ON THE ALCOHOLS OF FUSEL OIL.

BY ROBERT C. SCHÜPPHAUS.

About a decade ago fusel oil or commercial amylic alcohol could be procured for little more than the cost of cartage. In those days it was chiefly used in the manufacture of alkaloids, especially quinine. The quantities consumed in the preparation of valeric acid and its salts and various amylic ethers were unimportant. The conditions abroad were about the same. Though fusel oil was repeatedly proposed as a substitute for alcohol in the manufacture of spirit varnishes, its application did not meet with favor, both on account of its odor and its comparative lack of volatility. In the production of coal tar dyes it has been but rarely employed.

Cyanine or quinoline blue is obtained by treating quinoline with amyl iodide and subsequently treating with an alkali. Amyldiphenylamine furnishes, on heating with oxalic acid, a bluish green dye. The iodide and chloride of amyl required in these processes were prepared from fusel oil. In the manufacture of methyl green from methyl violet our method of purifying the dye stuff consisted in dissolving the crude product in water and agitating the solution with amyl alcohol, which dissolves the green, leaving the violet in the aqueous solution. All these processes are obsolete.

H. Briem* recommended the fusel oil from the fermentation of beet-sugar molasses as a crude material for the production of illuminating gas of superior quality, and in 1880 he† reported that several factories had introduced the process, among others a distillery. The latter concern enjoyed, of course, special facilities, putting a value of only eight cents a gallon on the material R. v.

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* Organ des Central-Vereins für Rübenzucker-Industrié in der Oest. Ung. Monarchie, 1877, p. 180, 1879, p. 265.

† Ib., 1880, p. 20.

Wagner* comments on Briem's proposition as follows: "It sems to me as if fusel oil could be utilized for something better than making gas. If there is no better outlet, let it rather go to waste, and wait for better times." And better times did come. In 1882 John H. Stevens† introduced fusel oil as a substitute of grain alcohol in the manufacture of celluloid. The mixture of alcohols constituting fusel oil forms, in conjunction with camphor, an efficient solvent of nitrocellulose, especially at elevated temperatures. In this connection it is worthy of note, that Arthur H. Elliott,‡ in his interesting paper on nitro-saccharose, mentions amyl alcohol as a solvent of this substance. From the very discovery of pyroxyline more or less successful attempts had been made to employ it as a base for varnishes. But the pyroxyline varnish industry did not begin to flourish until amyl acetate was utilized as a solvent, which was in 1879. John H. Stevens‖ patented its use in the manufacture of celluloid in 1882. Otto P. Amend§ introduced, in 1887, for similar purposes, the products of chlorination of amyl alcohol and acetate. In 1884 I found that pure amyl alcohol is far less useful in the manufacture of celluloid than the commercial article, which observation led me to the discovery that propyl and isobutyl alcohols are to be preferred to the higher homologue.** Mixtures of propyl and butyl alcohols can be procured at very moderate prices in European markets. At the same time I proposed propyl and butyl acetates for the manufacture of pyroxyline varnishes. Walter D. Field†† obtained a patent for such varnishes in 1887. Large quantities of the acetates of propyl, butyl and

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* Wagner's Jahresb., 1879, p. 1216.

† U. S. Patent 269,343, December 19th, 1882, filed June 12th, 1882.

‡ This Journal, 4 (1882), 147.

‖ U. S. Patent 269,340, Dec. 19th, 1882, filed June 12th, 1882.

§ U. S. Patent 371,021, October 4th, 1887, filed May 11th, 1887. U. S. Patent 372,100, Oct. 25th, 1887, filed May 4th, 1887. U. S. Reissue 10,879, Nov. 8th, 1887, filed Oct. 15th, 1887.

** U. S. Patent 410,204, Sept. 3d, 1884, filed Oct. 19th, 1886.

†† U. S. Patent 381,354, April 17th, 1888, filed August 13th, 1887.

amyl are consumed in the manufacture of photographic films. Amyl acetate has also been used in the preparation of some of the smokeless powders, the Wettern, for instance.

The burning fluid in Hefner's standard lamp for photometric purposes is amyl acetate. The acetate, butyrate and valerate of amyl enter into the composition of the artificial fruit essences and flavors. A few years since they found an ephemeral application in perfumery, when fashion, in one of her capricious moods, decreed that the delicate scents of flowers must yield to the more substantial odors of fruits.

E. Liebert* adds amyl nitrate to nitroglycerine to diminish its sensitiveness to cold and concussion. A variation of his process consists in mixing glycerine either with amyl nitrate or amyl alcohol before subjecting it to the action of the nitrating mixture. Amyl nitrate is employed in medicine ; in the chemical laboratory it serves in the preparation of diazo and kindred compounds.

The analyst makes use of pure amyl alcohol in the separation of alkaloids. Isobutyl alcohol or its chloride is employed in the manufacture of the artificial musks, trinitro derivatives of butyltoluol and butylxylol. Valeric acid is obtained through the oxidation of amyl alcohol. Le Bel† described a method of preparing inactive amyl alcohol from the fermentation product, and showed that valeric acid from this source is identical with the officinal *acidum valerianicum e radice parata*, a fact all the more important as the valerates made from active alcohol will not crystalize. Hydrated valeric acid, and the valerates of ammonium, sodium, iron, zinc, bismuth and quinine are well known remedies.

Pental (one of the amylenes), an anæsthetic, and hydrate of amylene, a hypnotic, are both derived from amyl alcohol. Prior to 1858, amylene was employed in dentistry, but owing to imperfect methods of manufacture, fell into disrepute. Fusel oil yields, on heating with zinc chloride crude amylene, which, through treatment with sulphuric acid and subsequent decomposition with water is converted into amylene hydrate or tertiary amyl alcohol.

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*D. R. P. 51022, of March 29th, 1889.

† Compt. Rend. 86 (1878), 213.

This alcohol, when heated with dilute sulphuric acid, furnishes pure amylene or "pental," i. e., trimethyl ethylene, B. P. 38° C.

This enormous increase in the consumption of fusel oil, or its separate constituents, has brought it about not only that the domestic article finds a ready market, but tnat large quantities are imported from abroad. But whilst the consumption is steadily on the increase, the production does not keep step with it. One gallon to each three hundred of crude spirit may be said to be the average yield, and from this a large quantity of ethyl alcohol may be extracted by cautious distillation. Moreover, every progressive distiller bends his whole energy to counteracting its formation, and Linnet's* researches, and Springer's† method of producing alcohol point to success in this direction. It must be borne in mind, however, that with free alcohol for the arts and manufactures the use of fusel oil would be abandoned in several branches.

Fusel oil was discovered by Scheele‡ in the tailings from the rectification of rye whiskey. Pelletan‖ obtained and examined a similar product from potato spirit. In the revised edition of Watts' Dictionary of Chemistry fusel oil is defined as a volatile liquid present in the product of the alcoholic fermentation of the saccharine liquids derived from potatoes, wheat, etc., and of the juice of grapes, beets, etc. It passes over in the latter portion of the distillate when these liquids are rectified. Fusel oil always contains amyl and ethyl alcohols, usually isobutyl and n. propyl alcohols, some fatty acids and some ethers. The three higher alcohols mentioned became first known to science through the examination of fusel oils.

Dumas§ isolated amyl alcohol, B. P. 131.5°, from potato fusel oil and ascertained its percentage composition, without recognizing, however, its alcoholic nature. Cahours** investigated the

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*Compt. Rend. 112 (1891), 663.

† Scientific American Supplement of Sept. 26th, 1891, p. 13125.

‡ Crell's Ann., 1785, I. 61.

‖ Ann. Chim. phys. [1] 30 (1825), 221.

§ Ann. Chim. phys. [1] 56 (1834), 314.

** Compt. Rend. 4(1837, 341, and Am. Chim. phys. [1] 70 (1839) 81, and [1] 75 (1840). 193.

same product and showed that it was a substance analogous to common alcohol and belonging to the same natural series of which methyl and ethyl alcohols form the first two members. Balard* obtained it from the fusel oil formed in the fermentation of grape skins, and prepared quite a series of amyl compounds. In a fusel oil of the same origin Chancel† discovered n. propyl alcohol. Wurtz‡ made the discovery of i-butyl alcohol in his investigations of fusel oils from potatoes and beet-sugar molasses.

The analytical chemist may regard fusel oil for all practical purposes as a mixture of water and ethyl, propyl, butyl and amyl alcohols. The quantity of ethers present, mostly amylic ethers, is usually minute. Kolbe,‖ Wurtz§ and Perrot** examined the ethers and fatty acids of fusel oil. Whilst in the crude product amyl alcohol preponderates, the composition of distillates varies greatly. Instances of fusel oil free, or nearly free, from amyl alcohol as reported in chemical literature, e. g., by H. Briem,†† do not bear close scrutiny. One such case‡‡ mentioned I found on consulting the original,‖‖ to refer to a distillate. This liquid, boiling at about 100° C., consisted of ethyl, propyl and chiefly isobutyl alcohols, with only very little amyl alcohol, and had been obtained from a large quantity of fusel oil by fractional distillation with the aid of a column.

G. L. Ulex§§ described, in 1873, a valuable method of determining the amount of ethyl alcohol in fusel oil, and incidentally remarked that "wine" fusel oil contains no amyl alcohol, because

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* Ann. Chim. phys. [3] 12 (1844). 294.

† Compt. Rend. 37 (1853), 410.

‡ Compt. Rend. 35 (1852), 310, and Ann. Chim. phys. [3] 42 (1854), 129.

‖ Ann. 41 (1842), 53.

§ Ann. Chim. phys. [3] 42 (1854), 129.

** Compt. Rend. 45 (1857). 309.

†† Organ des Central Ver. f. Rubenzucker-Ind. Oest. Ung. Monarchie 1877, p. 180.

‡‡ Wagner's Jahresb,, 1875, p. 882.

‖‖ August Freund, J. f. pr. Chem. N. F. 12 (1875), p. 25.

§§ Dingler's polyt. Journal, 208, 379.

all of it passes over below 130° C. when subjected to distillation Such superficial argument cannot convince the student who has ever investigated fractional distillation, especially as applied to such a complex mixture of analogous substances as represented by fusel oil. How imperfect a separation is effected by a single distillation of even so simple a mixture as amyl and ethyl alcohols, the boiling points of which are the farthest apart of all the substances concerned in this discussion, may be gathered from a communication in "A Treatise on Chemistry," by Roscoe and Schorlemmer.* A further complication ensues when the liquid contains water, as all commercial fusel oil does, and dehydration previous to anylysis is neglected. A mixture of water and amyl alcohol,† B. P. 130°, boils at 96°, and the distillate consists of two volumes of water and three of amyl alcohol: in the case of butyl alcohol, B. P. 108°, the boiling point is lowered to 90.5° and the constituents pass over in the proportion of one volume of the former to five of the latter. In the light distillates of fusel oil the amount of water may rise to considerable proportions. Where a rational separation is aimed at, complete dehydration is indispensable.

The Government chemist is chiefly concerned in a rapid determination of ethyl alcohol in fusel oil. The time-honored British method consists in shaking the sample with an equal volume of water and taking the gravity of the separated aqueous layer. Ulex‡ was the first to call attention to the serious error committed in calculating the percentage of ethyl alcohol from the gravity of the aqueous solution. He points out that commercial fusel oil is far from being a mixture of ethyl and amyl alcohols, and that the ready solubility of the lower alcohols is the cause of grave mistakes. The solubility of the alcohols chiefly concerned stands thus:

n-propyl alcohol is miccible with water in all proportions.

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* Vol. III., p. 147.

† Pierre and Puchot, Ann. Chim. phys, [4], 22 (1868), 234.

‡ l. c.

i-butyl alcohol requires 10.5 parts of water for solution at 18° C.
i-amyl alcohol requires 39 parts of water for solution at 16.5° C.

Ulex distilled three different fusel oils with the following results :

	Fusel Oil from		
	Beets.	Potatoes.	Rye.
Sp. gr. at 15° C.	.826	.832	.837
80-100° C.	13% by vol.	13% by vol.	31% by vol.
100-130° C.	53% "	30% "	26% "
above 130° C.	34% "	57% "	43% "

From these figures he concludes that two-thirds of beet fusel oil consist of the more soluble alcohols, a conclusion manifestly incorrect, as repeated fractional distillations would have yielded larger percentages of high boiling components. Neither does he mention any treatment to free the oils from water, though their gravities distinctly indicate its presence. It must be considered that he is speaking *pro domo.* However, his data were sufficient to justify his attack on the British excise method, on the basis of which a fusel oil containing eight per cent. of proof spirit had been declared to hold forty-four per cent.

According to his method 100 cc. of the sample is distilled until 5 cc. of distillate is collected. This is shaken with an equal bulk of a saturated solution of sodium chloride. If one-half or more of fusel oil is separated, it may be taken for granted that less than fifteen per cent. of proof spirit are present, *i. e.*, the sample is duty free. If, however, less or none separates, the sample under examination is shaken with an equal volume of a saturated solution of sodium chloride, which dissolves propyl and butyl alcohols much less readily than water does, and allowed to settle. The aqueous layer is subjected to distillation, and the gravity of the distillate is determined.

Alfred H. Allen* describes a very rapid method yielding satisfactory results, when mixtures of ethyl and amyl alcohols only are concerned. After agitating the sample in a graduated tube with

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* Commercial Organic Analysis. Vol. I. (1885), p. 179.

an equal volume of petroleum spirit, sufficient water is added to cause separation. The increase in the volume of the petroleum spirit indicates with approximate accuracy the amount of amyl alcohol.

The German Excise* authorities employ the following tests:

1. 10 cc. of fusel oil are shaken with 30 cc. of calcium chloride solution of sp. gr. 1.225 (made from 25 grms. of anhydrous calcium chloride and 100 cc. of water). After one minute's agitation at least 7.5 cc. must remain undissolved.

2. 100 cc. of fusel oil must show a decided turbidity, when shaken for one minute with 5 cc. of distilled water.

I have had occasion to examine several samples of distillates of fusel oil. A sample from a famous German factory was anhydrous, and consisted of nothing but propyl and butyl alcohols. Another distillate from a New York City firm had a similar composition with only very little amyl alcohol. But the most interesting and somewhat surprising results were revealed on a closer examination of several samples from a factory, where large quantities of domestic and foreign fusel oils are distilled. These liquids were guaranteed to be practically free from amyl alcohol, and a chemist, presumably more obliging than erudite, certified to the fact, that they contained propyl alcohol as their chief constituent, and that on an average not more than four per cent. of water was present. In spite of this favorable composition, and though they were used in conjunction with high grade wood alcohol, these fluids were responsible for some highly objectionable phenomena in the manufacture of celluloid. The determination of their gravities showed the presence of a large amount of water. If no dehydration had taken place previous to distillation, it was to be presumed that all the alcohols of fusel oil would be present, which my analyses proved to be the case.

To determine the quantity of water, 200 cc. of the sample were shaken in a graduated cylinder with freshly calcined potassium carbonate. More carbonate was added, until no further diminution of volume took place. The gravity of the liquid was carefully

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* Wagner's Jahresb. 1890, p. 1078.

taken both before and after this operation. All the gravities were determined by means of a pycnometer. A simple calculation gives us the percentage of water with sufficient accuracy for technical purposes.

For instance :

200 cc. Sp. gr. .8425=168.5 grms.
leave 179 cc. Sp. gr. .8095=144.9 grms.

23.6 grms. of water.
=14% by weight.

The larger quantities required for fractional distillation were dehydrated in the same manner, the operation being repeated. A further treatment with quick lime produced no decrease in the gravity. Calcium chloride cannot be recommended for quantitative work, being noticeably soluble even in the higher alcohols and thus interfering with distillation. 250 grms. of the anhydrous liquid were distilled from a flask fitted with a Glinsky column and connected with a long Liebig condenser, the rate of distillation being a drop a second. A platinum spiral was immersed in the fluid to ensure regular ebullition. In the first distillation the portions passing over between each five degrees were collected separately. These fractions were redistilled, and those portions which boiled between the same intervals of temperature were united, the interval in all subsequent distillations being two degrees. In this manner fractions boiling at 78–80°, at about 97° and 109°, and at 128–132° were obtained. The slight residue boiling above 132° possessed an odor suggestive of amyl valerate and probably consisted mainly of amylic ethers I append the results of my analyses of four different samples.

I.

Clear yellow liquid of neutral reaction.

Sp. gr. .8425 at 18° C.

100 grms. contain 1[illegible].0 of water.
30.0 of ethyl alcohol.
14.5 of n-propyl alcohol.
25.2 of i-butyl alcohol.
15.0 of fermentation amyl alcohol.
1.3 of residue.

II.

Clear yellowish liquid of neutral reaction.

Sp. gr. .8523 at 19.5° C.

100 grms. contain 20.0 of water.
19.4 of ethyl alcohol.
11.7 of n-propyl alcohol.
24.9 of i-butyl alcohol.
22.0 of ferm. amyl alcohol.
2.0 of residue.

III.

Slightly cloudy liquid of brownish tinge. Reaction neutral.

Sp. gr. .8434 at 21.5° C.

100 grms. contains 18.3 of water.
15.0 of ethyl alcohol.
8.2 of n-propyl alcohol.
19.9 of i-butyl alcohol.
36.8 of ferm. amyl alcohol.
1.8 of residue.

IV.

Colorless, clear liquid, of neutral reaction.

Sp. gr. .8630 at 16.5° C.

100 grms. contain 23.0 of water.
52.8 of ethyl alcohol.
5.7 of n-propyl alcohol.
11.0 of i-butyl alcohol.
7.0 of ferm. amyl alcohol.
.5 of residue.

It is evident that these liquids are the result of a simple distillation of fusel oil in the crudest kind of still. The temperature may never have exceeded 100°.

Kraemer and Pinner* found in the first runnings of fusel oil thirty per cent. of water, thirty per cent. of i-butyl, twenty per cent. of ethyl, and twenty per cent. of other alcohols, a good portion of which is n-propyl alcohol. Pierre and Puchot† found in

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*Ber. 2 (1869) 401, and 3 (1870), 75.

†Ann. Chim. phys. [4] 22 (1868), 234.

the crude fusel oils examined by them on an average 16 per cent. of water, 2.5–3 per cent. of n-propyl, 3–4 of i-butyl, and at least fifty per cent. of amyl alcohol. I learned later on that samples I. and II. had been specially redistilled, that my analyses might show more of the lower alcohols and less of amyl than otherwise would have been the case. A mixture of these distillates with methyl alcohol, in the proportions as used in practice, yields a clear camphor solution. Without the wood alcohol part of the water separates on the addition of camphor, and this behavior accounts for the disagreeable experience with these menstrua. Large blocks of celluloid, when cut into sheets, were found to be interspersed with cavities containing a liquid, which proved to be chiefly water. Their presence is easily explained when the peculiar composition of the solvent is considered. As stated, these liquids were represented to be free from amyl alcohol, and it became thus necessary to investigate the nature of the fraction 128–132°.

Its gravity was found to be .8113 at 19° C., *i. e.*, the gravity of i-amyl alcohol. With metallic sodium a gelatinous mass was obtained under copious evolution of hydrogen; on addition of water an oily layer collected on top of the lye. Heated with sulphuric acid and sodium acetate, an ether of the characteristic smell and boiling point of amyl acetate was produced. These tests leave no doubt as to its nature.

But the chief constituent was said to be propyl alcohol, and in view of Rabuteau's* researches on potato fusel oil it was at first thought possible that isopropyl alcohol might be contained in considerable quantities in the fractions of low boiling points. Isoprophyl alcohol is not totally freed from water even by distillation over barium oxide, as Friedel,† who was the first to prepare it from acetone, pointed out. Berthelot,‡ the discoverer of the compound, obtained it by absorbing propylene in sulphuric acid and treating the solution with water. He found the boiling point of the alcohol, which was not quite free from water, at 81–82°. The sepa-

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*Compt. Rend. 87 (1878), 500.

†Compt. Rend. 55 (1862), 53.

‡Ann. Chim. phys. [3] 43 (1855), 385.

ration had been effected by means of calcined potassium carbonate. Friedel's compound, boiled at 84–86,° after several rectifications over barium oxide, at 86–88°, after treatment with metallic sodium. It is to be noted that the acetone used by him was not remarkably pure, being a by-product gained in the manufacture of aniline. The subject was fully investigated by Linnemann*, who laid especial stress on starting with pure acetone. According to his investigations the boiling points of isopropyl alcohol and its three distinct hydrates, $3\,C_3H_8O_3+2\,H_2O$, $2\,C_3H_8O_3+H_2O$, and $3\,C_3H_8O_3+H_2O$, are 83–84°, 78–80°, 80° and 81° respectively. As these low alcohols absorb water, complete dehydration is rendered difficult; and as furthermore the boiling point of ethyl alcohol rises in the presence of water, it will be easily understood that a separation by fractional distillation alone must be well nigh impossible, as far as technical analysis is concerned. But a careful examination showed the entire absence of this alcohol. From each of the four samples 5 grms. of the fraction 78–80° and of intermediate fractions up to 88°, obtained by special distillations, were taken and subjected to oxidation. 5 grms. of the alcoholic liquid were dissolved in 45 grms. of water and a solution of

9.17 grms. of potassium dichromate,
11.90 grms. of sulphuric acid,
46.70 grms. of water,

was added, drop by drop. After complete reduction of the chromic acid the oxidation product was distilled off. Its odor was at once aldehydic and ethereal. To test for acetone, 5 cc., previously neutralized with caustic soda, were dissolved in 2 cc. of fifty per cent. alcohol and a drop of 10 per cent. caustic soda solution and a drop of pure benzaldehyde were added. After two days' standing there was no sign of the characteristic dibenzylidene acetone crystals, whilst a blank test with only 0.5 cc. of acetone yielded an abundant crop. Further tests with an alkaline sublimate solution gave likewise negative results. To a mixture of 1 cc. of $HgCl_2$ solution (1:20 of water) and 4 cc. of alcoholic potash (1:10) 1 cc. of the liquid was added, and the whole was thoroughly shaken. Ammon-

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*Ann. 136 (1865), 37.

ium sulphide failed to produce a precipitate in the filtered solution. Whenever alkali was added, the liquid turned first yellow, then reddish brown, and a pronounced smell of cinnamon was discernable, showing the presence of aldehyde. Ammoniacal silver solution was readily reduced. The odor of ethyl acetate could also be detected.

Rabuteau* found no less than 150 cc. of i-propyl alcohol, boiling at 85°, in one litre of potato fusel oil of Swedish origin. Nothing further has been published on the subject, the communication in the *Bulletin de la Société Chimique* 33 (1880), 178, being nothing but an abstract from the original in the Comptes Rendus.

The alcohol was identified by ultimate analysis, by its conversion into acetone and by its acetate boiling at 76°. Now it is ethyl acetate that boils at 76°, whilst the isopropyl ether boils at 90° according to Berthelot† and at 90–93° according to Friedel.‡ Rabuteau's figure may be simply an error, as 106.9° instead of 116.9° for n-butyl alcohol in the same article is. It is interesting to recall the fact that the very existence of n-propyl alcohol, and as a natural consequence its presence in fusel oil, was considered doubtful as late as 1868 by Mendelejeff.‖ He separated from 37 grms. of Chancel's§ alcohol 8 grms. of water, 25 grms. of ethyl and 1 grm. of amyl alcohol. The presence of the normal alcohol in fusel oil, not only in that from the marc of grapes, was placed beyond a doubt by the researches of Pierre and Puchot** and of Kraemer and Pinner.†† That Perrot‡‡ did not succeed in finding it in potato and beet fusel oils was due to his faulty method. From 60 litres he did not isolate enough of its iodide to be convinced of its presence. Without having recourse to dehydration, he separated a fraction boiling at 95°, treated it with desiccating

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*l. c.

†l. c.

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‖Zeitschrift für Chem., 1868, p. 25.

§Compt. Rend. 37 (1853), 410.

**Ann. Chem. phys. [4] 22 (1868). 234.

††Ber. 2 (1869), 401 and 3 (1870), 75.

‡‡Compt. Rend. 45 (1857), 309.

substances and converted it at once into the iodides. Yssel de Schepper* proceeded similarly with rye fusel oil. He freed a fraction passing over between 93 and 98° from water by agitation with anhydrous sodium carbonate. The liquid thus treated distilled at 83–84°, the mixture of iodides derived from it at 72–91°. Pirre and Pucheot say of the latter, that according to their extended investigations such mixture was liable to contain the iodides of the whole series of alcohols. Yssel de Schepper remarks that his experiments make the presence of an alcohol of the propylic series in rye fusel oil very probable. Pierre and Puchot, who experimented with very large quantities of fusel oils from various sources, with the facilities of a large distillery and with improved apparatus specially designed by them, found no i-propyl alcohol. A fraction of the boiling point 85–86° was at first thought to be the iso alcohol, but after treatment with potassium carbonate it was easily further separated by distillation. Rabuteau, however, was careful to free the crude fusel oil from water. Kraemer and Pinner, who also enjoyed the advantage of collaboration with a manufacturer, were unable to find i-propyl alcohol in a portion boiling at 84–86°, obtained from the dehydrated first runnings of fusel oil by repeated fractionating. The vapor density of these products was always found to be that of ethyl alcohol. It might be objected, that any of the hydrates of i-propyl alcohol would have shown a vapor density approaching that of ethyl alcohol. But these hydrates have a lower boiling point, and Kraemer and Pinner employed excellent apparatus. Barbaglia† found in isobutyl aldehyde from Kahlbaum's factory considerable quantities of acetone. Being unable to obtain acetone from pure isobutyl alcohol under the ordinary conditions of oxidation, he ascribed its formation to the presence of large quantities of i-propyl alcohol in the commercial i-butyl alcohol, from which the aldehyde had been made. Kraemer,‡ the manager of Kahlbaum's factory, replied that the i-butyl alcohol, prepared on a large scale from the first runnings of fusel oil by a series of frac-

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*Zeitschrift für Chem., 1868, p. 520.

† Ber. 6 (1873), 1064.

‡ Ber. 7 (1874), 252.

tional distillations, boiled at 106–109°, and that the absence of any noticeable quantity of i-propyl alcohol was further proved by converting the alcohol into its bromide. He showed that acetone was a constant product of oxidation of i-butyl alcohol under the conditions adhered to in their process of manufacturing i-butyl aldehyde. Lipp[*] described a method by which the formation of acetone may be almost wholly avoided. If we consider Rabuteau's data in the light of these facts, we are forced to the conclusion that the presence of such large quantities of i-propyl alcohol in potato fusel oil of Swedish origin is somewhat doubtful. The boiling point of 85° cannot assure us of the purity of the alcohol; the ultimate analysis is of little value, as any number of possible and probable mixtures can give results in accordance with the percentage composition of propyl alcohol; the boiling point of i-propyl acetate is not 76°; the formation of acetone is not sufficient proof, until it is shown that it is formed in such quantities as to preclude the possibility that it may owe its origin to a small quantity of i-butyl alcohol. It would have been desirable to learn how the acetone was identified. So far all the alcohols isolated from the fermentation products of saccharine liquids, about which there can be no reasonable doubt, are primary alcohols. They are methyl, ethyl, n-propyl, n- and i-butyl and i-amyl alcohols. Normal butyl alcohol was found by Claudon and Morin[†] in the heavy oils of French brandy (cognac), of which, however, it is not a normal constituent, but its presence is rather due to a secondary and objectionable fermentation. Morin[‡] proved its absence in normal brandies. Methyl alcohol is a product of the spontaneous fermentation of sugar cane juice in tropical climates, as discovered by Marcano.[‖] The yield of ethyl alcohol in this fermentation falls below the quantity produced by common yeast. The first runnings are methyl alcohol; the tailings are perfectly free from the higher alcohols and consist of a peculiar oily acid of disagreeable odor. Cultivations of the ferment in pure sugar solutions yield the same

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[*] Ann. 205 (1880), 1.

[†] Compt. Rend. 104 (1887), 1187.

[‡] Compt. Rend. 105 (1887), 1019.

[‖] Compt. Rend. 108 (1889), 955.

products. We are told that the domestic ardent spirits of our Southern neighbors are of the vilest quality. Marcano's research sheds a flood of light on this subject. Kraemer and Pinner* in 1869 expressed the opinion that methyl and hexyl alcohols might be found among the alcohols of fermentation. As far as methyl alcohol is concerned, their prediction was verified by Marcano's discovery. But Faget's† statements, who in 1853 isolated a substance from a fusel oil formed in the fermentation of grape skins, which he was inclined to regard as hexyl alcohol, have never been confirmed. Wurtz‡ demonstrated that potato and beet fusel oils contain no alcohols of any higher series than the pentylic. Perrot‖ was unable to find any hexyl alcohol in the same oils. Clandon and Morin§, and Morin**, who made the most thorough examinations of fusel oils extracted from large quantities of wine-brandy, report no hexyl alcohol.

It is to be hoped that Swedish potato fusel oil will be the subject of further investigation. If it contains 150cc. of isopropyl alcohol in each liter, there can be no difficulty in establishing this fact beyond any doubt. It is only necessary to subject the thoroughly dehydrated product to repeated fractional distillations and convert the portion boiling below 85° into the acetates. The difference in the boiling points of the acetates is about the same as in the case of the iodides, while the regeneration of the alcohols from the acetates is a much easier task. If the alcohol regenerated from an acetate of correct boiling point is transformed into acetone by oxidizing agents and if this alcohol furnishes a benzoate,†† which by heating is decomposed into propylene and benzoic acid, the existence of i-propyl alcohol in the original substance will be proved. Or the peculiar behavior of i-propyl benzoate above referred to may be utilized for the separation of i-propyl alcohol.

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*Ber. 2 (1869), 401.

†Compt. Rend. 37 (1853), 730.

‡Ann. Chim. phys. [3] 42 (1854), 129.

‖Compt. Rend. 45 (1857), 309.

§Compt. Rend. 104 (1887), 1187.

**Compt. Rend. 105 (1887), 1019.

††Linnemann, Ann. 161 (1872), p. 51.