

Synthesis in the Liquid Phase

The following is an account of the work of Dr. K lbel of Rheinpreussen in this field. A catalyst without a carrier was used, of composition Fe 100 : Cu 0.2 - 0.5 : K_2CO_3 1, precipitated in the way described for the Rheinpreussen medium pressure catalyst. The 1% alkali prevents the formation of methane, and if less alkali were used the main product would be low-boiling hydrocarbons instead of wax. Pretreatment is done for 1 day with a gas with $H_2/CO = 0.5$ at a temperature 10 - 20° above the initial synthesis temperature.

This catalyst is suspended in diesel oil so as to give a suspension containing 10 - 20% Fe, and synthesis is done in one stage at 230 - 245°C., 3 - 10 atm., with synthesis gas having $H_2/CO = 0.5$, at a space velocity of about 75/h. Recirculation is not necessary. The utilization ratio, X, is 0.5 as the reaction forms carbon dioxide and

no water. It is interesting that part of the Diesel oil reacts to form larger molecules, and in particular, that not only the olefines in it react in this way, but also the paraffins. As a result, the amount of wax obtained per cu.m. synthesis gas is extremely high, being 130 - 140 g. The yield of products produced from the synthesis gas, that is, not including the weight of material derived from the Diesel oil, is 180 g./cu.m., and this does not include methane because none is formed. Working to this yield, the catalyst life is 1 - 2 months, but for smaller yields the life is longer. The products contain 50 - 60% wax, b.p. > 290°C., 50 - 60% olefines, and 10 - 25% alcohols etc. The more alkali in the catalyst the more alcohols are formed.

The synthesis products are obtained by withdrawing oil and catalyst, filtering and returning the catalyst, all this being done in an atmosphere of synthesis gas. After 1,000 hours, the liquid in the reactor is renewed, being replaced by fresh Diesel oil.

The experimental plant was a tube 150 mm. diameter and 3 - 4 m. high, with cooling coils either inside or outside. This plant used 3 cu.m. gas/h. A pilot plant was constructed with internal cooling coils to deal with 750 cu.m./h. but this had not yet been used. For a full scale plant, very large reactors could be used, each capable of producing 7,000 t. products/year, on account of the simplicity of the design.

For this reason, coupled with the high yield of wax and negligible formation of methane, Rheinpreussen consider that this is the most promising of all the proposed modifications of the Fischer-Tropsch synthesis.

Rubro-ende have also done a large amount of experimental work on liquid-phase synthesis and they gave the following account of their results. Before 1941 they satisfied themselves that if the gas-rate were chosen to get a reasonable conversion it was insufficient to keep the catalyst suspended and that for this reason alone recirculation was necessary, so that a high gas velocity through the converter could be combined with the normal low throughput. With recirculation, results were very promising and work was continued on this basis.

Two reactors were available (see Figure 1 of EIOS Final Report 447), each consisting of a wide vertical tube, 6 m. high, fitted with jackets through which the heating oil circulated. The first contained 55 litres of the oil-catalyst mixture. The second contained 85 litres and differed in having a wider head so that less oil was carried off in the gas stream, particularly at higher gas rates. Whatever the gas rate, however, much oil is always carried off and the level of liquid in the converter sinks. Hence a condenser is arranged to condense out all the oil in the gas and return it continuously to the converter. The water also condenses here and is separated from the oil before the latter is returned. Only benzine and gasol remain in the gas and are absorbed in the active carbon scrubbers. The oil level in the reactor, as shown by a sight-glass, is then kept constant by drawing off the liquid synthesis products periodically through a filter stick immersed in the oil. As the oil level is altered by very small alterations in the pressure, if the latter is not kept absolutely constant the amount of oil drawn off, and hence the yield calculated from it will be very variable. Hence not only must the pressure be kept as constant as possible but yields must never be calculated for periods shorter than several days, or a week. In making alterations in the pressure, for starting or stopping an experiment, sudden changes must be avoided or the oil-catalyst mixture will froth over into the condenser and separator.

In the first experiments the gas was passed into the reactor through a ceramic plate which divided up the gas stream into small bubbles. After interruptions of the synthesis which allowed the catalyst to settle, this plate became blocked and pressure differences of up to 8 atm. across it were necessary to re-establish the correct gas rate. It was replaced therefore by a simple copper capillary tube. This never blocked and although the gas was not distributed nearly as well the conversion was just as good.

If the reactor has to be shut down for any purpose the whole contents are drawn off from a valve at the bottom, while gas is still passing to keep the catalyst in suspension. On cooling the mixture sets solid, and in doing so, partial separation occurs. But on remelting and putting the mixture back in the reactor the activity of the catalyst is undiminished. Emptying and refilling may be done many

times in this way without affecting the activity.

At the end of an experiment the contents of the reactor are emptied as just described, filtered hot, and the wax obtained used as the liquid medium for the next experiment. This is better than using fresh Diesel oil each time because it takes from 2 to 4 weeks, according to the nature of the catalyst, for this oil to be replaced by wax.

All the following data refer to synthesis with water-gas, and the temperatures required are the same as for ordinary medium pressure synthesis, being from 230 - 250°C. In general no increase in temperature is necessary during an experiment after the end of the running-in period. A pressure of 15 atm. is always used as there is no reason to suppose that the best pressure is different from that for ordinary synthesis.

The conversion of carbon monoxide, U_{CO} , is 70 - 75% in one stage, with recirculation ratios of 1 to 3, but at times it may be as high as 80 - 82%. If synthesis were being conducted in several stages, however, as it would be on a large scale, it is better to restrict the conversion in Stage I to 65 - 75% so as to minimize gas formation and get the best possible catalyst life. The residual gas from the first stage is perfectly suitable for use in a second stage, where a conversion of 70 - 75% can be obtained. In a two-stage test a total conversion of $U_{CO} = 93 - 94%$ was obtained.

The formation of methane is in all cases smaller than for the corresponding ordinary synthesis. During the early part of the catalyst life it is particularly low, being 1.5 - 2.0% or even less than 1% of the total products. For a catalyst which produces a high proportion of wax, the average amount of methane formed is 3 - 4% when working at a total conversion of 70 - 90%. In the later stages of the catalyst life the formation of methane increases.

The utilization ratio, H_2/CO , is bigger than for the ordinary synthesis under otherwise similar conditions. For Stage I it is usually above 1.3, being 1.4 - 1.5 in two examples quoted. Strangely enough it is hardly affected by the recirculation ratio, and changing this from 1.7 to 7 has little effect. Even without recirculation it is still above 1.3. The utilization ratio in Stage I will be smaller, and is in fact about 0.90. For the two stages together, the

utilization ratio is 1.24 - 1.28 which corresponds well with the composition of the water-gas. Further work has the aim of making the utilization ratio equal to this for each stage separately because in any stage, deviation of the utilization ratio from the composition of the gas supplied leads to a diminution in yield.

The effect of gas rate and of the concentration of the catalyst in the oil is shown in Table 46. The volume of catalyst is the volume of dry granules, before grinding, which is mixed with the requisite amount of oil to fill the reactor. When 10 litres of catalyst are used, 50 litres of oil are required, and when more catalyst is used rather less oil is employed. All results are for a recirculation ratio of 3.

Table 46.

Liquid-phase Medium Pressure Synthesis Iron Catalyst

(Ruhrchemie)		
Volume of Catalyst, litres	Gas Rate, cu.m./h.	Conversion U_{CO} %
10	1.0	73-75
10	1.5	62-64
10	2.0	48-52
20	2	73-75
20	3	62-64
20	4	48-53
30	3	70-75

The yield, calculated from the 90 - 93% conversion obtained for two stages, is 170 g./cu.m. but direct measurements of the yield have not yet been made, on account of difficulties in measuring the amounts of gases concerned.

Just as in ordinary synthesis, the nature of the products is dependent, in the first place, on the catalyst used, and in the second, on the synthesis conditions.

A catalyst which gives a high proportion of wax by ordinary synthesis will also do so in the liquid phase synthesis. It is uncertain whether hard wax is cracked slowly, to soft wax and Diesel oil due to its long contact with the catalyst. There is one difference from ordinary synthesis, and that is that the products are more saturated.

The longest test so far carried out lasted for $7\frac{1}{2}$ weeks without any marked deterioration of the catalyst, although the production of methane increased from 2 - 2.5% to 6 - 8% of the total products. It can be said therefore that the life of a catalyst for liquid phase synthesis is no less than for ordinary synthesis.

The effect of adding various substances to the oil-catalyst suspension has been investigated. In order to decrease the utilization ratio to the right value for water-gas, alkali was added, in the form of soda finely powdered and suspended in Diesel oil, sufficient to form 10% by weight of the iron present. This decreased the utilization ratio from 1.30 to 1.08 - 0.96 and did not change the conversion or the gas formation. But after 6 days the wax produced became brown, and was finally brownish black, jelly-like and only half solid.

In another experiment 5 litres C_{10-18} fatty acids were added. This put the utilization ratio up to 1.81 from the original value of 1.15, but it decreased again rapidly and after a few days was 1.05. The fatty acids had by this time been destroyed, as shown by zero acid or ester numbers for samples of the oil in the reactor. While the acids were still effective, the amount of methane ^{formed} increased to 3 - 10% and the conversion diminished somewhat.

The data in Table 47 give the results of a normal two-stage test.

Table 47.

Liquid Phase Synthesis in Two Stages with an Iron Catalyst
(Ruhrchemie)

	Stage I	Stage II	Total
Time, hours.	833	732	
Temperature, °C.	250	252	
Pressure, atm.	15.0	15.0	
Gas-rate, cu.m./h.	3.1	1.33	
Recirculation Ratio	2	3	
Contraction, %	50.2	35.5	67.3
Conversion of CO, %	64.0	75.0	91.0
CO converted to CO ₂ , %	25.0	31.3	27.6
CO converted to CH ₄ , %	3.3	6.3	4.3
CO converted to liquid products	71.7	62.4	68.1
H ₂ converted, %	69.3	73.0	91.6
CO + H ₂ converted, %	69.4	74.0	91.2
Utilization Ratio H ₂ /CO	1.36	1.05	1.28
Yield, g./N.cu.m.	126	93.0	170
Boiling Range of Products %			
- 200°C.	18.4	50.3	24.9
200 - 320°C.	21.9	30.1	29.8
320 - 460°C.	26.6	18.3	21.6
460 - °C.	32.1		23.6
Olefine contents %			
- 200°C.	63	78	65
200 - 320°C.	21	5	17
Residual Gas Analyses %			
CO ₂	24.7	48.3	
C ₂ H ₄	1.6	1.8	
C ₂	0.1	0.1	
CO	27.8	10.8	
H ₂	30.0	12.6	
CH ₄	2.1	5.6	
N ₂	13.7	21.2	

I.G. Farben have also investigated liquid phase synthesis, and Dr. Michael gave the following account of their work. The catalyst is prepared from carbonyl iron by burning in oxygen. Some 1% K₂CO₃ or borax is added and the mixture reduced at 250°C. until it contains 2/3 metallic iron and 1/3 ferrous oxide. It is then mixed with the oil

and milled with it to a size of 30 microns. Synthesis is carried out at 20 atm. pressure in a simple tube of capacity 1.5 cu.m., fitted with a porous plate. The oil is recirculated at such a rate as to change the contents of the reactor twenty times an hour, and with this rate there is a 10°C. rise of temperature through the reactor. The synthesis gas is passed in through the porous plate and a gas recirculation ratio of 1 is used. The resistance of the porous plate does not increase during synthesis. The progress of the synthesis can be judged from the analyses in Table 48.

Table 48.

Liquid Phase Synthesis. I.G. Farben

	Synthesis Gas	Residual Gas	
		No recirculation, 65% conversion.	Recirculation, with removal of CO ₂
		%	%
CO ₂	-	30	25
CO	53	30	14
H ₂	44	33	36
CH ₄	1	3	15
N ₂	2	4	12

A conversion of $\text{CO} + \text{H}_2 = 65\%$ was used, for a single stage, and this gave an output of products of 350 - 450 g./litre catalyst/day. From each N.cu.m. gas converted, the following products are obtained (Table 49).

Table 49.

Products from Liquid Phase Synthesis. I.G. Farben

	Weight g.	Olefines, % by weight	Oxygen, % by weight
C ₁ -2	10		
C ₃ -4	20	70	4
Benzin - 200°C.	81	70	3
Middle Oil 200- 325°C.	61	40-50	2-3
Wax 325- °C.	27		
Alcohols	9		

The benzin was of a poorer quality than that from the high gas recycle synthesis, but more wax than the amount stated could be produced if required.

Tests of this process have lasted three months, but after about two months, running trouble was experienced from deposits of ferrous carbonate which formed on the upper parts of the reactor walls and then fell off and interfered with the smooth working of the synthesis. It was thought that this trouble might be avoided by using shorter and wider reactors.

Reviewing the liquid phase synthesis, Lurgi point out the following objections:- It is very difficult to separate catalyst dust from the oil, and if this dust remains in it and is recirculated, acids are formed which attack the catalyst. There are also corrosion difficulties. On a large scale the very big mass of hot oil constitutes a fire hazard which is particularly dangerous in war time.

When the costs of the oil filtration and recirculation plant are considered, it is doubtful if the process is cheaper than the conventional, medium pressure, synthesis.