THE MANUFACTURE OF ALCOHOLS FROM HYDROCARBONS, WITH PARTICULAR REFERENCE TO PETROLEUM AS A RAW MATERIAL

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One of the few instances of the use of petroleum as a chemical raw material is the conversion of the simpler unsaturated hydrocarbons into alcohols. Curiously enough, this has been a very recent development although the essential elements in the chemistry of the processes now industrially employed have long been known; oil gas has been a familiar product of various industrial processes for many years. The present industrial development apparently arises from an effort to utilize the uncondensed gases from cracking processes for the manufacture of gasoline and has been greatly stimulated by the new demand for alcohols and their acetates for the manufacture of lacquers or varnishes in which esters of cellulose and certain varnish gums are incorporated.[1]

One might suppose that the formation of alcohols from the simpler olefins by the action of sulfuric acid and hydrolysis of the resulting alkyl sulfuric esters is one of the elementary reactions of organic chemistry, long known and well understood, but in the last four years, the United States Patent Office has granted twenty odd patents dealing with particular phases of this reaction. This is not meant as a criticism of the Patent Office but to emphasize that the discovery of the optimum conditions under which a reaction may be carried out, any peculiarities of certain raw materials or mixtures or the discovery of conditions which materially affect the utility or practical operation of a process, constitute improvements which are patentable. In spite of the large amount of published scientific information,

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[1] D. B. Keyes, *J. Ind. & Eng. Chem.*, **17**, 558 (1925).

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the subject is a very live one, industrially, and the following review will show that our knowledge of the subject is far from complete. Such substances as tertiary butyl alcohol, heretofore prepared by the well known synthesis of Butlerow by the action of acetyl chloride on zinc methyl, or by the Grignard reaction, is now available as an industrial product in large quantities.

The two raw materials of interest in this connection are petroleum and the unsaturated hydrocarbons derived therefrom by cracking, and natural gas. The relative cheapness of the gaseous olefins, as produced from petroleum in the form of oil gas, has heretofore not been taken advantage of, probably on account of the somewhat complex mixture of reactive hydrocarbons in oil gas and imperfect means of separating them usually employed.

TABLE 1

Per cent of ethylene and propylene in Pintsch gas made at different temperatures

TEMPERATURE	HIGHER OLEFINS	C_3H_6	C_2H_4	TOTAL OLEFINS
°C.	*per cent*	*per cent*	*per cent*	*per cent*
805–650	1.4	18.6	16.3	36.3
660–535	1.6	19.0	18.3	38.9
635–535	2.4	22.4	12.5	37.3
625–535	2.6	22.6	13.7	38.5
615–425	3.8	25.7	12.0	41.5

Thus, in the pioneer plant of Fritzsche, a large proportion of sulfuric acid was consumed in polymerizing or removing olefins other than ethylene without making or separating any products of value from these constituents.

Most of these products can be separated or reacted upon by chemical methods yielding reaction products of commercial value with good efficiency and also it is almost certain that by fractional distillation at low temperatures in the liquid air type of column that the major constituents of oil gas can be separated by this physical means in a state of purity satisfactory for commercial chemical synthesis. Some idea of the cost of these raw materials may be had from the fact that in commercial oil gas processes an average of 2300 cubic feet of gas per barrel (42 gallons) of oil used, can be obtained. The richest gas is produced at relatively low temperatures and as the yield of gas increases with higher temperatures, the per cent of ethylene propylene and higher olefins decreases, as is shown in the following tables. The Pintsch gas described in table 1 was purified from benzene and gasoline vapors by compressing to about 200 pounds and cooling to 15° to 20°; as the results show, it still contained some of the higher olefins, butylene and amylene.

The temperatures given are those at the beginning and end of the gas making period. The analyses were made by absorbing the higher olefins in 70 per cent sulfuric acid, the propylene in concentrated sulfuric acid, specific gravity 1.84 at room temperature and the ethylene in bromine water.[2]

TABLE 2

Composition of oil gas

TEMPERATURE	PRESSURE PER SQUARE INCH	ETHYLENE	PROPYLENE	HIGHER OLEFINS	TOTAL OLEFINS
°C.	*pounds*	*per cent*	*per cent*	*per cent*	*per cent*
600	57	19.3	28.0	3.2	50.5
650	72	19.0	28.4	4.2	51.6
700	83	17.7	23.9	3.5	45.1
730	95	17.5	20.0	3.1	40.6

TABLE 3

Per cent of oil gasified in Hall cracking unit

TEMPERATURE	OIL GASIFIED	ETHYLENE AND PROPYLENE
°C.	*per cent*	*per cent*
605	17.7	47.9
625	26.6	46.1
645	37.6	44.9
665	40.0	43.7
685	40.8 (?)	42.6
705	48.7	39.5
725	66.6	38.5

The composition of oil gas made in tubes maintained at definite temperatures in an industrial size apparatus of the Hall type is shown in table 2.

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[2] B. T. Brooks, *Chem. & Met. Eng.*, **22**, 630 (1920).

The relative amount of oil gasified is shown in table 3, the gas not being scrubbed or compressed for the removal of condensable light oil vapors.

As shown by M. C. Whitaker and C. M. Alexander[3] the composition of oil gas does not correspond to the equilibrium composition for the various temperatures at which it is produced, being much richer in illuminants than when the gas is subjected to these temperatures for any length of time. They suggest caution in dealing with such complex mixtures, in making deductions from one or two equilibria expressions.

The literature is very vague with respect to the composition of oil gas, the practice having been merely to condense only those tars and oils which would readily condense and only in the Pintsch gas practice has it been customary to remove light oil vapors from the gas (by compression and cooling). Consequently, the figures given for "illuminants" probably include 5 to 6 per cent of olefins other than ethylene and propylene. Nevertheless, the data for the volume of gas and its composition given by various authors is in good agreement, considering the various types of apparatus used and the many variables. The volumes of gas obtainable from various gas oils, having reference particularly to temperatures yielding gas rich in olefins, are given in table 4.

J. E. Zanetti[4] has shown that a mixture of propane and butane, separated from natural gas, gives a maximum percentage of about 38 per cent of olefins at about 750°.

If, from the above data, we take a yield of 900 cubic feet of olefins per barrel of gas oil and the proportion of ethylene, propylene and higher olefins, given first in table 1, we should have as an average yield 460 cubic feet of ethylene and 403 cubic feet of propylene. This is equivalent to 9.4 gallons of 95 per cent ethyl alcohol and 10.3 gallons of anhydrous isopropyl alcohol. This means that if the absorption of these two olefins, and their conversion to the corresponding alcohols is 80 per cent efficient, 15.7 gallons of the two alcohols are obtainable from one barrel

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[3] *J. Ind. & Eng. Chem.*, **7**, 484 (1915).

[4] *J. Ind. & Eng. Chem.*, **8**, 674 (1916).

of gas oil. In addition to these two alcohols, the butylenes and amylenes also produced yield about one gallon of secondary butyl and amyl alcohols and one-half gallon of tertiary butyl and amyl alcohols. This takes no account of the value of the gasoline fraction which may be produced and it has been shown that such gasoline, made by the so-called vapor phase method of cracking gas oil, has peculiar merit as an anti-knock motor fuel; a blend of ordinary gasoline containing 25 per cent of vapor phase gasoline has an anti-knock value corresponding approximately to the gasoline treated with tetraethyl lead as recommended for motor fuel use.[5] While the proportions of

TABLE 4

Yield of gas per barrel of oil

TEMPERATURE	GAS PER 42 GALLONS OIL	OLEFINS	OLEFINS	REMARKS
°C.	*cubic feet*	*per cent*	*cubic feet*	
743	2,990	36.6	1094	Hempel*
743	2,867	33.7	966	"
743	3,136	33.5	1050	"
785	3,320	27.3	906	"
782	3,365	27.7	932	"
682	2,490	35.8	891	Ross and Leather†
760	2,968	30.1	893	Ross and Leather
700	2,520	36.5	919	V. B. Lewes‡
800	2,870	46.2	1,325	J. F. Tocher (1)§
850	3,255	43.1	1,402	J. F. Tocher (2)
650	1,887	43.6	822	M. C. Whitaker and W. F. Rittman¶
750	2,884	30.6	882	M. C. Whitaker and W. F. Rittman

* *J. Gasbel,* **1910,** 77: various commercial gas oils used in experimental apparatus.

† *J. Gas Light'g.,* **1906,** 825: Pennsylvania Gas Oil.

‡ *J. Soc. Chem. Ind.,* **1892,** 585: Russian gas oil.

§ *J. Soc. Chem. Ind.,* **1894,** 231: Tocher used a retort 36 × 6 inches. In (1) a gas oil of specific gravity 0.847 was used and in (2) a burning oil of specific gravity 0.807 was employed.

¶ *J. Ind. & Eng. Chem.,* **6,** 478 (1914).

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[5] This fact does not appear to be in harmony with the theory regarding the effect of tetra ethyl lead which assumes that the lead atoms take up the ions in the gaseous explosion wave front.

the various products of cracking vary widely with the conditions of temperature and relative rate of oil passed through the cracking tubes, the above figures should indicate that this is a promising and, until recently, neglected field of industrial research.

The relative cheapness of ethylene and propylene from this source, as raw materials for the synthesis of other products, should also be pointed out. Thus, taking the catalytic conversion of ethyl alcohol to ethylene as practically quantitative, the cost of the alcohol (at 65 cents per gallon) would be \$6.11 as compared with \$2.73 for the gas oil, for the quantity of ethylene noted above. The difficulty, as illustrated by the attempt of Fritzsche, described below, to manufacture ethyl ether from oil gas, has been to obtain ethylene free from other olefins and to obtain values from these other products of oil cracking.

The two most important methods for the manufacture of alcohols from petroleum and natural gas are the addition of the elements of water to unsaturated hydrocarbons and the chlorination of saturated hydrocarbons (or addition of hydrogen chloride to olefins) and conversion of the chlorine derivatives to the corresponding esters or alcohols. The so-called hydration of the unsaturated hydrocarbons by means of sulfuric acid appears to be much the most important and most employed.

On account of the rather widely different properties of the different olefins and alkyl halides, the variant industrial importance of the several alcohols and the questions of considerable scientific interest in connection with these materials, the different alcohols will be discussed individually.

METHANOL

This alcohol is now being manufactured by the catalytic reduction of carbon monoxide, a subject, however, outside the plan of this review. A possible industrial synthesis is found also in the conversion of methyl chloride to methanol. The chlorination of methane has engaged the attention of a good many workers[6] and is the subject of numerous patents. No

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[6] Chlorination of Natural Gas, G. W. Jones and M. H. Meighan, Bur. Mines Techn. Paper 255, (1921): Cf. also F. Martin and O. Fuchs, *Zt. Elektrochem.*, **27**, 150 (1921).

industrially successful process for the manufacture of methyl chloride from methane has as yet been developed, although the conversion of methyl chloride to methanol can be accomplished with good yields by passing the chloride over hydrated lime. Methyl chloride is, of course, much more stable than the higher alkyl chlorides; E. Szarvasy[7] showed that it is slowly hydrolyzed by heating with alkali solutions at 140° (under 20 to 24 atmospheres pressure). J. R. H. Whiston[8] states that methyl chloride and steam do not react appreciably below 270° but that the formation of methanol was almost quantitative when passed over slaked lime at 300°. R. H. McKee and S. P. Burke[9] have published further details and shown that the use of steam with the lime and methyl chloride is beneficial. They estimate that with chlorine at two cents per pound, the gross cost of methanol by this method would be 70.8 cents per gallon, which figure would be somewhat reduced if the hydrochloric acid from the original chlorination could be sold. The cost of producing methanol by the catalytic reduction of carbon monoxide is probably much below this figure.

ETHYL ALCOHOL

The relationships between ethylene, ethyl hydrogen sulfate, ethyl ether and ethyl alcohol, were pointed out by H. Hennell,[10] as long ago as 1828, who stated "thus ether may be formed from alcohol, and alcohol from ether at pleasure by throwing the hydrocarbon of these bodies into that peculiar state which it assumes when combined with sulfuric acid. We may even proceed beyond this, and form either alcohol or ether, using olefiant gas as the hydrocarbon base; for as I have shown . . . . olefiant gas, by combining with sulfuric acid, forms sulfovinic acid, and the acid so produced forms either ether or alcohol, according to circumstances which are under perfect control."

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[7] *J. Soc. Chem. Ind.*, **35**, 707 (1916): B. S. Lacy, U. S. Pat. 1, 253, 615 (1918), heats methyl chloride with milk of lime in an autoclave to temperatures above 100°.

[8] *J. Chem. Soc.*, **117**, 190 (1920).

[9] *J. Ind. & Eng. Chem.*, **15**, 682, 788 (1923).

[10] *Phil. Trans. Royal Soc.*, **1828**, 365.

M. Berthelot[11] absorbed ethylene in concentrated sulfuric acid, diluted the acid mixture with 5 to 6 volumes of water and distilled, thus obtaining a very good yield of ethyl alcohol. He also showed that by adding sodium acetate, potassium butyrate or benzoate directly to the acid solution and distilling, the corresponding ethyl ester could be obtained.[12]

The manufacture of ethyl alcohol from the ethylene in coal gas was suggested at an early date and alcohol made in this way was exhibited at the London Exhibition in 1862. An industrial attempt was made about that time in St. Quentin, France, but was soon abandoned.[13]

In an early English patent, E. A. Cotelle stated that the gas should first be purified from oil vapors and hydrogen sulfide and also that the propylene, amylene and similar hydrocarbons should be removed by scrubbing with sulfuric acid.[14] He also suggested the use of oil gas for this purpose and describes diluting the resulting acid mixture with water and distilling to obtain the alcohol.

An industrial plant for the conversion of ethylene into ethyl ether was operated by P. Fritzsche in Richmond, Va., in 1900 and 1901. Oil gas was the source of the ethylene. In his English Patent 20,225 (1896) Fritzsche claims the preliminary treatment of oil gas, coal gas and similar gases containing ethylene and other olefins, with cold concentrated sulfuric acid to absorb olefins other than ethylene, and following this by scrubbing with concentrated sulfuric acid at 100 to 140°. In another patent[15] he describes treating the gas first with acid containing 80 per cent H_2SO_4 at 70° to 80° to remove propylene

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[11] *Ann. de Chim. et de Phys.* (3), **43**, 385 (1855).

[12] C. Ellis and M. J. Cohen, U. S. Pat. 1,365,050 (1921), have patented the process adding sodium acetate to the sulfuric acid solution, containing alkyl sulfuric esters, obtained from oil gas, and distilling to get ethyl, propyl and butyl acetates: in U. S. Pat. 1,365,051 the mixture of acetates is claimed as a new composition of matter and in U. S. Pat. 1,365,049, the use of this mixture of esters as a solvent is patented.

[13] Payen, *Dinglers Polytechn. J.*, 167, 236 (1863).

[14] English Pat., 2062 (1862): Eng. Pat. 1924 (1863).

[15] German Pat. 89,598 (1897).

and butylene. The ethylene was passed through four scrubbing towers in which sulfuric acid at 100° to 120° was passed, countercurrent to the ethylene. He pointed[16] out that temperature control is necessary and that provision must be made to hold the temperature of the first scrubbing towers below 40°, and that if the acid from these preliminary scrubbers is diluted with three to four parts of water and distilled isopropyl alcohol is produced; oily polymers were also formed.

Apparently undeterred by the failure of Fritzsche's plant, which made use of oil gas containing a large percentage of ethylene, others have more recently taken up the problem and endeavored to use coal gas containing up to about 2.5 per cent of ethylene. The gas must first be well purified from hydrogen sulfide and other sulfur compounds as well as aromatic hydrocarbon vapors and all ethylene homologues.[17] E. Bury has described the work done at the plant of the Skinninggrove Iron Co.,[18] and reports that at 60° to 80° about 71 per cent of the ethylene in the gas was absorbed and that 70 per cent of the absorbed gases were recoverable as ethyl alcohol, the amount of the latter being equivalent to about 1.6 gallons of alcohol per ton of coal.

The earlier observations, with regard to the conditions for the reaction of ethylene and sulfuric acid were only qualitative, but S. G. P. Plant and N. V. Sidgwick[19] have studied the reaction of ethylene and propylene with sulfuric acid and found that at 70° the reaction with ethylene could be carried out practically to completion with 98.8 per cent of 100 per cent acid without any sign of decomposition; considerable decomposition was noted after 2.5 hours at 100°. Their results for the absorption of ethylene at 50° and 70° are given in tables 5 and 6. The formation of diethyl sulfate in substantial proportions is of

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[16] *Chemische Ind.*, **35**, 638 (1912).

[17] F. S. Sinnatt, (*Gas Journal*, **1920**, 695) prepared the dibromides of the olefins in a typical coal gas and on the basis of the fractional distillation of this mixture gives the following *relative* percentages, ethylene 84.3 per cent, propylene 11.8 per cent, butylene 2.3 per cent, amylene, etc., 1.5 per cent.

[18] *Gas Journal* (**1919**) 718.

[19] *J. Soc. Chem. Ind.*, **40**, 15T (1921).

particular interest and since it is readily separated as a heavy oil merely by diluting the acid reaction mixture, this should prove to be an excellent method for the manufacture of this valuable ethylating reagent.

C. F. Tidman[20] also states that in large scale work the best temperature for ethylene absorption by 95.4 per cent acid is 60° to 80°.

TABLE 5

Absorption of ethylene at 50°

TIME	CONCENTRATION OF H_2SO_4		
	93.1 per cent	97.6 per cent	99.3 per cent
hours			
3	1.24	1.70	2.52
9	3.63	5.49	9.38
15	6.39	10.90	21.63
26	12.51	24.49	32.01*

* This analyzed 72.7 per cent ethyl hydrogen sulfate and 22.2 per cent diethyl sulfate.

TABLE 6

Absorption of ethylene at 70°

TIME	CONCENTRATION OF H_2SO_4		
	93.1 per cent	95.8 per cent	98.8 per cent
hours			
2.5	1.36	1.28	2.75
10	6.59	8.05	17.16
15	10.59	13.95	28.50
20	18.19	24.48	34.39

C. Maimeri[21] has recently published data which show the benefit of absorbing the ethylene in acid under pressure. His investigation was evidently carried out with pure ethylene but he states that 1300 cubic meters of coke oven gas containing 4 per cent ethylene (much higher ethylene content than gas made by American practice) will yield 64 kgm. of ethylene by absorption in ethyl alcohol, 100 kgm., under pressure. After

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[20] *J. Soc. Chem. Ind.*, **40**, 86T (1921).

[21] *Chem. Abst.*, **19**, 1402 (1925).

absorbing the ethylene in sulfuric acid, 98 to 100 per cent the mixture was diluted with water and ice to separate diethyl sulfate. Working at 3.5 atmospheres pressure the yield of diethyl sulfate was 35 per cent and ethyl hydrogen sulfate 51 per cent based on the acid used; at 10 atmospheres the yield of diethyl sulfate was 62 per cent and ethyl hydrogen sulfate 30 per cent; the total yield of ethyl alcohol, at 10 atmospheres absorption pressure, was 76.7 per cent. The temperatures employed are not given. Maimeri alludes to the high acid consumption of earlier work but it should be noted that, as in the operation of Fritzsche's plant, the excessive acid consumption is caused largely by the acid required for preliminary purification of industrial gases such as oil gas or coke oven gas. Present developments in this country utilize oil gas from various sources for the ethylene homologues and only one manufacturer is making use of ethylene and in this case it is converted into ethylene chlorohydrin and glycol.

A. Damiens[22] states that small proportions of water greatly retard the reaction, 99.5 per cent acid absorbing ethylene at three to five times the rate shown by 95 per cent acid; the rate of absorption at 60° is three times the rate at 25°. He also confirms the fact that decomposition of the acid solution is appreciable above 60°. As noted above, the formation of diethyl sulfate is considerable when 100 per cent acid is employed, and at 15° an equilibrium mixture is reached containing 35.6 parts of diethyl sulfate per 100. Increase in temperature or dilution shifts the equilibrium in favor of ethyl hydrogen sulfate. The rate of absorption of the gas is also directly proportional to the pressure and the surface of contact. A semi-commercial plant, using oil gas, is described by Damiens and E. de Loisy,[23] the gas being given a preliminary washing with sulfuric acid as in Fritzsche's process.

A number of patented processes deal with the purification[24] of

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[22] *Bull. Soc. Chim. de France,* (**4**), **33**, 71 (1923): *Compt. rend.,* **175**, 585 (1922).

[23] *Chimie et Industrie,* **1923**, 664.

[24] C. Still, Eng. Pat. 147,737 (1920), specifies a sequence of operations, finally treating the gas with sulfuric acid 50° Be and later with acid of 66° Be.

the gas and with the concentration or isolation of ethylene. F. Soddy[25] separates ethylene from hydrogen, methane and carbon monoxide by absorption of the ethylene in activated charcoal. E. Berl and O. Schmidt[26] show the enrichment of ethylene by successively treating a gas containing 17.08 per cent ethylene with activated charcoal, of 64.2 per cent, 90.9 per cent and by the third treatment 98.8 per cent ethylene. They note that vapors of heavier hydrocarbons displace the ethylene from the charcoal.

G. O. Curme[27] prepares a gas rich in ethylene by compressing, cooling and absorbing the ethylene in acetone, releasing the ethylene by releasing the pressure. I. Brown[28] purifies the gas and separates nearly pure ethylene by liquefaction and fractional distillation at low temperatures.

The rate of the reaction of ethylene and sulfuric acid is affected catalytically by certain substances. A Damiens[29] states that cuprous salts are most effective, iron salts less so and R. Engehardt and W. Lommel[30] state that silver sufate has a very pronounced effect on the rate of absorption. With silver, mercurous and cuprous salts, the reaction proceeds in two stages, ethylene first forming a compound with the metal salt and later reacting with the acid. With silver sulfate this absorption takes place readily even in very dilute acid solution; thus a silver sulfate solution containing 3 per cent sulfuric acid readily absorbed one mol. of ethylene. W. Glund and G. Schneider[31] state that the reaction of ethylene and sulfuric acid is accelerated by the sulfates of calcium, lead, iron, copper, ferrous ammonium sulfate and silver, the last being most effective. The compounds of ethylene with mercury salts have long been known. J. Sand and F. Breest[32] noted that the formation of mercuric ethanol chloride

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[25] U. S. Pat. 1,422,007 and 1,422,008.

[26] *Z. f. Angew. Chem.*, **36**, 247 (1923).

[27] U. S. Pat., 1,422,184.

[28] German Pat. 338,358 (1916).

[29] *Compt. rend.*, **175**, 585, (1922): Brit. Pat. 180,988 (1922).

[30] *Ber.* **57** B, 848 (1924): U. S. Pat. 1,458,646.

[31] *Ber.* **57** B, 254 (1924).

[32] *Z. f. physik. Chem.*, **59**, 424 (1907): **60**, 237 (1907).

was reversible and W. Schoeller[33] showed that mercuric acetate in methanol solution readily absorbed 1 mol. of ethylene, the gas being expelled by warming with hydrochloric acid. One process of separating ethylene from inert gases is based upon the use of mercuric sulfate.[34] W. Manchot and W. Brandt[35] have called attention to the fact that the absorption of ethylene by copper salts causes serious errors in gas analyses unless entirely removed before determining carbon monoxide.

Ethylene and water react only very slightly, in the absence of catalysts, at elevated temperatures and pressures. H. W. Klever and F. Glaser[36] found that in 17 hours at 150° and 190 atmospheric pressure only 0.00011 mol. of ethylene was hydrated; at 200° and 100 atmospheric pressure 0.0008 mol. was hydrated, but by adding 1.93 per cent of hydrochloric acid more than one mol. was hydrated from which they concluded that ethyl chloride was first formed and this then hydrolyzed.

When pure ethylene and steam are passed together over alumina or aluminum sulfate at 360°, very small proportions of acetaldehyde are formed, from which J. P. Wibaut and J. J. Diekmann[37] conclude that ethyl alcohol is first formed. They also note that at 156° to 160°, 55 per cent sulfuric acid does not react with ethylene and 65 per cent acid only very slowly.

Ethylene reacts readily with chlorosulfonic acid and 86 per cent of the reaction product is hydrolyzed by water to form ethyl alcohol and 16 per cent to form ethyl chloride. W. Traube and R. Justh[38] recommend the use of equal parts of 100 per cent sulfuric acid and chlorosulfonic acid.

Ethylene and hydrogen chloride react to give ethyl chloride; E. Berl and J. Bitter[39] report a yield of 36 per cent using anhydrous aluminum chloride and HCl at 130° to 170°. G. Curme[40]

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[33] *Ber.* **46**, 2864 (1913).

[34] U. S. Pat. 1,315,541 (1919).

[35] *Ann.*, **370**, 286 (1909): **420**, 170 (1920).

[36] *Chem. Abs.*, **18**, 1976 (1924).

[37] *Chem. Abs.*, **17**, 3858 (1923).

[38] *Brennstoff-Chem.*, **4**, 150 (1923).

[39] *Ber.* **57 B**, 95 (1924).

[40] U. S. Pat. 1,518,182 (1924).

states that satisfactory commercial yields of ethyl chloride can be obtained by treating ethylene with hydrogen chloride under a pressure of about 160 atmospheres without a catalyst and also at about 35 atmospheres in the presence of aluminum chloride; no temperatures are given.

Very little has been published regarding the conditions advantageous for the conversion of ethyl chloride to ethyl alcohol or other products. B. S. Lacy[41] passes the chloride over calcium oxide at 250° to 450°. Williamson's well known synthesis of ethyl ether was carried out with ethyl iodide. In J. U. Nef's researches on ether formation from alkyl halides, ethyl bromide and iodide were employed, but not the chloride, although with other alkyl halides he showed that in a series of so-called double decomposition reactions the formation of the olefins was maximum with the alkyl iodides and minimum with the alkyl chlorides.[42] The reactions of ethyl chloride and its preparation from industrial gases offers an attractive field for investigation with industrial possibilities.

ISOPROPYL ALCOHOL[43]

Berthelot[44] showed that alcohols could be made from ethylene homologues by combining the olefins with sulfuric acid and hydrolyzing the resulting sulfuric acid ester; he made isopropyl alcohol in this way and believed that the reaction was a general one. He showed that one volume of concentrated sulfuric acid absorbed about 860 volumes of propylene at 18°, and on subsequent treatment with water both isopropyl alcohol and oily

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[41] U. S. Pat. 1,245,742 (1917), Lacy chlorinates ethane at temperatures above 300° and states that it chlorinates much more readily than methane; U. S. Pat. No. 1,242,208.

[42] *Ann.*, **309**, 126 (1899).

[43] In 1920 C. Ellis gave an account of the manufacture of isopropyl alcohol from cracking still gases (*Chem. & Met. Eng.*, **23**, 1230 (1920)). A small experimental plant was built near the Bayonne plant of the Tidewater Oil Co. and later the Standard Oil Co. of New Jersey secured the rights to the process and is now producing isopropyl alcohol, under the name of petrohol, at its Bayway refinery.

[44] *Ann.*, **127**, 69 (1863): *Ann de chimie et de phys.*, (5) **9**, 289 (1876); (7) **4**, 104 (1895).

hydrocarbon polymers were obtained. Fritzsche and others who converted the ethylene of oil gas, coal gas and the like into ethyl alcohol employed sulfuric acid to remove the propylene and other olefins; Fritzsche[45] removed propylene by treating with cold concentrated sulfuric or by sulfuric acid of not over 80 per cent at 70° to 80°.[46] He examined the products of hydrolysis of the acid used for removing the propylene and found isopropyl alcohol but he apparently made no attempt to conserve this product or to determine the best operating conditions to obtain this alcohol. Plant and Sidgwick[47] state that propylene is readily absorbed by 97 per cent sulfuric acid at 25° and that 80 per cent and 90 per cent acid also absorbs propylene at roughly the rate that ethylene is absorbed by 100 per cent acid at 70° but beyond noting the formation of hydrocarbon polymers say nothing as to the yield of isopropyl alcohol obtained by hydrolysis. J. U. Nef[48] was obviously in error when he stated that ethylene, propylene and butylene could be estimated by treating the gas mixture with concentrated sulfuric acid at 0°; he stated that the ethylene passed through unchanged; the propylene formed isopropyl sulfuric acid which could be determined by hydrolyzing to the alcohol and distilling and that the butylenes were polymerized to heavy hydrocarbon oil. Both propylene and butylene yield hydrocarbon polymers and some of the corresponding alcohols under these conditions.

The patents having to do with the industrial manufacture of isopropyl alcohol from the propylene in oil gas, the uncondensed gas resulting from cracking heavy oil for gasoline and usually known as cracking still gas, deal with particular features not fully disclosed by the older literature. They are chiefly of interest as illustrating the improvements or new details of operation which are patentable.

M. D. Mann and R. R. Williams[49] describe passing gas con-

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[45] English Pat. 20,225 (1896): *J. Soc. Chem. Ind.*, **16**, 824 (1897).

[46] *J. Soc. Chem. Ind.* 16,630 (1897): *Chem. Industrie*, **35**, 637 (1912).

[47] *Loc. cit.*

[48] *Ann.*, 318, 26 (0000).

[49] U. S. Pat. 1,365,043 (1921).

taining propylene through an agitated mixture of sulfuric acid of about 1.8 specific gravity and neutral oil at temperatures below 30°. C. Ellis[50] claims as a solvent the mixture of the acetates derived from the simpler iolefins or their alcohols, such as ethyl, isopropyl and secondary butyl alcohols.

C. Ellis and M. J. Cohen[51] claim the treatment of the sulfuric acid solution resulting from the treatment of oil gas and the like with sodium acetate to obtain a mixture containing ethyl, isopropyl and secondary butyl acetates. H. E. Buc[52] has patented the chlorination of isopropyl alcohol at 35° to 75°, and continuing the chlorination above 70° to obtain pentachloroacetone. In another patent[53] Buc describes raising the temperature as the chlorination proceeds. When isopropyl alcohol is partially chlorinated a mixture consisting principally of di- and tri-chloroacetones results.[54] Buc[55] has also patented the conversion of isopropyl alcohol to isopropyl chloride by treating with dry or aqueous hydrochloric acid and distilling the mixture. C. Ellis and A. A. Wells[56] pass chlorine into a solution of olefins in sulfuric acid but the products are not very definitely characterized. M. C. Mann[57] has patented the dehydration of isopropyl and other alcohols, the process consisting in adding caustic soda and separating the two layers thus formed. Buc has also patented the dehydration of alcohols by mixing with kerosene and heating with lime.

R. R. Williams and D. H. White[58] have patented the oxidation of isopropyl and other secondary alcohols to ketones by passing the vapors with air over brass at 500° to 800°. The polymerization of propylene and other olefins to hydrocarbon oils has been referred to above; the polymerization of the olefins in oil gas

[50] U. S. Pat. 1,365,049 (1921).
[51] U. S. Pat. 1,365,050 (1921).
[52] U. S. Pat. 1,391,757 (1921).
[53] U. S. Pat. 1,391,758 (1921).
[54] U. S. Pat. 1,436,378 (1922).
[55] U. S. Pat. 1,436,377 (1922).
[56] U. S. Pat. 1,440,976 (1923).
[57] U. S. Pat. 1,452,206 (1923): 1,455,072 (1923).
[58] U. S. Pat. 1,460,876 (1923): also A. A. Wells, U. S. Pat. 1,497,817 (1924).

by means of sulfuric acid (conditions not definitely specified) has been patented by C. Ellis.[59] The use of alcohols or ketones, derived from petroleum olefins, mixed with gasoline as a motor fuel has also been claimed by C. Ellis.[60] Another patent issued to Ellis[61] specifies the preliminary purification of the gas, treating with sulfuric acid specific gravity 1.8 together with several volumes of inert oil to remove propylene and then treating the gas with an acid stronger than 1.8 at above 60°. The conversion of isopropyl alcohol to isopropyl ether by boiling with sulfuric acid, 70 to 85 per cent, is claimed by M. D. Mann:[62] the yield is stated to be about 40 per cent of the theory. When the usual process of esterification is carried out with isopropyl alcohol and acetic acid W. W. Clough and C. O. Johns[63] find that a constant boiling mixture is formed containing about 47.5 per cent isopropyl acetate and 52.5 per cent isopropyl alcohol. Various special processes of refining isopropyl alcohol have also been patented, for example treating with potassium permanganate,[64] alkaline hypochlorite solution,[65] dissolving in sulfuric acid of about 1.57 specific gravity and diluting, distilling or extracting the alcohol,[66] filtering through sawdust.[67]

According to W. W. Clough and C. O. Johns[68] the industrial manufacture of isopropyl and other secondary alcohols, from oil gas or petroleum cracking still gas was due largely to the efforts of M. D. Mann, Jr. An important step in this work was the discovery by M. D. Mann and R. R. Williams that a mixture of inert hydrocarbon oil and sulfuric acid absorbed propylene from gases lean in this constituent much more readily than when sulfuric acid alone was used. Clough and Johns

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[59] U. S. Pat. 1,464,152 (1923).

[60] U. S. Pat. 1,412,233 (1922).

[61] U. S. Pat. 1,464,153 (1923).

[62] U. S. Pat. 1,482,804 (1924).

[63] U. S. Pat. 1,485,071 (1924).

[64] M. D. Mann, U. S. Pat. 1,518,339 (1924): 1,491,916 (1924) and U. S. Pat. 1,502,149 (1924).

[65] H. E. Buc, U. S. Pat. 1,498,229 (1924).

[66] C. Ellis and M. J. Cohen, U. S. Pat. 1,365,048 (1921).

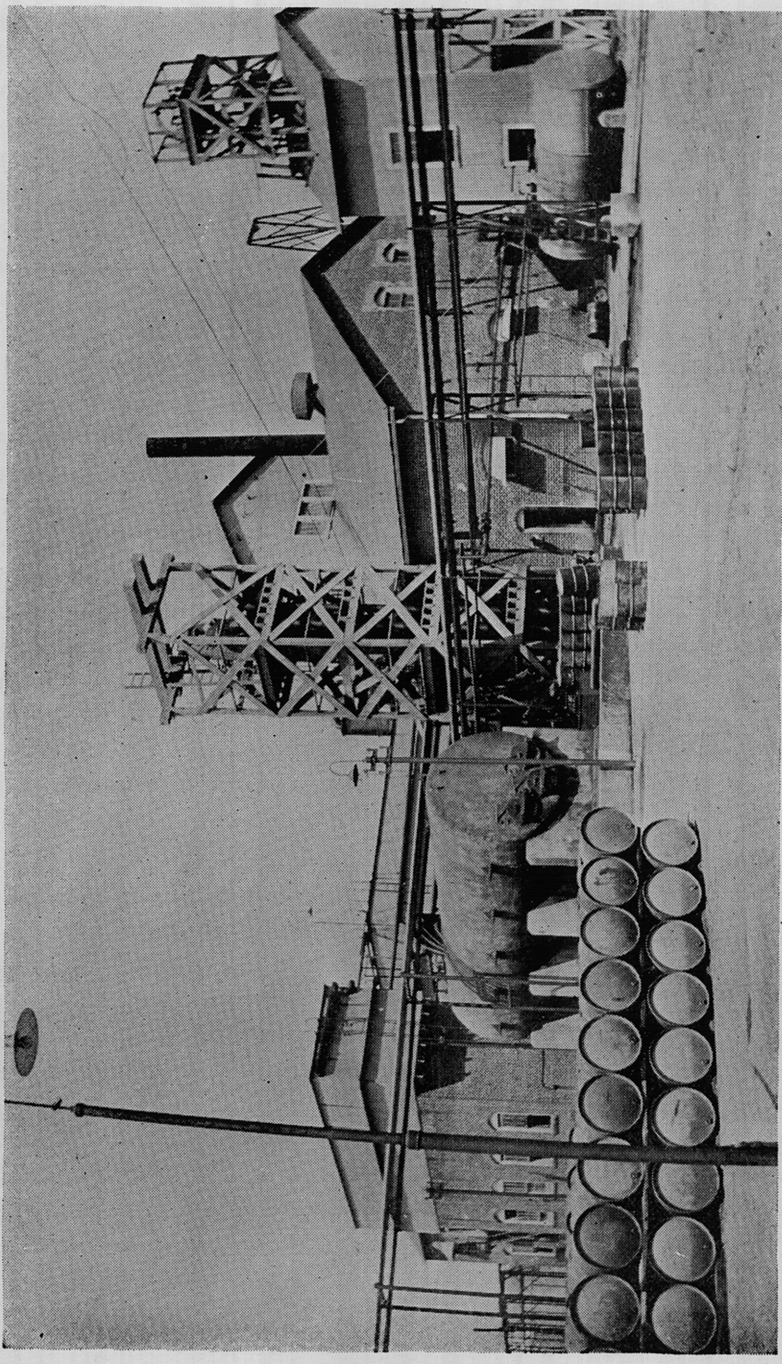
[67] M. D. Mann, U. S. Pat. 1,413,864 (1922).

[68] *Ind. & Eng. Chem.*, **15**, 1030 (1923).

note an azeotropic mixture containing 91 per cent of alcohol and 9 per cent of water (by volume) boiling at 80.4° and having a specific gravity at 20°/4° of 0.816. The anhydrous alcohol boils at 82.4°. Isopropyl alcohol and the acetate also form an azeotropic mixture containing 52.3 per cent of the alcohol and 47.7 per cent of the ester (by weight).

INDUSTRIAL OPERATION

Isopropyl alcohol is at present the most important, industrially, of the several alcohols now being manufactured from oil gas, or cracking still gases. Three manufacturers have a combined production of about 575,000 gallons of isopropyl alcohol annually. The oil gas, or cracking still gas is first treated to remove all condensible hydrocarbons valuable as gasoline. This practice is now quite general in the larger refineries, whether the residual gases are chemically utilized or not. Usually all of the waste gases, including uncondensed vapors from the stills, are brought together and treated by well known methods for removal of gasoline vapor, and where the residual gas is to be chemically treated, this should include scrubbing the gas with heavy oil under pressure. The scrubbed gas is then given a preliminary treatment with dilute sulfuric acid to remove butylenes and amylenes, the concentration and temperature of the acid varying with different manufacturers, the object being to convert as large a percentage as possible of the butylenes and amylenes into alcohols. As noted above, Fritzsche merely polymerized these olefins, which accounts largely for the very high acid consumption in his process. In accordance with well known practice in handling sulfuric acid, the scrubbing towers using dilute sulfuric acid are lead lined, but where the concentration is 80 per cent or more, cast iron or steel is used. The gas is passed counter-current against the acid in the scrubbing towers, several such towers being arranged in series. The acid from the last tower containing isopropyl hydrogen sulfate together with polymers and small proportions of di-isopropyl sulfate is diluted with water, separated from the oily mixture of polymers and distilled with steam to obtain



Plant of Empire Refining Co. for Manufacturing Alcohols from Cracking Still Gases dilute isopropyl alcohol. A small proportion of hydrocarbon polymers are separated from the dilute isopropyl alcohol distillate and the dilute alcohol then concentrated by fractional distillation. The crude isopropyl alcohol contains traces of malodorous substances, probably mercaptans, which are removed by hypochlorite or other oxidizing reagents. Well refined isopropyl alcohol has an odor closely resembling ethyl alcohol, and the solvent power and physical properties of the anhydrous isopropyl alcohol make it an excellent substitute for ethyl alcohol for certain uses, and with the further advantage of not being subject to the manifold government regulations, applied to ethyl alcohol.

Secondary butyl, amyl and hexyl alcohols are recovered by diluting the acid employed for removal of the corresponding olefins, prior to the absorption of the propylene. The diluted acid solution is distilled with steam and the dilute mixture of alcohols thus obtained are concentrated and separated by fractional distillation. Final dehydration may be carried out by adding solid caustic soda, which causes separation into two layers, and distilling the alcohol layer, or by adding a low boiling liquid such as benzol and distilling, the benzene carrying over the water present.

Butyl alcohols

The ease with which isobutylene reacts with dilute sulfuric acid was recognized by Butlerow[69] who dissolved isobutene in a mixture of equal parts of sulfuric acid and water; at ordinary temperatures the hydrocarbon slowly dissolved without appreciable discoloration or separation of hydrocarbon polymers. After neutralizing the acid solution and distilling, a nearly theoretical yield of *tertiary butyl alcohol* was obtained. If the acid solution is warmed the hydrocarbon polymers quickly form. He also noted that normal butene-2 was noticeably less reactive to sulfuric acid than isobutylene, but could similarly be converted to normal secondary butyl alcohol. In this case, an acid mixture of two parts of acid to one of water required several

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[69] *Ann.*, **180**, 245 (1875).

days at ordinary temperature to effect solution, whereas isobutene was completely converted in a few hours, under the same conditions. He later[70] stated that this acid mixture and also one consisting of three parts of acid to one of water gave "small quantities" of hydrocarbon oil at ordinary temperatures: concentrated sulfuric acid promptly gave a mixture of hydrocarbon polymers of high boiling point. The polymer formed by warming with equal parts of acid and water, to 100°, is chiefly di-isobutylene.

A. Michael and R. F. Brunel[71] found that isobutene is the most reactive olefin known, to sulfuric acid and halogen acid. The greater reactivity of isobutene as compared with normal butene was found to be as follows, the hydrocarbons in gaseous form being passed through the acid.

	PARTS H_2SO_4 TO 1 PART H_2O (BY WEIGHT)	TEMPERATURE OF ACID	PER CENT ABSORBED
Isobutene	2	17°	100
Butene (2)	2	15°	12
Butene	3.5	18°	None
Butene	3.75	18°	37
n. butene (1)	3.75	17°	33
n. butene	4	17°	49

With dilute sulfuric acid, 50 per cent by weight, isobutene dissolved completely in twenty minutes, trimethyl ethylene in two hours. Tetramethyl ethylene is still much less reactive: in 66 per cent acid trimethyl ethylene readily dissolves but tetramethyl ethylene was not appreciably dissolved after six hours. Since oil gas contains isobutene, butene -2 and probably butene -1, and probably all the isomeric amylenes with the possible exception of isopropyl ethylene and normal pentene -1 it is apparent that the concentration of the acid employed is of the greatest importance.

W. W. Clough and C. O. Johns[72] have described secondary

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[70] *Ann.*, **189**, 46 (1877).

[71] *Am. Chem. J.*, **41**, 118 (1909).

[72] *J. Ind. & Eng. Chem.*, **15**, 1030 (1923).

butyl alcohol made by treating pressure still gases with sulfuric acid and hydrolyzing the butyl sulfuric ester and have noted that this alcohol forms an azeotropic mixture with water which boils at 87.5° and contained 72.7 per cent of the alcohol by weight, or 77.72 per cent by volume. They give the physical constants of this alcohol as follows: boiling point of the anhydrous alcohol, 99.40° at 760^{mm}, D at 15°/4° 0.8104, 20°/4° 0.8063. These authors have also determined the specific gravity of aqueous solutions of the alcohol; the saturated aqueous solution at 20° contains 17.85 per cent by weight or 21.55 per cent by volume of the alcohol and has a density of 0.9732 20°/4°: the alcohol phase at 20° contains 64.17 per cent by weight or 69.97 per cent by volume of the alcohol and has a density of 0.8792, 20°/4°. They also note that secondary butyl alcohol and its acetate form an azeotropic mixture boiling at 99.60° (758^{mm}) and consists of 86.3 per cent alcohol and 13.7 per cent of the ester, by weight.

R. R. Read and F. Prisley[73] converted isobutene to the tertiary alcohol by treating it in solution in kerosene with cold 50 per cent sulfuric acid. As noted by others[74] a rearrangement of butylenes occurs on heating and on dehydrating isobutyl alcohol over alumina at 450° to 475° these authors obtained 30 to 35 per cent of butene -2, which was not absorbed by the 50 per cent acid at 0° to room temperature. From 1000 g. of isobutyl alcohol they obtained 550 g. tertiary butyl alcohol melting above 15°. The acid solution containing the alkyl sulfuric ester was run into an excessive of alkali, vigorously stirred.

In connection with the conversion of the butenes and amylenes to alcohols by means of sulfuric acid, it is of interest to note that none of the many workers who have prepared secondary and tertiary alcohols in this way have observed the formation of any primary *alcohols.* According to A. Michael and Leighton,[75] who were interested in a study of Markownikows rule,

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[73] *J. Am. Chem. Soc.*, **46**, 1512 (1924).

[74] Nef. *Ann.*, **318**, 22 (1901): Senderens, *Compt. Rend.*, **144**, 1110 (1907); Ipatiev, *Ber.* **36**, 2012 (1903).

[75] *J. Prakt. Chem.*, **60**, 286, 443 (1899).

propylene and hydriodic acid yields a very small proportion of normal propyl iodide, and isobutene and hydrogen bromide in acetic acid yields about 93 per cent tertiary butyl bromide and 7 per cent of the primary isobutyl bromide.

Amyl alcohols

Commercial amylene as used by earlier workers was a mixture of amylenes prepared by the decomposition of fermentation amyl alcohol. Berthelot[76] stated that ordinary sulfuric acid almost completely polymerizes this hydrocarbon mixture. Erlenmeyer[77] tried sulfuric acid of various concentrations but on diluting and distilling (without neutralization) obtained no amyl alcohols. A little later Flavitsky[78] stated that he obtained a mixture of amyl alcohols boiling from 100° to 108° by treating a commercial amylene mixture with dilute sulfuric acid, containing 2 parts of concentrated acid to one part of water. He diluted the acid mixture but did not neutralize it before distilling. The yield is not stated but he notes the formation of the polymer boiling at 155° to 160°. A Wischnegradsky[79] worked more carefully and treated commercial amylene (made from fermentation amyl alcohol) with a mixture of equal parts by volume of concentrated sulfuric acid and water, keeping the mixture cold by snow and salt. About half of the amylene was dissolved, the resulting mixture passed into a mush of snow and neutralized by caustic soda. The alcohol obtained was chiefly the tertiary alcohol, the so-called amylene hydrate or dimethyl ethyl carbinol. Wischnegradsky also noted that normal pentene -2 and isopropyl ethylene were much less reactive to sulfuric acid than trimethyl ethylene. He converted fermentation amyl alcohol to the iodides and from this made the amylenes by caustic potash. On treating the amylene mixture with acid containing two volumes of acid to one of water, at 0°, about 38 per cent went into solution. The residual oil contained some

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[76] *Ann.*, **127**, 69 (1863).
[77] *Zt. fur. Chemie & Pharm.*, **1865**, 362.
[78] *Ann.*, **165**, 157 (1873).
[79] *Ann.*, **190**, 328 (1878).

polymer but isopropyl ethylene boiling sharply at 21.5° was easily separated from it.

No accurate work on the nature of the amylenes produced by cracking petroleum oils at different temperatures, the relative amounts of each present or the relative stability of the different amylenes to heat, has been published. The nature of the oils which separate when sulfuric acid, which has been used for refining gasoline or kerosene, is diluted with water long remained a mystery, although the odor of secondary alcohols in such "acid oils" is usually very pronounced. R. Zaloziecki[80] stated "by the dilution of the sludge acid with water, the constituents soluble in concentrated acid separate out again, while other reactions take place which give rise to alcohols, ketones and ethers, but principally to polymers."

J. Hausman[81] showed the presence of so-called sulfo acids in the diluted mixture which form water-soluble barium salts. It is now known that on treating mixtures of unsaturated hydrocarbons, such as the commercial cracked gasolines, with sulfuric acid 85 to 93 per cent, cooled or at ordinary temperatures, alcohol formation results chiefly in the case of the simpler olefins and that while some polymers and alkyl sulfuric esters are formed, polymerization is the chief result with olefins of more than six carbon atoms.[82]

In the treatment of amylenes or hexylenes with sulfuric acid 85 to 93 per cent and subsequently diluting the acid solution with cracked ice and water a certain amount of secondary alcohol is immediately precipitated as an oil. The slight amount of alcohol left in solution can then be extracted, as by ether—and further dilution or continued extraction does not cause hydrolysis of the alkyl sulfuric esters in the solution. These esters are relatively stable and do not readily hydrolyze below 100°. This led Brooks and Humphrey to state that since the original sulfuric acid contained not only H_2SO_4 but the hydrate

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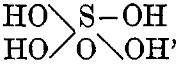
[80] *Chem. Rev. d. Fett.-u Harz-Ind.*, **5**, 27 (1898).

[81] *Petroleum*, **6**, 2301 (1911).

[82] B. T. Brooks and I. W. Humphrey, *J. Am. Chem. Soc.*, **40**, 822 (1918).

$H_2SO_4 \cdot H_2O$ or  alkyl esters of both acids were probably formed, the ester of $H_2SO_4 \cdot H_2O$ being the one to hydrolyze most readily to give the free alcohol.

Since the per cent of unsaturated hydrocarbons in gasolines made by the thermal decomposition (cracking) of heavier oils, is relatively high, frequently being 40 per cent or more, the tendency in refinery practice is to use acid less dilute than 93 per cent acid, or by minimizing the proportion of acid used to selectively polymerize or remove the di-olefines present in such oils. It is well known that di-olefines are much more reactive and polymerize much more readily, than the simple olefines. The volume of such "cracked" gasoline now manufactured is so great that the quantity of amyl and hexyl alcohols which could be made from them without seriously affecting the amount of motor fuel of this kind, would exceed any conceivable demand for such alcohols for solvent or chemical purposes.

W. W. Clough and C. O. Johns have described a very pure grade of secondary amyl alcohol, pentanol-2, made from petroleum amylene. The boiling point is given as 119.2° (760^{mm}) and the specific gravity as 0.8088 at 20°/4°. At 20° 100 grams of the alcohol dissolves 11.2 grams of water and 100 grams of water dissolves 4.2 grams of the alcohol.

It is possible that for the successful preparation of alcohols from the actylenes or other olefines higher in the series, the addition of hydrogen chloride followed by hydrolysis would be more effective, thus avoiding the excessive polymerization, which sulfuric acid causes with the higher olefines. Berthelot[83] showed that commercial amylene readily yields tertiary amyl chloride boiling at 85°, and A. Michael[84] showed that n-butene and isobutene, and the amylenes all react readily with hydrogen chloride. This is a favorite reaction employed in the terpene series and usually proceeds quantitatively, each double bond adding hydrogen chloride. In the olefin series however, the

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[83] *Ann.*, **127**, 72 (1863).

[84] *J. Prakt. Chem.*, **60**, 372 (1899).

addition of halogen acids (hydrogen chloride) has been very little studied with the higher members. It is probable that the reactivity of the higher members of the olefin series for hydrogen chloride falls off very markedly, as is the case with sulfuric acid, since Butlerow[85] showed that di-isobutylene is much less reactive to hydrogen chloride than isobutylene and the tri-isobutylene still less so.

LeBel described a method for separating the amylenes based on their capacity to unite with hydrogen chloride; those hydrocarbons which can form a tertiary halide by the addition of HCl do so most readily, i.e., at ordinary temperatures. Thus, trimethylethylene and unsymmetrical methylethylethylene react most readily, of the amylenes.

By direct chlorination of petroleum pentane (usually a mixture of normal pentane and isopentane) a mixture of monochloropentanes is obtained from which the corresponding alcohols or acetates can be made. By heating the mono-chloropentanes with sodium acetate in acetic acid at 190° to 200° the yield of amyl acetate is about 50 per cent of the theory.[86] The cost of chlorine and the difficulty of securing a good yield of monochlorides are unfavorable factors. The simple water hydrolysis of such alkyl chlorides does not appear to have been studied. Hexyl, heptyl and octyl alcohols can be made from unsaturated hydrocarbons by means of sulfuric acid, though with diminishing yields, and pure individual alcohols made in this way have not been described.

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[85] *Ann.*, **189**, 51 (1877); *Ber.*, **12**, 1483 (1879).

[86] B. T. Brooks, D. F. Smith and Harry Essex, *Ind. & Eng. Chem.*, **10**, 512 (1918).