

## CHAPTER IV

# SYNTHETIC PROCESSES

THE recovery of oil from coal by dry distillation is essentially a destructive method based upon the thermal decomposition of the ulmins, and particularly of the bituminous constituents of coal. Products of low boiling range are formed only to a small extent and by a far-reaching breaking-up of the large molecules of the higher primary tar constituents. The large size of the molecules of the compounds forming coal itself explains its behaviour on distillation, *i.e.*, the fact that thermal decomposition of the bitumen and the other coal constituents yields predominantly products of high boiling points.

It is to be expected that a synthetic method, starting from very small molecules, is more likely to lead to low-boiling motor fuels than the destructive method. The simplest way of resolving coal into small molecules is to gasify it, or its carbonising residue, semi-coke or coke. It is undoubtedly advantageous first to recover the primary tar—if the coal is suitable—and then to gasify the semi-coke, as explained in Chapter III.

Carbon may be gasified by passing carbon dioxide over it at about 900° to 1000°, forming carbon monoxide according to the equation:  $C + CO_2 = 2CO - 37,320$  cal. If steam is substituted for carbon dioxide the reaction is:  $C + H_2O = CO + H_2 - 26,990$  cal. The water-gas, thus produced, is the most convenient raw material for the preparation of "Synthol."\* The fact that in generators semi-coke and coke can be almost completely converted into water-gas, with a thermal efficiency of about 80 per cent., is a promising basis for attempts at synthesising liquid combustibles from this gas.

### (a) THE ACTION OF ELECTRIC DISCHARGES

The first experiments successful in effecting a combination of carbon monoxide with hydrogen, with the formation of liquid products, were probably those using electric discharges. Losanitsch and Jovitschitsch<sup>158</sup> submitted mixtures of CO and H<sub>2</sub> to the silent electric discharge. The chief product obtained was formaldehyde, which was transformed into oily condensation products among which they found glycollaldehyde to predominate.

In a similar way, Berthelot<sup>159</sup> obtained a solid compound which he regarded as a carbohydrate.

Slosse<sup>160</sup> claims to have obtained from 1 vol. of carbon monoxide and 2 vols. of hydrogen, a water-soluble body of the general character of a sugar; other investigators, *e.g.*, Löb,<sup>161</sup> are not in agreement with these findings.

De Hemptinne<sup>159a</sup> replaced carbon monoxide and hydrogen by carbon monoxide and hydrocarbons, and obtained peculiar condensation products of aldehydic or ketonic character. From methane and carbon monoxide he obtained

\* The term "Synthol" has been chosen as a brief designation of the oxygenated synthetic oils produced from carbon monoxide by catalytic processes.

an aldehyde; from ethane and carbon monoxide, acetone, possibly according to the equation:  $C_2H_6 + CO = C_3H_6O$ .

Losanitsch<sup>162</sup> obtained a yellow-brown solid mass from acetylene and carbon monoxide, whilst ethylene and carbon monoxide gave a clear thick yellow-red oil. Benzene also combines with carbon monoxide under the influence of the silent electric discharge, forming a thick dark fluid.

Hultgrén<sup>163</sup> heats gaseous hydrocarbons, carbon monoxide or dioxide, in an electric high-tension arc or a spark gap to temperatures between 2000° and 4000°. The mixtures are said to condense directly, without application of pressure, to volatile oils, with heavy hydrocarbons as intermediate products. The gases are passed in a continuous stream through an electric arc, and then through a cooler, in which a portion is condensed to a very volatile liquid; 2 kilowatts are stated to be required per litre of liquid. The yield of liquid obtained varies with the material; acetylene gives 60 per cent., carbon monoxide and hydrogen give 80 per cent., carbon dioxide and hydrogen 50 per cent. of the quantity used. The unconsumed gases can be returned to the furnace. The liquid produced from acetylene boils at 85.3°, has a specific gravity of 0.723, and consists of hydrocarbons intermediate between the methane and the acetylene series. These results sound very promising, but they have so far not been confirmed by other workers.

#### (b) CATALYTIC EXPERIMENTS AT ORDINARY PRESSURE

The action of hydrogen on carbon monoxide has been the subject of many investigations. In the most noteworthy of these Sabatier<sup>164</sup> showed that, in the presence of finely-divided nickel, carbon monoxide with three times its volume of hydrogen can be converted almost completely into methane and water. At the temperature recommended, 230–250°, methane is formed rapidly, without side reactions. Above 250°, the reaction becomes more complex; carbon monoxide is then partly decomposed in the presence of nickel to carbon and carbon dioxide:  $2CO = C + CO_2$ , and this reaction becomes steadily more marked as a temperature of 250° is exceeded. The carbon dioxide formed may itself be again hydrogenated by hydrogen in contact with nickel, so that the extent of the secondary reaction:  $2CO = C + CO_2$ , must be judged not so much by the carbon dioxide formed as by the carbon deposited. At 380°, the theoretical mixture ( $CO + 3H_2 = H_2O + CH_4$ ) gives a gas of a totally different composition:  $CH_4$ , 67.9 per cent.;  $H_2$ , 21.6 per cent.;  $CO_2$ , 10.5 per cent.

At the same temperature, water-gas (equal volumes of hydrogen and carbon monoxide) in the presence of nickel gives 52.6 per cent.  $CO_2$ , 39.8 per cent.  $CH_4$ , and 7 per cent.  $H_2$ . If the carbon monoxide in the gas mixture is increased above that in water-gas, hydrogenation is further depressed, much hydrogen and carbon dioxide remaining unaltered.

Sabatier found further that carbon dioxide, like carbon monoxide, can be easily reduced to methane with nickel as catalyst:  $\text{CO}_2 + 4\text{H}_2 = 2\text{H}_2\text{O} + \text{CH}_4$ . This reaction required a somewhat higher temperature; between  $300^\circ$  and  $400^\circ$  it proceeded rapidly without appreciable side reactions. With an excess of hydrogen above the four volumes required by theory, the carbon dioxide disappears almost entirely. The gas resulting at  $300^\circ$  consists of methane, an excess of hydrogen and some carbon dioxide, and there is no deposition of carbon nor formation of carbon monoxide.

Neither the experiments of Sabatier nor corresponding technical investigations (Cedford process) indicated the formation of intermediate products, or of liquid hydrocarbons.

There are a few observations which suggest reactions in the reduction of carbon monoxide other than the formation of methane. Orloff<sup>165</sup> states that a mixture of equal volumes of hydrogen and carbon monoxide, heated to about  $95$ – $100^\circ$  in the presence of a special catalyst, yields a few per cent. of ethylene. This catalyst consisted of pieces of coke coated with nickel and palladium by impregnating them with a solution of nickel nitrate, drying and calcining them in a nickel dish over a flame; they were then impregnated with a solution of ammonium-palladium chloride, dried, and calcined. To effect reduction, they were heated in a copper tube in a current of methyl alcohol vapour, the last traces of the alcohol being expelled in a drying oven. It is not stated why hydrogen was not used for the reduction, instead of methyl alcohol, traces of which might make the results of the subsequent experiments doubtful. Two glass U-tubes were filled with the catalyst and placed in a water-bath. A current of hydrogen and carbon monoxide in equal proportions was passed through the tube, when a gas was formed of the composition: Oxygen 1.5 per cent., carbon monoxide 42.9 per cent., hydrogen 43 per cent., ethylene 6.6 per cent., nitrogen 6 per cent. An objection to these experiments is that the ethylene could not be removed with bromine water, but that after absorbing oxygen and carbon monoxide in the usual way, hydrogen and ethylene were mixed with air and burned over palladium asbestos, and the  $\text{CO}_2$  formed was absorbed by caustic potash. The objection to this course of analysis is that incomplete absorption of carbon monoxide would account for carbon dioxide in the palladium combustion. Orloff states expressly that no methane was formed at the low temperatures he employed.

In contradiction to Orloff, Breteau<sup>164</sup> claims to have found that carbon monoxide can be hydrogenated to methane with palladium as catalyst, in the cold and better at  $100^\circ$ .

Fester,<sup>166</sup> repeating Orloff's experiments, took pieces of pumice stone, impregnated them with nickel nitrate, calcined them in a nickel crucible, impregnated again with ammonium palladium chloride (1 gram of solid salt per 10 grams of pumice of pea size) and calcined again. The pumice thus prepared

was reduced by hydrogen, charged with methyl alcohol vapours, in a copper tube at 600°. After 1 hour, the tube was cooled in a current of hydrogen. Why Fester also used the quite unnecessary methyl alcohol is not intelligible; it certainly casts some doubt on the results. To repeat Orloff's experiment strictly, he would have had to use coke instead of pumice stone. The reduced pumice stone was charged into an electrically-heated glass tube, and a mixture of equal parts of hydrogen and carbon monoxide was passed over it at the rate of 2 litres per hour and at 90–100°; before entering the tube the gas mixture was bubbled through water and dried over soda-lime. There is, unfortunately, no analysis of the gas before treatment. After leaving the catalyst tube it contained 4.7 per cent. by volume of unsaturated compounds, absorbed by bromine water. In agreement with Orloff, no methane was found. Fester states that the catalyst rapidly became ineffective, and that after a few experiments no reduction would take place.

One cannot but conclude that neither in the experiments of Orloff, nor in those of Fester, the conditions of ethylene formation were clearly recognised. It is regrettable that in both cases the catalyst was reduced with the aid of methyl alcohol; the suspicion naturally arises that the appearance of ethylene at the beginning of the experiments was due to traces of this alcohol.

Fester<sup>167</sup> recently repeated his experiments under conditions free from objections, when he did not succeed in establishing the formation of ethylene.

Medsforth<sup>168</sup> recently studied from a novel point of view the formation of methane by the hydrogenation of carbon monoxide with nickel as catalyst. He observed that the reaction is much accelerated by the addition to the nickel of promoters\*† which favour dehydration. Thoria and alumina‡ were found to be particularly active in this respect. Medsforth discusses the possibility of arresting the reaction by suitable additions to the catalyst before it reaches the methane equilibrium, and thus of obtaining interesting intermediate products. The results of several attempts made in this direction were, however, negative. Winkelmann§ has succeeded in obtaining very small quantities of formaldehyde as an intermediate product by passing water gas quickly through narrow quartz tubes, heated to 450°.

The experiments so far discussed in this section prove that liquid combustible products are not formed at ordinary pressure.

\* Kita and Mazume, *Z. angew. Chem.*, 1923, 36, 389, also proposed promoters such as alumina, magnesium oxide, magnesium phosphate, calcium phosphate and borate for the catalytic hardening of fats. The promoters to be efficient must be added before reduction of the nickel oxide, and there is an optimum quantity in each case.

† The need of securing an intimate mixture of the promoter and the catalytic metal, e.g. by common precipitation, was pointed out in a patent (D.R.-P. 307580) published in 1918, of the B.A.S.F., concerning both the reduction of carbon monoxide to methane and fat hardening.

‡ Adkins and Nissen (*J. Amer. Chem. Soc.*, 1923, 45, 809) connect the catalytic activity of  $\text{Al}(\text{OH})_3$  with the distance between the atoms, which is said to vary with the size and structure of the salt molecule from which the  $\text{Al}_2\text{O}_3$  has been prepared by calcination.

§ Unpublished.

## (c) LIQUID HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN UNDER PRESSURE

In Friedländer's *Fortschritte der Teerfarbenfabrikation*, 12, 899 and 901, patents of the Badische Anilin- und Soda-Fabrik are recorded, dealing with the production of liquid hydrocarbons and their derivatives by submitting carbon monoxide and hydrogen to a contact process under pressure. The patents emphasise the fact that mainly liquid hydrocarbons are formed, and it is pointed out that in order to obtain liquid products, the hydrogen content should be reduced to, say, 1 part of hydrogen for 2 or more parts of carbon monoxide. All that is known about the process is that it does not yield the uniform products anticipated for the purposes of the chemical industry, but a very complex mixture of the most diverse bodies.

In the absence of other data in the literature, and as in the chapter on the "Synthol Process" a method will be described which works with an excess of hydrogen, whereby other products are obtained, the patents are here quoted *in extenso*.

British Patent No. 20488 of 10 Sept., 1913. Improvements in the Manufacture of Hydrocarbons and Derivatives thereof. (Corresponding German Patent No. 293787.)

"It is known that methane can be obtained from carbon monoxide, or carbon dioxide, and hydrogen at a raised temperature by means of catalytic agents (particularly nickel), and it has also been stated that by altering the conditions of the experiment, small quantities of formaldehyde and ethylene are also sometimes produced. Lipinski, in the Specification of Letters Patent No. 1325, 1913, describes the conversion of coal gas, or similar gases containing carbon monoxide and hydrogen, into methane mixture by passing the highly compressed gas, or gases, over a catalytic agent, so that the rate of reaction is increased and the conversion takes place more rapidly and efficiently.

"We have found that a new result can be obtained, and a number of organic compounds be built up, when working under pressure under suitable conditions as hereinafter explained, that is to say, we have found that easily liquefiable hydrocarbons, and oxygen compounds of hydrocarbons, can be obtained by passing a mixture, containing carbon monoxide and hydrogen in the proportion of at least two-thirds of a volume of carbon monoxide to each volume of hydrogen, over a heated catalytic agent under high pressure, that is to say, a pressure exceeding that of 5 atmospheres. The carbon monoxide and hydrogen can be passed either alone, or in admixture with other gases, over the heated catalytic agent. According to the nature of the catalytic agent employed and the conditions of working, different compounds, or mixtures, for instance, liquid hydrocarbons, either saturated, or unsaturated, and alcohols,

aldehydes, ketones and acids, are obtained. In order to obtain larger quantities of liquid compounds, it is often advantageous to employ gas mixtures in which the percentage of hydrogen contained is comparatively small, for instance, the quantity of carbon monoxide is preferably two, or three, times as much as the hydrogen reckoned by volume. As instances of catalytic agents which can be employed for the purposes of this invention, I mentioned cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, zinc, and oxides, or other compounds of these metals, and, if desired, mixtures of two, or more, of these catalytic agents can be employed; and it is often advantageous to add a basic compound, such, for instance, as alkali hydroxide, but this invention is not limited to the use of the foregoing specific catalytic agents.

“Although the advantages of this invention can be obtained by working at any pressure above about 5 atmospheres, we prefer to employ pressure ranging say from 20 atmospheres upwards.

“The following examples will serve to illustrate how this invention may be performed, but it is not confined to these examples.

#### *Example 1*

“Impregnate pure asbestos with pure cobalt oxide, or osmium oxide, together with a little caustic soda and then, while employing a coppered iron vessel with steel jacket and working at a pressure of 100 atmospheres and a temperature of from 300° to 400° Centigrade, pass over the catalyst thus prepared a mixture containing 1 part of pure hydrogen and 2, or more, parts of pure carbon monoxide. During the reaction some carbon is deposited and some water and carbon dioxide are produced, while, in addition to methane, higher hydrocarbons, as well as oxygen derivatives of the hydrocarbons, are formed and can be at once condensed, or absorbed, in a cold receiver. Generally an aqueous solution of aldehydes and the like is obtained in addition to a light oily liquid consisting chiefly of saturated and unsaturated hydrocarbons of boiling points up to 250° Centigrade, or even higher. It is preferred to maintain the receiver under the same pressure as the reaction space and to effect the condensation by cooling. If desired, fractionated cooling can be effected, either releasing the pressure, or not.

#### *Example 2*

“Impregnate a suitable carrier (for instance, calcined magnesia, pumice stone, or diatomite) with potassium carbonate solution and then dry the mass and introduce it into a concentrated solution of zinc nitrate. Pour off the liquid, and dry and heat the contact mass and place it in a suitable vessel and, whilst employing a pressure of 120 atmospheres, and a temperature of from 360° to 420° Centigrade, pass through the vessel a gas mixture

containing 62 per cent. of carbon monoxide, 28 per cent. of hydrogen, 4 per cent. of carbon dioxide, 2 per cent. of methane and 4 per cent. of nitrogen. The products consist chiefly of higher hydrocarbons and derivatives thereof. In this case carbon is generally not deposited, or it is at most deposited to but a slight extent. The greater part of the products capable of liquefaction, or absorption, can be separated at ordinary temperature, and the remaining gas generally contains olefines, such as ethylene and propylene, and paraffins, such as methane and possibly ethane. Analysis of the products obtained shows that the oily layer consists chiefly of hydrocarbons of boiling points of from 20° to well above 200° Centigrade. For instance, one experiment yielded a mixture of which paraffins, olefines, and benzene hydrocarbons each constituted about one quarter, while the remaining quarter consisted of other hydrocarbons, both saturated and unsaturated, but these proportions will vary considerably. In addition to the said hydrocarbons, organic oxygen compounds of various kinds are contained dissolved in the hydrocarbons. The oily layer, either before, or after, special purification, has the character of the natural ethereal oils. Analysis of the aqueous layer shows a varying content of saturated and unsaturated organic compounds consisting, for instance, of alcohols, ketones (such as acetone), aldehydes (such as formaldehyde), acids (such as acetic acid and higher homologues thereof), and also other condensation products.

“When the gas mixture employed is not sufficiently pure, but contains traces of substances deleterious to the reaction, the gases may be specially purified, for instance, by passing them, before use, and at a raised temperature, through a purifier containing material similar to that employed as the catalytic agent. The gases leaving the receiver can be used over again after correcting their contents; for instance, by removing carbon dioxide and adding hydrogen, and the whole process can be carried out under continuous pressure.

#### *Claims*

“1. The manufacture of easily liquefiable hydrocarbons and oxygen compounds of hydrocarbons, by passing a mixture containing carbon monoxide and hydrogen in the proportion of at least two-thirds of a volume of carbon monoxide to each volume of hydrogen over a heated catalytic agent under high pressure, that is to say, a pressure exceeding that of 5 atmospheres.

“2. The manufacture of easily liquefiable hydrocarbons and oxygen compounds of hydrocarbons, as described in each of the foregoing examples.”

German Patent No. 295202. Process of Manufacture of Hydrocarbons and their Derivatives. Addition to Patent No. 293787.

According to Patent No. 293787, hydrocarbons, particularly of liquid or liquefiable nature, and compounds derived from hydrocarbons are obtained by making oxides of carbon react at high pressure with hydrogen in the presence of catalysts.

In carrying out this process, especially in the presence of carbon monoxide in the gas mixture, it has proved advantageous to use contact materials of high thermal conductivity. By this means it is possible to avoid the possibly violent dissociation of carbon monoxide with deposition of carbon and consequent local superheating.

In the preparation of contact materials of high thermal conductivity, the catalyst deposited upon ceramic carriers may be mixed with pieces of metals such as copper and the like, granulated or in rod form; or the catalyst may be deposited upon metals of high heat-absorbing and conducting powers, or the catalytic metal may be used directly, compact in the shape of chips, wool, or wire gauze, suitably activated previously. It will be advisable at the same time to provide, by proper temperature control in the reaction chamber, for a constant temperature.

#### *Example*

Pure nickel wire gauze (*e.g.*, in the shape of rolls) suitably etched and activated by means of materials like alkali, zinc oxide, cobalt oxide, etc., is introduced into a tube capable of resisting high pressure and lined internally with copper. The tube is uniformly heated, *e.g.*, in a bath to about 350° to 400°, and a gas mixture containing 1 to 2 vols. of carbon monoxide to 1 vol. of hydrogen preheated and compressed to 100 atm., is introduced. As soon as the reaction sets in, the rate of gas feed and the heat supply and heat withdrawal are regulated; higher hydrocarbons are then formed at a uniform rate. The gas may contain small amounts of iron carbonyl.

In the special case of the preparation of acetone from acetic acid, good thermal conductors have already been used as carriers for the reacting material. This method, in an entirely different branch, did not offer any guarantee, however, that it would be possible to avoid, in the catalytic treatment of carbon monoxide-hydrogen mixtures under pressure, the diminution in the yield, sometimes occurring with deposition of carbon and the equally undesirable and occasionally dangerous, spontaneous sudden rises in temperature and pressure, by the application of the contact materials of high thermal conductivity claimed. This constitutes a surprisingly new recognition, by virtue of which an extraordinarily important effect is realised.

#### *Claim.*

The manner of carrying out the process according to Patent 293,787 by the application of contact materials of high thermal conductivity.

German Patent No. 295,203. Process for the Manufacture of Hydrocarbons and their Derivatives. Addition to Patent 293,787.

In the treatment of gas mixtures containing carbon monoxide and hydrogen under pressure with catalysts according to the process of Patents 293,787 and 295,202, the reaction is sometimes retarded when metallic catalysts are



being used, the reaction starting at a slow rate and only gradually increasing in intensity.

It has now been found that a satisfactory reaction may be secured from the beginning, when metallic catalysts are used which contain carbon chemically bound or dissolved. Suitable materials of practical utility under this heading are particularly the carbides of the metals of the iron group, as well as the metals mentioned in partly carburised form such as are obtained, *e.g.*, by treating iron with hydrocarbons or carbon monoxide with heating. Other suitable materials are, *e.g.*, cast iron, high-carbon steel, etc., in the shape of shavings, cuttings, etc., or carbides of molybdenum, tungsten, and of other suitable metals. The masses may further be activated by means of alkali and the like. For example, the reaction may be started with a gas mixture which contains, in addition to hydrogen, the same or a larger amount of carbon monoxide; this mixture is treated at 300° to 400° and at a pressure of from 50 to 100 atm.

In the synthetic preparation of ammonia from its elements, use has already been made of the carbides of the rare earths. This reaction, however, did not give any indication that it would be advantageous to use metals containing carbon as catalytic materials for this catalysis, which is of an entirely different kind.

#### *Claim.*

The special manner of carrying out the process of Patent No. 293,787 and the additional Patent 295,202 by the use as catalysts of metals containing carbon.

A patent application of F. Uhde deals with the production of liquid hydrocarbons from methane, in which he proposes to pass a mixture of methane and carbon monoxide over nickel at a temperature between 350° and 500° and to cool the products rapidly (U.5629, class 12 o). The point he emphasises is that the gases should only be left for a short time in contact with the catalyst, perforated nickel sheet coated with spongy nickel placed in a high-pressure nickel tube. He uses equal parts of carbon monoxide and methane at 400°, and does not mention any impregnation of the nickel. The light oil produced is stated to amount to 45 to 50 per cent. of the weight of methane used and to consist of the lower aliphatic hydrocarbons; unconsumed gas is to be re-used.

#### (d) ALCOHOLS AND FORMALDEHYDE FROM CARBON MONOXIDE AND HYDROGEN UNDER PRESSURE

Several other methods have recently been proposed for the reduction of carbon monoxide, by hydrogen under pressure, to formaldehyde and alcohol.

G. C. Calvert,<sup>169</sup> of the Metropolitan Laboratories, claims to have worked

out a new process for the production of alcohols, especially of methyl alcohol, by mixing water gas with gases varied according to the alcohol desired, and passing them through a special apparatus, particulars of which are not given. The alcohol yield is said to be 80 per cent. of the theoretical, at a cost much lower than that from wood distillation. Using products like coke dust, coal dust, or wood waste as raw materials, the alcohol would be cheap enough to serve as liquid fuel.

J. Lush <sup>170</sup> (Brit. Pat. 180,016) passes a mixture of carbon monoxide and hydrogen under a pressure of 10 atm. rapidly over catalysts consisting of a mixture of 4 parts of nickel, 1 part of copper and 5 parts of alumina, and claims to obtain large yields of formaldehyde or of its polymerised derivatives. The residual gas consists mainly of methane and hydrogen. The gas is preferably forced through the catalyst tube at an initial temperature of 300° to 400° under 10 atm. pressure, at a velocity such that the temperature does not drop below 160° to 180° before the gas leaves the catalyst. In order to promote rapid cooling, the compressed gas is led through a constriction and then into water to scrub out the formaldehyde. The activity of the catalyst is restored by periodically blowing steam through it, or by mixing steam with the compressed gas.

Patart <sup>171</sup> (French Pat. 540,543) makes mixtures of gaseous hydrocarbons, carbon monoxide and hydrogen react at high pressures, and at temperatures of 300° to 600° in the presence of Ni, Ag, Cu, Fe or other metals known to be catalysts for hydrogenation, in order to produce alcohols, aldehydes and acids of various kinds. In some cases he also mixes hydrocarbons with oxygen for the same purpose under similar conditions. The patent specification does not explain how the process is conducted in practice, nor what products have been obtained.

#### (e) METHYL ALCOHOL AND OILS BY DECOMPOSITION OF FORMATES

The supposition that the formation of reduction and condensation products of carbon monoxide would be facilitated by conditions favouring the intermediate production of formates has led to a number of investigations concerning the formation and decomposition of formates. A review of the literature on the subject will be found in *Abh. Kohle*, 1921, 6, 366. The decomposition of formates has been studied by K. A. Hofmann <sup>172</sup> <sup>173</sup> and his collaborators. More recently the formation and decomposition of calcium formate have been the subject of a detailed research.<sup>174</sup> The formation takes place at 160° to 180° when compressed carbon monoxide is heated at 10 to 50 atm. in a shaking or stirring autoclave, with milk of lime prepared from pure or commercial calcium oxide.

As regards the decomposition of calcium formate it was shown that

heating to a few hundred degrees will yield gas and in addition an aqueous distillate smelling of aldehyde, with a thin supernatant layer of a brownish oil. The residue of this dry distillation being calcium carbonate, the principle of a cyclic process seemed obvious, viz., to calcine the calcium carbonate to calcium oxide, to slake the lime and to reconvert it into formate by means of carbon monoxide. In this way the production of oil from carbon monoxide is undoubtedly possible.

The aqueous distillate of the decomposition of calcium formate has been investigated by Lieben and Paternò.<sup>175</sup> From 170 grams of calcium formate they obtained 12 c.c. of a liquid containing 5 c.c. of methyl alcohol, that is, about 3 per cent. of the weight of the formate. The oily film, of which only very little was obtained, yielded on steam distillation a light yellow oil, lighter than water and containing carbon 82.71 per cent. and hydrogen 11.6 per cent.; the substance thickened but did not solidify at  $-12^{\circ}$ , and it burned with a highly luminous flame.

In their study of the decomposition of calcium formate into liquid combustible products, Hofmann and Schumpelt<sup>172</sup> observed that it undergoes decomposition above  $380^{\circ}$  when it is mixed with dry, calcined quartz sand and heated in a current of moist carbon dioxide, the residue being calcium carbonate, grey with carbon particles. Calcium formate gave under the experimental conditions of Hofmann and Schumpelt a maximum of 4 per cent. of formaldehyde, acetone and methyl alcohol. In a subsequent paper, Hofmann and Shibsted<sup>173</sup> state that cautiously heated calcium formate gives little formaldehyde, but certainly acetone, a fair amount of methyl alcohol and much empyreumatic and carbonaceous matter. Not more than 17 per cent. of the total decomposition products, including gas and carbon, could be distilled.

Franz Fischer, Tropsch, and Schellenberg<sup>174</sup> investigated the decomposition of calcium formate in the aluminium retort, with and without steam, and with accurate temperature control. In the presence of steam the decomposition does not leave any carbonaceous residue; the resulting calcium carbonate was of a pure white colour. The temperature was maintained between  $420^{\circ}$  and  $430^{\circ}$  for a period of from 1 to 2 hours. The essential result is that the yield of liquid distillate (chiefly methyl alcohol) rose to 53 per cent. of the theoretical, a figure which has not yet been realised by other workers. Small quantities of oil are formed, of which the portion volatile in steam gave on analysis carbon 80.1 per cent., hydrogen 9.9 per cent., and oxygen 10 per cent. by difference. The portion not volatile in ordinary steam was distilled in a current of superheated steam; this oil differed from the other portion by being heavier than water, and gave on analysis carbon 73.7 per cent., hydrogen 8.7 per cent., and oxygen 17.6 per cent. The iodine number of the first oil was 55.2; that of the second, 31.4. An excess of lime in the