West Texas aviation	71.0	1.66

* See literature reference (41) for method determining the tetraethyl lead susceptibility values given in this column; the higher the numerical value, the greater the lead response.

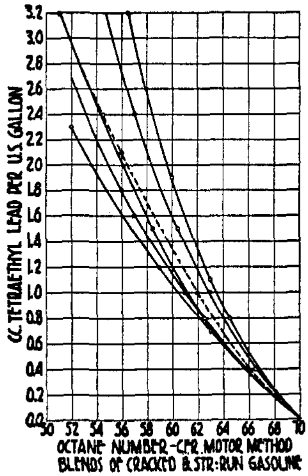

FIG. 32. Tetraethyl lead susceptibility of base stocks used for commercial gasoline

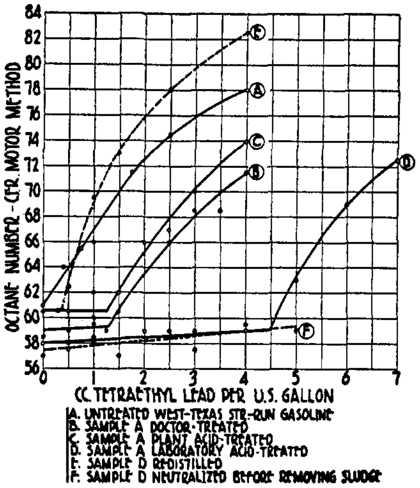

FIG. 33. Effect of treating and sweetening on tetraethyl lead susceptibility

lieved to be due to an increase in volatility, but to the removal of disulfides and other sulfur compounds" (41). In this connection, a sample of an apparently similar West Texas straight-run gasoline was doped with 0.35 per cent of dimethyl sulfate, with the following results (41):

WEST TEXAS STRAIGHT-RUN GASOLINE	OCTANE NO., C.F.R. MOTOR METHOD	TEL SUSCEPTIBILITY
Undoped	60.0	0.83
+ 0.35 per cent dimethyl sulfate	59.2	0.73

Although the gasoline doped with dimethyl sulfate did not show the above-mentioned lag in the action of the tetraethyl lead, both the octane rating and the lead susceptibility were reduced.

Other investigators (10) have also found the presence of sulfur compounds to affect tetraethyl lead susceptibility adversely, as shown in table 85.

Additional data on the effect of sulfur compounds on tetraethyl lead susceptibility are given in table 86.

Tetraethyl lead susceptibility has a distinct bearing on the refiner's problem of "reforming" versus "leading." Both methods are used to raise a low-octane straight-run gasoline to a marketable product. In certain cases it has been found more economical to use a combination of both methods. A recent report (36) on the subject summarizes the magnitude of the differential revenue derived for optimum reforming and leading versus no reforming, as follows (using gasoline at 6 cents per gallon and fuel oil at 60 cents per barrel):

TABLE 85

Effect of sulfur compounds on tetraethyl lead susceptibility (10)

SAMPLE	OCTANE NO., C.F.R. MOTOR METHOD		
	Nonleaded	With TEL per gallon	
		1 cc.	3 cc.
Venezuelan straight-run gasoline:	64.4	73.8	82.3
+ 0.1 per cent sulfur as EtSH	63.6	68.7	74.3
+ 0.1 per cent sulfur as Et_2S	64.6	70.5	76.6
+ 0.1 per cent sulfur as Et_2S_2	64.0	68.8	73.4
+ 0.1 per cent sulfur as Et_2S_3	62.0	66.6	73.0
Iranian gasoline:	55.3	66.3	75.6
+ 0.1 per cent sulfur as EtSH	55.0	61.7	68.2
+ 0.1 per cent sulfur as Et_2S	55.4	62.8	69.8
+ 0.1 per cent sulfur as Et_2S_2	55.4	61.5	68.2
+ 0.1 per cent sulfur as Et_2S_3	52.5	59.7	66.3
Heptane–octane:	55.3	68.3	77.8
+ 0.1 per cent sulfur as Et_2S_2	55.3	61.4	67.3

OCTANE ELEVATION	OCTANE TEST METHOD	REFORMER CHARGE BARRELS PER DAY	INCREASED REVENUE PER YEAR
70	Motor	5,000	$365,000
73	Motor	5,000	425,000
73	Research	5,000	470,000
73	L-3	5,000	515,000

B. Nitrites, nitrates, etc., for Diesel fuels

The demand for Diesel oils of high cetane number is increasing. Highly selected stocks of paraffinic characteristics are in demand. To increase the cetane number many compounds have been proposed to accomplish this purpose such as: (*1*) alkyl nitrates, e.g., ethyl, isopropyl, and butyl nitrates; (*2*) alkyl nitrites, e.g., ethyl, isopropyl, butyl, and amyl nitrites;

TABLE 86

Effect of sulfur compounds on tetraethyl lead susceptibility of reference fuels

SAMPLE	OCTANE NO., C.F.R. MOTOR METHOD	
	Nonleaded	With 2 cc. TEL per gallon
Reference fuel A-3	44	58
+ free sulfur	41	54
+ ethyl sulfate	43	47
+ ethyl sulfide		56
+ diethyl sulfide	42	
+ ethyl mercaptan	42	
+ butyl sulfide	43	56
+ diphenyl sulfide	44	57
+ isoamyl sulfide		56
+ diphenyl disulfide	43	53
+ isoamyl disulfide	42	
+ isoamyl mercaptan	43	53
+ thiophene	44	57
+ thiophenol		54

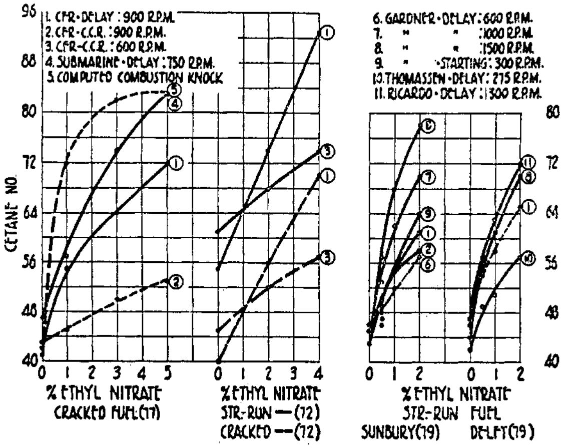

FIG. 34. Effectiveness of ethyl nitrate for improving ignition quality of Diesel fuels

(*3*) nitro compounds, e.g., nitrobenzene, nitrotoluene, nitroxylol, nitroglycerol, and nitropentane; (*4*) oxidizing agents, e.g., nitrogen dioxide, percarbonates; (*5*) peroxides, e.g., cyclodiacetone, cyclotriacetone, acetyl, tetralin, tetrahydronaphthalene, and benzoyl peroxide; (*6*) aliphatic hydrocarbons, e.g., allylene, diacetylene, and butadiene; (*7*) bromine compounds, e.g., benzyl, butyl, and butylene bromides and isobutylene dibromide; (*8*) oxygenated copper compounds, e.g., copper oleate and copper stearate; (*9*) hydroxylamines, diketones, etc. Few data are to be found as to the relative values of these dopes. The effectiveness of ethyl nitrate (47, 37, 11), acetyl peroxide (11), and tetralin peroxide (60) is illustrated in figures 34 and 35.

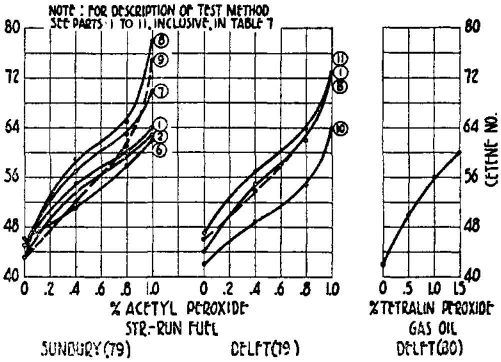

FIG. 35. Effectiveness of acetyl peroxide and tetralin peroxide for improving ignition quality of Diesel fuels

IX. 100-OCTANE AIRCRAFT FUELS

The general procedure for producing 100-octane aircraft fuels is to blend commercial isoöctane with an aviation straight-run gasoline and add up to 3.0 cc. of tetraethyl lead per gallon. In many cases, 5 to 15 per cent of isopentane is used to supply the front-end volatility which isoöctane lacks.

Toluene, benzene, ethylbenzene, isopropyl ether, mixed ethers, alcohols, ketones, and other high-octane blending agents may be used in the preparation of 100-octane aircraft fuels, provided the finished product meets specifications. The advantages and disadvantages of these various fuels have been discussed to a limited extent in the respective sections of this paper.

The high vapor pressure (20.4 lb. per square inch) of isopentane limits to less than 15 per cent the amount of isopentane that can be used and still meet the 7- and 7.5-lb. Reid vapor pressure specifications which are now in force in the United States.

Because of the high freezing point (approx. 42°F.) of benzene, usually not more than 10 per cent can be blended and still meet the conventional freezing-point specification of −76°F.

The relatively low heating value of isopropyl ether (19 per cent lower than isoöctane on a weight basis) and its reaction to the acid-heat test tend to prevent its use to any great extent under existing specifications.

TABLE 87

Various combinations of high-octane blending agents and straight-run base gasolines to produce 100-octane fuel, with and without addition of tetraethyl lead

	C.F.R. MOTOR METHOD PER CENT HIGH-OCTANE FUEL FOR VARIOUS ADDITIONS OF TEL PER GALLON				
	0 cc.	1 cc.	2 cc.	3 cc.	4 cc
(1) Per cent blended with 74-octane straight-run gasoline* (46):					
Isoöctane (100 octane No.)	100	69	58	51	43
Isoöctane (95 octane No.)	100+ 0.4 cc.	84	70	60	50
Isoöctane (90 octane No.)		100	85	72	62
(2) Per cent blended with 70-octane straight-run gasoline* (46):					
Isoöctane (100 octane No.)	100	74	63	55	48
Isoöctane (95 octane No.)	100+ 0.4 cc.	85	72	63	55
Isoöctane (90 octane No.)		100	88	81	72
Isopropyl ether (98 octane No.)	100+ 0.1 cc.	68	56	42	34
Isopentane (90 octane No.)	100+ 0.7 cc.	88	74	62	52
Benzene (100+ octane No.)	86	84	82	81	76
Toluene (100+ octane No.)	87	85	83	81	77
Xylene (mixed) (100+ octane No.)	86	84	82	80	77
Ethylbenzene (96 octane No.)	100+ 0.7 cc.	97	88	82	76

* Blend of straight-run reference fuels C-9 and A-4.

It is apparent, therefore, that isoöctane is destined to remain one of the principal blending agents in the manufacture of high-octane aircraft fuels. This is because of its high octane rating, good susceptibility to tetraethyl lead, high heating value, good stability without the use of inhibitors, and its ability to "stand up" best under the widest variety of engine operating conditions.

The dollar value of high-octane fuel when used in the high-compression aircraft engine has been discussed quite completely in the literature (46, 7, 13, 50, 8, 19). The following statements presented by D. P. Barnard (8) illustrate the economic value of octane ratings: *(1)* Depending upon design and operating conditions, the revenue-earning power of 1 gallon of gasoline may be increased from 2 to 5 cents per octane number improvement. *(2)* If the octane number increase involves a decrease in energy content, the apparent improvement must be discounted by about two octane numbers for each per cent reduction in heat content below that of gasoline. *(3)* It is evident that the earning power of octane increase is so great that within practical limits its cost cannot influence the trend toward higher octane numbers to any appreciable extent.

In tables 87 and 88, data are given showing various combinations of fuels and tetraethyl lead which rate 100 octane number by the C.F.R. motor method. In a number of cases octane ratings by the Army method are included. Most of the data have already been presented in the respective sections of this paper.

TABLE 88

Various combinations of high-octane blending agents, straight-run base gasolines, and tetraethyl lead to produce 100-octane fuel

	PER CENT HIGH-OCTANE FUEL FOR VARIOUS ADDITIONS OF TEL PER GALLON			
	Motor method		Army method	
	2 cc.	3 cc.	2 cc.	3 cc.
1. Components (67):				
Per cent straight-run (74-octane No.)		38 37 37		
Per cent isoöctane (100-octane No.)		62 53 46		
Per cent isopentane (90-octane No.)		0 10 17		
2. Components:				
Per cent straight-run (70-octane No.)*	25 24	32 31	26 25	35 34
Per cent isoöctane (95-octane No.)	75 66	68 59	74 65	65 56
Per cent isopentane (90-octane No.)	0 10	0 10	0 10	0 10

* California straight-run gasoline.

X. SUMMARY

Motor fuels of any desired octane rating are available from many sources in ample quantities for years to come. The fuel requirements for internal-combustion engine use can be met at any time and in any quantity.

The sources of motor fuels are petroleum, natural gas, coal, oil shale, plants and wood. Compounds added to motor fuels play their part in obtaining greater efficiencies.

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