# Liquid Fuels from Water Gas[1]

By Franz Fischer[2]

KAISER WILHELM INSTITUT FÜR KOHLENFORSCHUNG, MÜLHEIM, GERMANY

IN ALL countries the need for liquid fuels, particularly for light motor fuels, is continually increasing. America is in the fortunate position of having abundant supplies of petroleum and gasoline-containing natural gas, which may be used partly directly and partly through cracking processes. Europe, on the contrary, particularly Middle and Western Europe, is poor in petroleum resources and is therefore forced to import, or to prepare artificial liquid motor fuels. The sources of the latter are the coals and shales, which by suitable distillation processes yield a small percentage of their weight of such fuels. Larger quantities may be obtained from coal by hydrogenation under pressure by the Bergius processes. This paper, however, describes only the newest synthetic processes.

Our teacher in the art of synthesis, Nature, starts in the plants with carbon dioxide, adds it to the chlorophyl, which thus acts as the catalyst, and under the influence of the energy of light, splits off oxygen, while simultaneously by the action of water carbohydrates are formed, a process which is universally known as assimilation. In the synthesis of fuels the chemist starts, not with carbon dioxide, but because of its lower oxygen content, with carbon monoxide, which is easily produced by direct technical processes. Attempts to prepare formaldehyde by the direct addition of hydrogen to carbon monoxide according to the equation

$$CO + H_2 = CH_2O$$
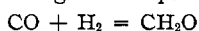
were made long ago, but without success. Equally unsuccessful have been attempts to produce methanol by the addition of twice this amount of hydrogen according to the equation

$$CO + 2H_2 = CH_3OH$$
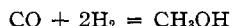
Even the master in the field of catalysis, Sabatier, has failed completely. The reasons are well known today. These reactions require the use of high pressures, just as with Haber's ammonia synthesis, so that the decomposition of the new molecules formed may be suppressed.

Known Carbon Monoxide Reactions

Of the reactions of carbon monoxide which must be considered in the present case, the following were known twelve years ago:

1—The so-called decomposition of carbon monoxide in contact with finely divided metals of the iron group according to the equation

$$2CO = C + CO_2$$

This reaction could only be of interest if hydrogenation of the liberated carbon could be carried to the point of yielding higher hydrocarbons. This seemed possible since the oxidation of this carbon with nitric acid forms not only carbon dioxide, but also much mellitic acid. By hydrogenation, on the other hand, we have up to now been able to obtain only methane, which can be obtained in much simpler ways.

2—The catalysis of Sabatier and Senderens, using finely divided nickel and an excess of hydrogen, yields methane and water almost quantitatively according to the equation

$$CO + 3H_2 = CH_4 + H_2O$$
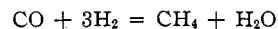
However, it had not been possible to stop the reaction at the stage of formaldehyde or methanol formation, although strong efforts were made by many investigators, particularly through the addition of substances which could stabilize or cause the rearrangement of these intermediary products.

3—Indirectly, however, methanol and higher boiling products were obtained long ago by Lieben. It is known that under pressure carbon monoxide and metal hydroxides react easily to yield formates.

$$KOH + CO = HC\overset{\displaystyle OK}{\diagup}\!\!\!= O$$

and analogously

$$Zn(OH)_2 + 2CO = Zn$$

The starting point in the synthesis of liquid fuels from water gas is always carbon monoxide. The various known reactions with carbon monoxide and various catalysts are discussed with regard to their possible use in devising a process for the production of synthetic fuels. Processes are finally developed for the formation, first, of synthetic methanol, then of a mixture of synthetic alcohols called "Synthol," and finally from Synthol of a mixture of products similar to benzine or gasoline, called "Synthin."
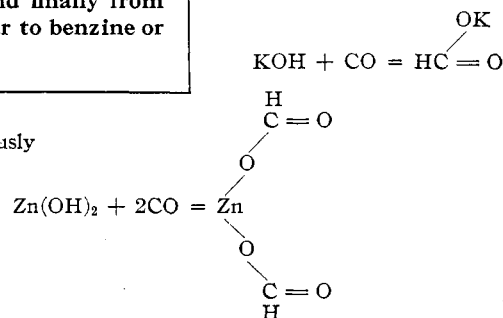
When these formates are decomposed by heating they behave quite differently. Whereas potassium formate gives first potassium oxalate and hydrogen, zinc formate gives in good yields formaldehyde, methyl formate, and methanol. This remarkable property of zinc formate was shown about eight years ago by K. A. Hofmann. Tin formate, according to Goldschmidt, decomposes almost quantitatively to yield formaldehyde, but from the solid residue the formate cannot be regenerated by carbon monoxide, as is the case with zinc formate.

As opposed to the reaction of hydrogen with carbon monoxide at ordinary pressures in the presence of finely divided nickel, the formation and decomposition of the formates give a means of preparing methanol from carbon monoxide. Immediately there arises the idea of combining the formation and decomposition of the formates into one process. Although the formation of sodium and potassium formates takes place readily at ordinary or low pressures, the other formates require carbon monoxide under high pressure, so that for the unification of these processes the use of compressed gases cannot be avoided. As already mentioned, other considerations also point to the necessity for the use of a high pressure.

If we assume that in Sabatier's experiments no formaldehyde or methanol was obtained because at the temperatures necessarily used these compounds break down again at ordinary pressures, or because the amount that remains at equilibrium with carbon monoxide and hydrogen at atmospheric pressure is almost zero, then we may hope to obtain better results at high pressures, just as in the ammonia synthesis. In fact, various patents of the Badische Anilin und


Sodafabrik for 1913 and 1914 contain claims for the production of liquid reduction products from carbon monoxide. The gas mixture used was carbon monoxide and hydrogen, preferably with an excess of the former. Pressures over 100 atmospheres and temperatures of 360° to 420° C. are stated to be suitable, the catalyst being metals, especially of the iron group, impregnated with basic substances. Zinc and zinc oxide are also proposed. The reaction products are described as a mixture of oily substances consisting mainly of hydrocarbons and a mixture of water-soluble substances, said to comprise aldehydes, acids, ketones, and alcohols. Except for this and a few other patent claims, until two years ago there were no exact scientific publications concerning the high-pressure hydrogenation of carbon monoxide.

In 1923, Tropsch and the writer published an article concerning the formation and composition of Synthol, and there recently has appeared an article by Patart concerning the exclusive formation of methanol using zinc oxide as a catalyst. For the sake of completeness it may also be mentioned that for a year previous to the appearance of Patart's article the Badische Anilin und Sodafabrik was producing many tons of methanol daily, and it is reported that several shiploads of synthetic .methanol have already been exported to America.

As opposed to the ammonia synthesis in which hydrogen and nitrogen unite to form one product, we have here three components—hydrogen, carbon, and oxygen—and therefore the almost endless possibilities of organic chemistry before us. The formation of three synthetic products—methanol, Synthol, and Synthin—will be described. A trace of the first reduction product of carbon monoxide, formaldehyde, may be shown to exist in the products of the high-pressure catalysis, but it seems to be too unstable at the formation temperature and, therefore, to decompose again or to rearrange into more stable substances, such as methyl formate or methanol.

Methanol

The first and until now the only publication in the scientific literature concerning the formation of methanol of high purity is that of Patart.[3] Before this, there appeared, in 1922, a brief note by Calbert which gave no exact data but claimed a production of methanol in 80 per cent yields, Patart's patent of 1922, and new patents of the Badische Anilin und Sodafabrik in 1923 concerning the synthesis of methanol. In the Badische patents, and especially in Patart's article, the more exact reaction conditions are set forth. The most suitable gas mixture is the theoretical one, methanol being obtained with zinc oxide as a catalyst at 400° C. and over 150 atmospheres pressure according to the equation

$$CO + 2H_2 = CH_3OH$$
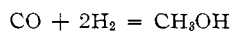
To avoid side reactions metals of the iron group must be absent. The contact chamber must therefore be lined with copper. The writer can confirm Patart's statements that zinc oxide is the best catalyst for methanol formation, but it is not the only one. Patart used zinc oxide because he found in the literature that at temperatures below red heat it decomposed methanol readily into carbon monoxide and hydrogen, in opposition to other catalysts. He concluded from this that the same catalyst at high pressures should cause the reverse reaction, and success followed.

Nevertheless, we really know nothing as yet concerning the mechanism of the process. Audibert tends to assume that the hydrogen partly transforms the zinc oxide to the lower or suboxide, and that this suboxide acts as a hydrogen carrier—as, for example, does finely divided nickel. Although

[3] See Lormand, This Journal, **17**, 430 (1925).

the nickel-hydrogen compound has actually been isolated by Schlenk, the similar compound of zinc is not yet known. We seem, therefore, entitled to consider other explanations beside that of the catalytic addition of hydrogen—for example, the transitional formation and decomposition of zinc formate, which has already been mentioned. This explanation contains some difficulties, however, since the presence of water is necessary for the formation of formates from zinc oxide and carbon monoxide. Perhaps some addition compound of carbon monoxide with the zinc oxide is formed, which easily takes up hydrogen to form basic zinc methylate, the latter decomposing again to zinc oxide and methanol.

Zinc oxide evidently has special properties—it is not reduced by hydrogen to the metal; if carbonate is formed, it decomposes again below 400° C. to zinc oxide and carbon dioxide; it therefore cannot be easily changed permanently, although it is a fairly strong base. These three properties place it in a special position, which is perhaps the cause of its exceptional activity in the present case.

The yield of methanol, using zinc oxide as catalyst, is almost theoretical, as Patart has stated and as the writer's results also show. The crude reaction product distils 93 per cent below 80° C. and contains only traces of acids. If the temperature is kept below 400° C., there is only a 1 per cent yield of methane in the residual gas, since the undesired side reactions which lead to methane formation are thus avoided. After weeks of constant operation the zinc oxide catalyst was found to be still pure white, showing the absence of that even less desirable side reaction, the splitting of carbon monoxide to carbon and carbon dioxide. The remarkable yields of methanol are thus explained.
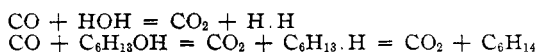
Formation of Synthol

From the standpoint of the catalytic preparation of good motor fuels from carbon monoxide and hydrogen, the methanol process is not especially suitable. It is even less useful than ethyl alcohol, which, when used as such, has few friends. If we consider the splitting of water from the various alcohols, then with methanol we have 1 molecule of water per CH_2 group, with ethyl alcohol $1/2$ molecule, with propyl $1/3$, with butyl $1/4$, and so forth, and the heating value becomes increasingly better. Moreover, a mixture of such alcohols is more suitable than a single one.

Experiments conducted by the writer have been directed toward the study of the formation, not of pure methanol, but of the higher alcohols. With the information afforded by the Badische Anilin und Sodafabrik patents of 1913–14, but without further knowledge of their actual plant processes, investigation was made of the best conditions for the formation of the previously mentioned synthetic oils, which for the sake of simplicity have been called "Synthol," and to study the composition and properties of these products. Contrary to the directions given in these patents, the writer worked with an excess of hydrogen, hoping thus to avoid the highly disagreeable splitting of the carbon monoxide to carbon and carbon dioxide—this hope being in fact realized. The patents state that, in addition to an aqueous layer, an oily layer is formed which is lighter than water and consists mainly of hydrocarbons. On the contrary, the writer has obtained an oily layer which contains almost no hydrocarbons but which consists largely of the higher alcohols and ketones with smaller amounts of aldehydes and acids. It might well have been expected that, using excess hydrogen, the product would consist, not largely, but almost exclusively of hydrocarbons. The astonishment was therefore great, and the interpretation of the observed results will be of interest. At 400° C. in the presence of the iron-alkali catalyst, excess carbon monoxide as present in the Badische process has the same deoxygenating

action on alcohols that it has upon water (the water-gas equilibrium).

$$CO + HOH = CO_2 + H.H$$
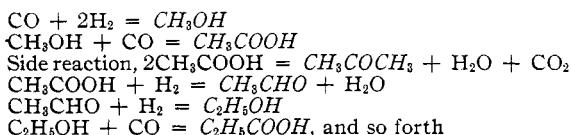$$CO + C_6H_{13}OH = CO_2 + C_6H_{13}.H = CO_2 + C_6H_{14}$$

Thus, the unexpected results are easily explained on the basis of the conditions of the experiments, excess carbon monoxide transforming the alcohols into hydrocarbons.

The formation of Synthol takes place best at pressures of 150 atmospheres, using as a catalyst iron filings impregnated with strong bases. The most favorable temperature is about 400°–420° C. Moreover, although the use of strong bases leads to the formation of oily products, with weak bases only water-soluble products are obtained. The relationship between these reactions and the methanol synthesis is shown by the following experiment: If a contact tube containing zinc oxide is used, and behind this but separated from it is an iron-alkali catalyst, Synthol is formed. Without the iron catalyst but with all other conditions the same, methanol only is obtained.

It can therefore be concluded that the methanol formed by the zinc oxide is further changed in the presence of carbon monoxide and hydrogen and under the influence of the iron-alkali catalyst, larger molecules being formed by condensation or other reactions. This idea is confirmed by experiments reported two years ago in an article from the writer's laboratory, which showed that methanol heated at 400° C. with an iron-alkali catalyst in a steel autoclave gives partial decomposition to gases and also yields oily reaction products.

It is not yet clearly evident in just what way the formation of Synthol takes place. A possible scheme may be set up as follows:

$$CO + 2H_2 = CH_3OH$$
$$CH_3OH + CO = CH_3COOH$$
Side reaction, $2CH_3COOH = CH_3COCH_3 + H_2O + CO_2$
$$CH_3COOH + H_2 = CH_3CHO + H_2O$$
$$CH_3CHO + H_2 = C_2H_5OH$$
$$C_2H_5OH + CO = C_2H_5COOH, \text{ and so forth}$$

It is thus seen that carbon monoxide and hydrogen are used up in the same proportions in which they are present in the starting gas (1 part CO to 2 parts H_2).

The writer has found all of the above italicized products, partly in the aqueous layer, partly in the oily layer. The higher homologs, which are formed by the alternating action of carbon monoxide and hydrogen, are found only in the oily layer—that is, in the Synthol. This synthesis apparently yields compounds with as many as nine carbon atoms, but small quantities of solid white waxy substances have also been obtained. It is not remarkable that at 400° C. these reactions do not go beyond compounds with nine carbon atoms, since we know from the cracking process that at this temperature the higher aliphatic compounds are unstable, breaking down to smaller molecules. In addition to the compounds specifically mentioned above, the following have been found in Synthol, the principal products being alcohols and ketones:

Propyl alcohol, and higher alcohols up to C_9
Isobutyric acid and higher acids up to C_9
Isobutyraldehyde, and higher aldehydes
Acetone, methylethyl ketone, diethyl ketone,
methyl-*n*-propyl ketone
About 2 per cent of various esters
About 1 per cent of hydrocarbons

As for the practical utilization of Synthol, it should be stated that 87 per cent distils below 200° C., so that almost all of the crude product, after washing free from acids, can be used as light motor fuel, as practical experiments with motor vehicles have proved. Some of the physical data of Synthol are therefore of interest.

**Properties of the Oil Distilled below 200° C.**

Color, light yellow, not darkening on standing
Specific gravity 20°/4° C. = 0.8289
Carbon 69.3 per cent, hydrogen 12.3 per cent
Higher heating value, 8200 calories per kg.
Lower heating value, 7540 calories per kg.
Thickening point; At −30° C. separation begins, but the oil is still
nonviscous. Complete solidification occurs at
−90° C.
Boiling range;

Temp., ° C.	62–80	100	120	140	160	180	200
Per cent	11	37	64	76	84	91	97

The utilization of the heating value of the original gas mixture (1CO + 2H_2) is not so efficient in the case of Synthol as with methanol, as Audibert has recently pointed out. The reaction

$$CO + 3H_2 = CH_4 + H_2O + x \text{ cal.}$$
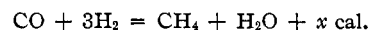
is exothermic, heat being liberated. The heat content of the 1 molecule of methane on the right-hand side of the equation is only 77 per cent of that of the 4 molecules on the left; 23 per cent of the available heat on the left-hand side has thus been lost in the formation of methane. The formation of methanol is similar, the reaction being likewise exothermic:

$$CO + 2H_2 = CH_3OH + y \text{ cal.}$$
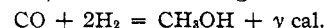
Eighteen per cent of the available heat is lost, the right-hand side thus having only 82 per cent of the heating value of the left-hand side. In the isopropyl alcohol formation the loss in available heat is 23 per cent; with dimethyl ketone it being about the same. Thus, although in the formation of methanol the exothermic character of the reaction causes a heat loss of 18 per cent, the loss in the formation of Synthol must be about 25 per cent. The writer does not believe, however, that this unavoidable loss in the heating value is of practical significance, because a molecule of methanol or, on the other hand, an "average molecule" of Synthol is much more valuable economically than the molecules of carbon monoxide and hydrogen necessary for its formation. However, although in the case of methanol it has been possible to obtain almost theoretical yields on material, and hence almost the theoretical 80 per cent yield of available heat, in the case of Synthol it has not yet been possible to attain more than about half of the theoretical 70 to 75 per cent yield in heating value. The reason appears to be the complexity of the reactions involved. If no carbon is deposited on the catalyst, this loss is represented mainly by the hydrocarbons of the residual gas—that is to say, by its content of methane, ethylene, and their homologs. It seems certain, however, that technical developments in the process will bring improvements in this respect.

Formation of Synthin

If Synthol is heated alone at 400° C. in a steel autoclave (at ordinary pressures it decomposes at 400° C. into gases) it is transformed in one hour into a petroleum-like liquid with the simultaneous formation of water and gases. About half of this liquid consists of saturated hydrocarbons, the other half being soluble in concentrated sulfuric acid. The saturated hydrocarbons have a petroleum-like odor, on analysis giving a carbon-hydrogen ratio of 1:2, while their fraction boiling over 150° C. gives a ratio of 1:1.8 to 1:1.6. Apparently, the first reaction is the splitting of water from the alcohols of the Synthol to form olefins, while from these in some way naphthenes are formed. The fact that the Synthol, composed mainly of alcohols, is thus transformed into a synthetic mixture of products similar to benzine or gasoline was the reason for giving the name "Synthin" to this product.

To be sure, this transformation of Synthol into Synthin is of no practical significance, but it is nevertheless interesting in many respects. For example, it shows that under the proper circumstances, naphthenic petroleums can be formed from water gas of volcanic origin.