Industrial Production of Synthetic Methanol[1]

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IN A recent Paris Letter the writer briefly mentioned the interesting results obtained by Patart, Inspector General of the Bureau of Explosives, on the synthesis of methanol by catalysis under pressure. Patart summarized his work at a lecture on January 31, 1925, before the Société d' Encouragement pour l' Industrie Nationale. The present article is based on this lecture, supplemented with notes that M. Patart was kind enough to place at the disposal of the writer.

M. Patart was in charge of the negotiations undertaken by the French Government with the Badische for the purchase of the Haber patents, and he will be in charge of the plant for the synthetic production of ammonia by that process, which will be installed by the Toulouse Powder Works. His interest in this work led him to experiment with the application of high pressures to the synthesis of methanol.

The reaction

$$\begin{array}{ccccc} CO & + & 2H_2 & = & CH_3OH + 23.9 \text{ cal.} \\ \text{1 vol.} & & \text{2 vols.} & & \text{1 vol.} \end{array}$$

can be compared with the reaction

$$\begin{array}{ccccc} N_2 & + & 3H_2 & = & 2NH_3 + 24.4 \text{ cal.} \\ \text{1 vol.} & & \text{3 vols.} & & \text{2 vols.} \end{array}$$

Previous Work

Sabatier and Senderens[1,*] called attention to the tendency of carbon monoxide to add certain elements, as evidenced, for example, in the formation of carbon oxychloride and carbon oxysulfide. The possibility of the fixation of hydrogen on the carbon monoxide molecule by means of reduced nickel led these chemists to the hope of obtaining both formaldehyde and methanol. Although not successful in their experiments, they pointed out the great industrial significance that such a reaction would have. Their experiments never yielded methanol, but only water and methane in accordance with the reaction

$$CO + 3H_2 = H_2O + CH_4 + 47.8 \text{ cal.}$$

The heat evolved by this reaction is twice the heat of formation of methanol. It appeared, therefore, that the reaction could not be made to take place in a different way. In the synthesis of ammonia, by the union of nitrogen and hydrogen, the only possible product is ammonia. In the system of carbon monoxide–hydrogen the possibility of these two reactions made it appear that the more exothermic reaction would be the one to take place.

The synthesis of ammonia had been forecast by Kuhlmann as early as 1836, but the problem was not practically solved until 1908 by Haber and Le Rossignol. The result with methanol has been much more quickly brought to a practical basis, since the early experiments on this synthesis date only from 1877.

Berthelot[2] submitted to the action of the silent discharge various mixtures of carbon monoxide and hydrogen. He obtained some carbohydrates of the general formula $(CH_2O)_n$. Losanitch and Jovitschich,[3] as well as Hemptine,[4] had obtained traces of formaldehyde by the action of the silent discharge on mixtures of equal parts of carbon monoxide and hydrogen. Jahn[5] also obtained formaldehyde by passing the same mixture over platinum sponge. Berthelot and Gaudechon,[6] studying the action of ultra-violet light on the same mixture, showed not only that formaldehyde was obtained but that the reaction was reversible. Orlow[7] obtained ethylene by passing a mixture of carbon monoxide and hydrogen at 100° C. over a catalyst consisting of coke impregnated with nickel nitrate and ammonium chloroplatinate, in accordance with the reaction

$$2CO + 4H_2 \rightarrow C_2H_4 + 2H_2O$$

It appears, therefore, that under ordinary atmospheric pressure one obtains from this reaction, according to the catalyst, formaldehyde or ethylene hydrocarbons. The Badische undertook some experiments on this hydrocarbon formation, when in 1913 the industrial synthesis of ammonia had become a reality. The formation of ethylene from carbon monoxide and hydrogen at low temperatures is now an accomplished fact,[8] but when the proportion of carbon monoxide is double that of hydrogen certain oxygen derivatives make their appearance—for example, alcohols, aldehydes, ketones, and acids.[9] The catalysts employed are chromium, cobalt, manganese, molybdenum, osmium, palladium, and zinc, their oxides, and mixtures of these with alkali hydroxides. To avoid a decomposition of carbon monoxide with the formation of carbon, it is advisable to employ a catalyst with high thermal conductivity, which is obtained by using either the metal in a granulated form or in filings, or carbon mixed with carbides of molybdenum, tungsten, or even cast iron.[10] The gaseous mixture must contain an excess of carbon monoxide, and it is possible to employ carbon dioxide in place of carbon monoxide. In the latter case the yield of liquid hydrocarbons is considerably diminished.[11]

Such was the state of affairs in 1913, and it appears rather extraordinary that these processes should not have been utilized on an industrial scale at that time. Franz Fischer, Director of the Kaiser-Wilhelm Institute at Mülheim-Ruhr,[12] was of the opinion that, inasmuch as these processes yielded a complex mixture, they could not be utilized on an industrial scale.

In 1916, Dreyfuss[13] developed on an industrial scale the synthesis of acetic acid and ethyl alcohol, from acetylene as starting material. It occurred to him that in this reaction the intermediate product, acetaldehyde, could be replaced by carbon monoxide so as to form formaldehyde and methanol. He worked only at atmospheric pressure, however, using salts of nickel and platinum sponge. He does not appear to have obtained any results in this direction.

In 1921, Lush[14] prepared formaldehyde by passing a mixture of hydrogen and carbon monoxide over a catalyst composed of four parts of nickel, one part of copper, and five parts of aluminium oxide. He used a pressure of 10 atmospheres and a temperature of from 300° to 400° C. This aldehyde contained considerable methane.

Finally Calvert,[15] using water gas, claims to have obtained methanol with a yield of 80 per cent of the theoretical. Unfortunately, the process has not come into commercial use, and no details are given.

Patart's Work

It was during 1921 that Patart conceived the idea of carrying out the synthesis of methanol, basing his process on van't

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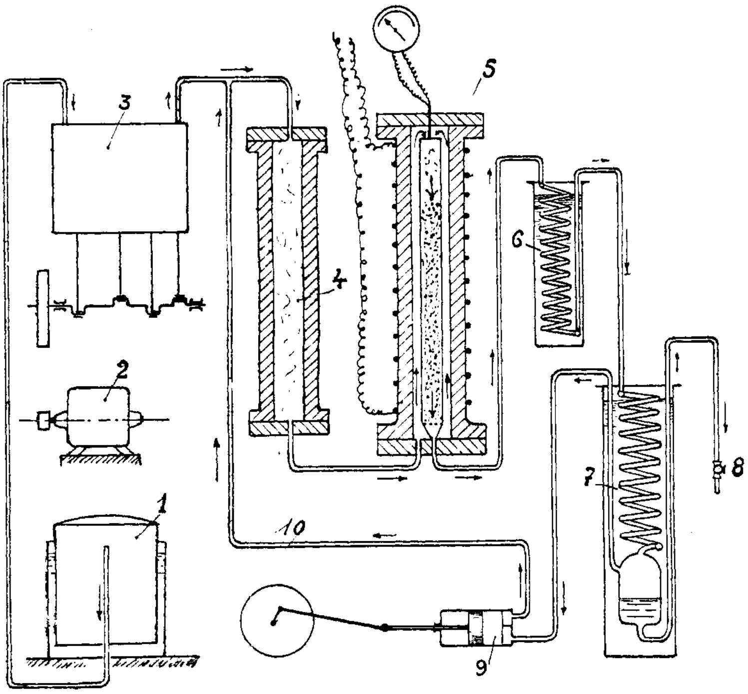
[1] Received February 27, 1925.

* Numbers in text refer to bibliography at end of article.

Hoff and Le Chatelier's law for the displacement of the equilibrium point. It occurred to him that the reversible reaction

$$\underset{\text{3 vols.}}{CO + 2H_2} \rightleftharpoons \underset{\text{1 vol.}}{CH_3OH}$$

should go in the direction of the formation of methanol if the pressure of the system were increased; further, that the reaction leading to the formation of methane, water, and carbon dioxide, involving no change in volume, would not be favored by the rise in the pressure, and that, therefore, if the temperature was not too high, methanol could be taken out of the system by condensation before it could go over into methane and water, or into methane and carbon dioxide.



Arrangement of Plant for Production of Synthetic Methanol

On this basis a patent was issued to Patart.[16] That patent disclosed as catalytic agents all metals, their oxides, and their salts, which are known to favor hydrogenations or oxidations, and a range of temperature from 300° to 600° C., the gaseous mixture consisting of two volumes of hydrogen to one of carbon monoxide. The gases were led over the catalytic agent rapidly, the temperature being sufficiently low to prevent the decomposition of the methanol formed. The pressure range was between 150 and 200 atmospheres.

M. Patart, with the help of the Bureau of Explosives of the Ministry of War and the Petroleum and Gasoline Bureau of the Ministry of Commerce, was able to put up a small industrial plant in the works of the Oxylite Company at Asnieres, near Paris. This plant is diagrammatically represented in the accompanying figure.

The gaseous mixture (generally two volumes of hydrogen to one volume of carbon monoxide), stored in gas holder (1), is withdrawn by a four-stage compressor (3), operated by an electric motor (2), and therein compressed to as high as 500 atmospheres. The gases are passed over a filtering device (4) where oil and other impurities are removed, then enter into an autoclave containing the catalyst (5), which is maintained at the desired temperature by external electric heating. From there they pass through two water-cooled coils (6 and 7), the second coil being provided with a reservoir for the condensed liquid, which is drawn out through a tap (8). The gases that have not been condensed by the cooling are taken up by a circulating pump (9), which sends them again through the return line (10) into the catalyzing autoclave, a proper speed of circulation being maintained.

From the very beginning this installation was utilized for a study of the yields with various catalysts.

The decomposition of methanol has been studied by Sabatier and Senderens[17] and Sabatier and Mailhe.[18] Their results are summarized in Table I. The volumes indicated are those of the gases obtained at a temperature of 350° C. with the same volume of catalytic agent under identical conditions and for the same quantity of alcohol.

Table I—Gas Production with Various Catalysts

Catalyst	Cc. per minute	Catalyst	Cc. per minute
I—Gas is nearly pure hydrogen			
BeO	Trace	ZrO_2	1.8
SiO_2	0.3	MnO	2.0
TiO_2	1.2	Al_2O_3	6.0
ZnO	1.5	Cr_2O_3[a]	6.0
II—Gas consists of hydrogen with some carbon monoxide			
Catalyst	Cc. per minute		
PbO	45.0 (start)		
Mo_2O_3	54		
CdO	57 (start)		
III—Gas has nearly the composition $CO + 2H_2$			
Fe_2O_3	106 (start)		
V_2O_3	140		
SnO	160 (start)		
Cu (powder)	152		

[a] Data obtained by Patart.

Platinum at 250° C. is as effective as copper. Nickel at 350° C. gave a mixture of methane and carbon dioxide. Iron and cobalt have an activity intermediate between that of copper and that of nickel. An inspection of this table would lead to the conclusion that powdered copper is the most active catalyst when used in methanol synthesis. This conclusion, however, was contradicted by experience. Pure copper gave very poor results— i. e., it caused the formation of carbon. On the other hand, the oxides of vanadium, chromium, and zinc led to the desired result— i. e., the formation of methanol. Another curious fact is that these oxides alone gave comparatively small yields, whereas their mixture with copper increased the yields considerably. A catalyst containing 90 per cent metallic copper and 10 per cent zinc oxide is more effective than one consisting entirely of zinc oxide. Commercial zinc dust is entirely ineffective as a catalyst, but when mixed with copper powder, which by itself was also ineffective, a good yield is obtained. These facts are fully in accord with what is generally known about the mixtures of catalysts.[19] Metallic salts, such as chromates, manganates, vanadates, molybdates, and tungstates, give better yields.

The circulating pump has a capacity of 2000 liters per hour at atmospheric pressure, and the proportion of the gases, which are combined at each passage over the catalyst, is between 8 and 10 per cent. The methanol, which is condensed, contains neither aldehydes nor acetone; it is slightly yellowish in color and contains small traces of amines and acids, in the proportion of 0.1 to 0.2 per cent. The water content is about 5 per cent. The liquid contains in addition 0.1 to 0.2 per cent of higher alcohols, the proportions of these, however, varying with various catalysts.

From a cubic meter of carbon monoxide and 2 cubic meters of hydrogen a yield of 476 grams of methanol is obtained— i. e., for 1 kg. of methanol 0.7 cubic meter of carbon monoxide and 1.4 cubic meters of hydrogen are required.

After the plant has been running for about 10 hours only small proportions of carbon dioxide and methane are found in the gaseous mixture. The composition of the mixture of hydrogen and carbon monoxide can be varied between wide limits and can even reach the composition of equal volumes of the two gases, if one is careful to supply hydrogen as fast as it is taken out by the formation of methanol. The presence of inert gases, such as carbon dioxide, methane, and nitrogen, does not prevent the reaction, but retards it. Increase in temperature brings about the formation of methane and an increase in the yield of higher alcohols.

It is to be noted that the reaction chamber must be externally, and not internally, heated, as in the latter case carbon and methane are produced. The pressure can be increased without deleterious results, and can even be raised as high as 900 atmospheres.

If hydroxides of the alkalies or of the alkaline earths are introduced in the system, the distillation residues from the methanol will show the presence of a certain number of derivatives of higher alcohols; this phase of the problem, however, still demands considerable study.

Following these experiments, which date from 1922, the Badische, in 1923, developed the industrial synthesis of methanol. This process is covered by German patents taken out beginning February 22, 1923, and French patents beginning September 30, 1923—i. e., more than eighteen months after the French patent taken out on August 19, 1921.[20] The German patents cover only developments of the process disclosed by the Patart patents. All the disclosures of these patents coincide with the principles brought out by the French patent. There is, however, a decided difference in the two methods regarding the behavior of the catalyst. According to the patents of the Badische it would be necessary to employ thoroughly purified gases. Patart believes, on the contrary, and his beliefs are confirmed by experiments, that the catalysts employed are far less susceptible to poisoning than is indicated in the German patent, inasmuch as he has always employed water gas which has been only slightly purified. He has never detected a diminution in the yield, which could be ascribed to the poisoning of the catalyst.

Industrial Development

The synthesis of methanol on a commercial scale is less difficult than the synthesis of ammonia, inasmuch as it appears to be unnecessary to employ pure gases and because the apparatus required is practically identical with that developed for the synthesis of ammonia. The raw materials are water gas and hydrogen, both easily obtainable. Standard forms of compressors can be had of satisfactory capacity. The reaction chambers are also available in capacity up to 20 tons per day. There appears to be, therefore, no insurmountable obstacle from the point of view of either equipment or raw materials. At the end of 1923 the Badische plant at Merseburg was producing from 10 to 20 tons of methanol per day.

So far as the market is concerned, the use of methanol for denaturation of ethyl alcohol, the methylation of organic compounds, the synthesis of dimethylaniline and its derivatives, and the manufacture of formaldehyde and of methyl esters constitutes a growing demand. The formaldehyde required for the manufacture of synthetic resins alone constitutes a market of several thousand tons annually. The current American price for 95 per cent methanol in tanks is 65 cents, and for 97 per cent in tanks 67 cents per gallon (March 18). Synthetic methanol of German origin is offered in the American market at a price slightly below the American makers' schedules, though it seems certain that this price could be materially lessened and might under competitive conditions decline to one-third the present quotations.

The cost of producing a hectoliter (26 gallons) in a plant having a daily capacity of 7.5 tons, or 32,800 hectoliters, a year, is as follows:

Raw Materials	Francs
150 cu. m. of water gas at 0 fr. 16 per cu. m.	24
67 cu. m. of hydrogen at 0 fr. 25 per cu. m.	16
Overhead	65
Total:	
Per hectoliter	105
Per 100 kg.	130

(or, on a gold basis, approximately 5 to 7 cents per liter or 18 to 26 cents per gallon)

It is worthy of note that an important consideration from the economic point of view would be the simultaneous manufacture of methanol and formaldehyde, since, by the decomposition of methanol in accordance to the reaction

$$CH_3OH \rightarrow CH_2O + H_2$$

the hydrogen liberated could be immediately used. This process would, in addition, permit the use of any fuel, even a cheap one and, as fundamentally all these problems of fuels consist in transformations of carbon compounds, it appears that the manufacture of methanol would be cheaper than the liquefaction of carbon by hydrogenation by the Bergius or other similar processes, which after ten years of researches have not yet passed the laboratory scale.

There are other products in view, which are at present being investigated by Patart. It had occurred to him that acetone could be obtained by replacing in part hydrogen by ethylene; contrary to expectations, he found the two reactions would run concurrently under such conditions: first, the normal reaction forming methanol, and then polymerization of the ethylene, which resulted in the formation of liquid fluorescent hydrocarbons similar to petroleum.

Bibliography

1—Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 418 (1905).

2—Berthelot, *Ibid.*, [5] **10**, 72; "Les Carbures d'Hydrogène," Vol. II, p. 333.

3—Losanitch and Jovitschich, *Ber.*, **30**, 135 (1897).

4—Hemptine, *Bull. acad. roy. med. Belg.*, [3] **34**, 269; *Chem. Zentr.*, **76**, 171 (1905).

5—Jahn, *Ber.*, **32**, 989 (1899).

6—Berthelot and Gaudechon, *Compt. rend.*, **150**, 1690 (1910).

7—Orlow, *Chem. Zentr.*, **80I**, 735 (1909).

8—*Brennstoff-Chem.*, **3**, 244 (1922); **4**, 197 (1923).

9—German Patents, 293,787 (March 8, 1913, with addition of August 23, 1913); 295,202 (May 31, 1914); 295,203 (June 23, 1914). See also French Patent 468,427 (February 13, 1914).

10—German Patents 295,202 (May 31, 1914) and 295,203 (June 23, 1914).

11—French Patent 468,427, p. 1 (February 13, 1914).

12—Fischer, *Brennstoff-Chem.*, **4**, 276 (1923).

13—Dreyfuss, French Patent 492,154 (August 12, 1916, with addition of March 27, 1917).

14—Lush, British Patent 180,016 (February 12, 1921).

15—Calvert, *Chem. Age* (*London*), **5**, 153 (1921).

16—Patart, French Patent 540,343 (August 19, 1921, published July 12, 1922).

17—Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 469 (1905).

18—Sabatier and Mailhe, *Ibid.*, [8] **20**, 302 (1910). See also Sabatier, "La Catalyse en Chimie organique," **1920**, p. 256.

19—Lamb, Bray, and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920); Armstrong, *Proc. Roy. Soc.* (*London*), **102A**, 714 (1922); Medsforth, *J. Chem. Soc.* (*London*), **123**, 1452 (1923).

20—German Patents of February 22, 1923 (with addition of March 19, 1923), February 24, 1923 (with additions of March 19, April 4, and September 15, 1923), March 3 and 16, 1923, April 5, 1923 (with addition of April 11, 1923), April 21 and 30, 1923, May 8, 1923, May 22, 1923 (with addition of January 19, 1924), and July 2, 1923. These patents to the writer's knowledge have not yet been issued by the Patent Office. French Patents 571,285 (September 29, 1923), 571,354, 571,355, and 571,356 (October 1, 1923), 575,913 (January 17, 1924), 580,915 (April 30, 1924), 580,949 (May 1, 1924), 581,816 (May 19, 1924), 585,169 (September 2, 1924).

Gold chloride in consignments exceeding 50 grams net weight and silver nitrate and silver chloride in excess of 500 grams may now be exported from Germany without an export license.