

The Oil-Recirculation Process

Some of the advantages of the liquid phase synthesis can be retained and some of the disadvantages avoided if a catalyst is arranged in a fixed bed and oil circulated over it to remove the heat of reaction and the products. Such a method was developed by Dr. Duftschmidt, of the I.G. Farben, and the present opinion of the company is that this is the

best method of conducting synthesis with iron catalysts, although it does not give quite such high yields as synthesis in the usual Ruhrchemie type of reactor. At the end of the war they were planning a 40,000 t./year plant for this process.

A melted iron catalyst was to be used in 8 - 12 mm. pieces, and reduced with hydrogen. The rate of oil recirculation used on the small scale was 550 - 750 litres/hour for a reactor of capacity 60 litres. The pressure was 20 atm. and carbon dioxide the main oxygen product.

It was pointed out that this process, in which the whole reactor is filled with oil is very different from that developed by Ruhrchemie in which a fixed bed of catalyst is sprayed with oil to keep the catalyst free from wax and to remove the heat of reaction by the latent heat of evaporation of the oil.

Direct Synthesis of Alcohols

Ruhrchemie gave the following details of a semi-technical scale test of the catalyst Fe 100 : Cu 5 : CaO 10 : Kieselguhr 5 : KOH 3, whose laboratory scale preparation and testing have already been described (BIOS Report 447, Appendix VI).

The catalyst was precipitated with sodium carbonate, half of the kieselguhr being added before and half after the precipitation. It was filtered on the filter press and washed for 30 minutes and then repasted with 70 litres hot water per kg. iron and filtered. The repasting and filtering were repeated twice. After the last of these filtrations, washing was continued for 100 minutes. The filter-cake was impregnated with the 3% KOH in the extrusion press and then dried at 140°C. or less and the threads broken to 1 - 3 mm. pieces.

Pretreatment was done at 225°C. with 75% hydrogen (the rest nitrogen) for 24 hours at a space velocity of 6,000/h., and this caused reduction so that 71.8% of the iron was soluble in 2% acetic acid.

Synthesis was carried out in a semi-technical scale plant with 16 full sized double tubes, using water-gas at a space velocity of 100/h., pressure 10 atm., temperature 200 - 214°C. and no recirculation. For the 750 hours of the

experiment the conversion $U = 60 - 65\%$, the utilization ratio $X = 0.65 - 0.72$, and of the gas converted, 14% went to form methane. The yield was 95 g./N.c.u.m. and of this, about 15 g. was gasol. The composition of the products is shown in Table 50.

Table 50.

Products from the Direct Alcohol Synthesis

		Weight %	Total S.P.L. (i.e. Volume soluble in $\text{H}_2\text{SO}_4 - \text{H}_3\text{PO}_4$ mixture), % ^{3 4}
Benzin	- 200°C.	60	75
Diesel Oil	200- 320°C.	12	70
Wax	320- $^\circ\text{C.}$	28	

Synthesis at Atmospheric Pressure

Dr. Kölbl, of Rheinpreussen, gave the following particulars of his latest results in this field. The best catalyst had the composition $\text{Fe } 100 : \text{Cu } 1 - 10 : \text{kieselguhr } 50 - 100 : \text{K}_2\text{CO}_3 \frac{1}{2} - 15$, although attempts were being made to replace the kieselguhr by dolomite as in the other Rheinpreussen iron catalysts. It is prepared by dissolving the iron in nitric acid to give a 10% solution, adding the copper nitrate, boiling, adding the kieselguhr, precipitating with boiling 10% sodium carbonate solution, filtering and washing. The potassium carbonate is dissolved in water and is stirred into the filter cake which is then dried and granulated to $1 - 3 \text{ mm.}$ pieces. It is not submitted to any process involving forcing through dies.

The success or failure of this catalyst depends on the pretreatment, which is done for 1 or 2 days at $230 - 235^\circ\text{C.}$ with synthesis gas, $\text{H}_2/\text{CO} = 2$, which has been carefully freed from both carbon dioxide and water vapour, and is passed at 20 times the normal synthesis gas rate either directly or with recirculation (recirculation ratio 3), at atmospheric pressure.

Synthesis can either be done with water-gas using recirculation, or with a gas richer in hydrogen, approaching the composition of ordinary synthesis gas, without recirculation, and in both cases the results are essentially the same. The longest run so far was with water-gas, and lasted for 2 months at 218°C. without any sign of the activity falling off. No regeneration treatment was done during this period and it is estimated that the catalyst life will be at least 4 months, taking into account the fact that iron catalysts do not respond to regeneration treatments nearly as well as cobalt ones. The yield of products, including methane, is given as 130 - 135 g./N.cu.m. (CO + H₂) for one stage at a space velocity of 250/h., and for two stages at a total space velocity of 100/h. it is 160 g./N.cu.m. (CO + H₂), including methane, or 150 g. without methane. Half of the oxygen product is water, half carbon dioxide, and the utilization ratio X is about 1. It is rather higher in Stage I than in Stage II, and is not affected very much by the amount of alkali in the catalyst. The conversion of carbon monoxide, U_{CO}, is 85 - 90% for Stage I and 97% for the two stages together.

The products contain as high a proportion of wax as those from cobalt medium pressure synthesis, and the amount of olefines in the total products is very much higher, being 40 - 50%. The more alkali there is in the catalyst, the bigger the proportion of wax in the products; the total yield of products is however independent of the amount of alkali in the catalyst.

For synthesis at atmospheric pressure, the K.W.I. used the Fe 100 : Cu 20 : K₂CO₃ 1 catalyst whose preparation and pretreatment have already been described (see p. 122). Synthesis was done with water-gas at 205°C. with a space velocity of 50/h. or at 215°C. with a space velocity of 100 - 150/h. For either set of conditions the conversion was U_{CO} = 90 - 95% and the yield, including methane, 140 - 145 g./N.cu.m. inert-free gas. The methane amounted to 2 - 4 g. for the lower space velocity and to 5 - 6 g. for the higher one. This yield was maintained for 3 months by carrying out a solvent extraction every 2 or 3 days, and by allowing the temperature to rise 5° by the end of the 3 months. The formation of methane increased a little during this period.

The products contain some 30 - 40% wax, of b.p. >300°C., and they vary in colour from yellow to bright

brown due to resins formed from unsaturated products. More oxygen compounds are formed than in synthesis with cobalt catalysts, the amount being the same as in the medium-pressure iron Reichsanversuch experiments. The utilization ratio $X = 0.6$ so that no second stage is possible.

Reviewing the prospect of synthesis at atmospheric pressure with iron catalysts, Lurgi are certain that from the point of view of costs the position is worse than for synthesis at medium pressure.