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MEDIUM PRESSURE SYNTHESIS WITH IRON FIXED - BED
CATALYSTS, AND OPERATION OF THE FISCHER TROPSCH
SYNTHESIS IN THE LIQUID PHASE.

INTERROGATION OF DR. H. KOLBEL.

by

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Report of Interview at Fuel Research Station December 5th 1947.

Dr. H. Kölbel, Steinkohlenbergwerk Rheinpreussen Homburg, Niederrhein.

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Dr. Kölbel was in charge of research and development at the Homburg works of Steinkohlenbergwerk Rheinpreussen. His work consisted mainly of investigations on the Fischer process, in which he had also had experience at the Kaiser Wilhelm Institut, Mülheim, under Professor Fischer in 1934-5. The information obtained at the present interview amplifies that obtained in Germany by Drs. Hall and Craxford in the course of B.I.O.S. Trip 2505. References to the report prepared on this Trip are indicated by (2505).

Dr. Kölbel's main fields were the development of iron catalysts for use in conventional fixed catalyst bed reactors, and the investigation of the possibilities of carrying out the Fischer synthesis in the liquid phase; the interview was accordingly directed towards obtaining detailed information on these subjects.

NOTE

The report on Trip No: 2505 is being published as B.I.C.'S. Final Report No: 1722.

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I Medium Pressure Synthesis with Iron Fixed-bed Catalysts

Catalyst Composition The composition of a good catalyst which had been prepared on the semi-technical scale was given as (parts by weight):-

Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	CuO	K ₂ O	CO ₂
3.4	46.3	40.7	6.5	3.1	0.5	40.1

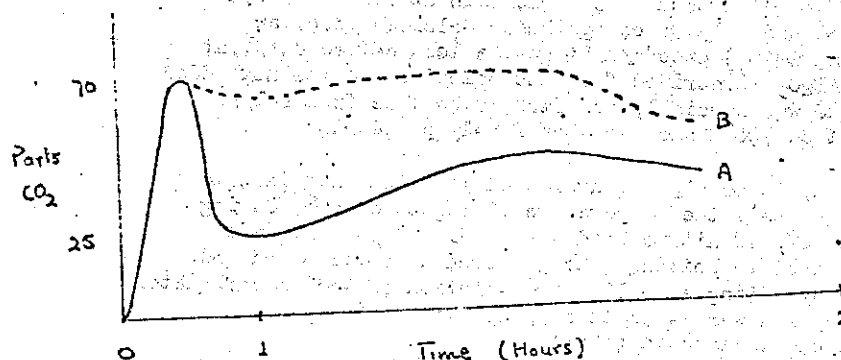
the exact composition being of great importance. The main constituents were iron and dolomite. Dr. Kislbel had only tried synthetic dolomite (i.e. an equimolar mixture of Mg CO₃ and CaCO₃) once and it gave a less active catalyst than natural dolomite. The Al₂O₃ is derived from the dolomite and was not added separately. The dolomite used was specially selected to be free from sulphur and phosphates, was roasted at ca 700°C and was then finely powdered.

Catalyst Preparation The iron, as metal, was dissolved in dilute nitric acid to give a 10% solution (based on Fe), the temperature rising to ca 50°C during solution. A small excess, 5-10%, of nitric acid was used. Copper nitrate was then added, the mixture heated to boiling, the powdered dolomite added and the precipitation carried out by adding a boiling 10% solution of sodium carbonate. The amount of sodium carbonate used was as small as possible, so that a considerable amount of magnesium remained in solution.

Filtration was carried out immediately, followed directly by washing till the filtrate was free from NO₃ by the brown ring test. This took about 45 minutes for a laboratory-scale preparation, the filter funnel being refilled with fresh water six or seven times; no redispersal of the precipitate in water was necessary. The wet filter cake was then impregnated with an aqueous solution of cobaltous carbonate, dried and granulated.

Pretreatment of the Catalyst This stage is very critical. It was carried out in synthesis gas (H₂: CO :: 2:1) at 240-260°C and atmospheric pressure. The gas was recirculated in the proportions of nine parts of recycle gas to one part of fresh gas, the total minimum space velocity being 1000 vol. gas per vol. catalyst per hour. The gas must be freed from carbon dioxide, which could be done satisfactorily with soda-lime, but the presence of water vapour has no deleterious effect. The time required for pretreatment is usually between 3 and 24 hours. It can be judged exactly by following the evolution of carbon dioxide. As shown in the attached graph, the carbon dioxide concentration in the gas rises to a maximum during the first hour possibly owing to the decomposition of the metallic carbonates, then falls to a minimum and rises slowly to a second maximum during carbide formation. Ideally the pretreatment should be ended when the second maximum is reached. (Curve A, Figure (1))

Figure 1



If carbon formation occurs during pretreatment a curve of a type similar to B (Figure 1) is obtained, and the catalyst will be useless for synthesis.

Synthesis:- When the pretreatment has ended the temperature of the catalyst is decreased and synthesis is started at 10 atmospheres and the full space velocity. There is very little danger of bolting if pretreatment has been done in synthesis gas; pretreatment with carbon monoxide gives a catalyst which is more liable to bolt. The temperature at which synthesis is started is critical but it varies from catalyst to catalyst, and even from batch to batch of the same catalyst, and K6lbel could give no exact figure.

K6lbel could give few results for laboratory scale plant working in a single stage unit, as most of his work had been carried out with two or three stages. Using the above catalyst, however, in one stage he obtained the following data in a reaction tube 3 m. high by 16 mm. diameter.

Synthesis gas:- Water gas of normal composition ($\text{CO}:\text{H}_2 : 1 : 1.25$)

Space Velocity:- 100-150

Reaction Temperature:- 225°C . (This was limited by the reactor design)

Residual Gas:	After 96 hours running	CO	CH_4	CO
" 30000 "	"	38.9	1.9	0.7
" 30000 "	"	38.1	1.7	6.3

The corresponding figures for the residual gas from Stage I in a 2 stage pilot plant after 1000 hours running with synthesis gas were CO_2 14.3 CH_4 0.4 CO 22.0.

For a catalyst of this type, which was designed for multi-stage operation, K6lbel advocated running with 2 or preferably 3 stages, or with recirculation of the residual gas. With 3 stages a CO-conversion of 90-95% could be obtained with an overall space velocity of 150 i.e. ca. twice that used on the normal technical scale plants, and higher throughputs (3 to 4 times normal) could be achieved with very active batches of catalyst. No adjustment of the CO : H₂ ratio of the gas was carried out between stages. As an example of the results obtained K6lbel gave the following data.

Composition of	CO ₂	CH ₄	O ₂	CO	H ₂	C _n H _{2n+2}	N ₂
Synthesis Gas	9.3	0.0	0.2	28.2	54.6	0.5	7.2
Residual Gas	32.5	1.5	0.1	4.0	32.6	8.1	21.0

Reaction temperatures, C.,	Stage 1	Stage 2	Stage 3
after 640 hours.	210	215	205
CO-conversion %	45	75	ca. 95

Space Velocity:- Stage 1: 500 v./v./hr.; overall 150. v./v./hr.
 Gas Contraction: 55% overall
 Utilisation ratio: CO/H₂ : : 1 : 1.52
 Yield, including CH₄ 159 gm/cu.m. CO+H₂.

The catalyst life could not be determined as the run was cut short by bombing after 1200 hours. During this time the reaction temperature in Stage 1 was increased from 205°C to 213°C. The space velocity was adjusted to give a total conversion of carbon monoxide of the order of 95%.

In general K6lbel had found that the catalyst had a longer life with synthesis gas than with water gas.

II. Operation in the Liquid Phase

Dr. K  lbel has carried out investigations on the operation of the Fischer-Tropsch synthesis in the liquid phase over a period of several years, and considers this technique of great importance for the future development of the synthesis. He pointed out that its main advantages derive from the rapid transfer of heat away from the catalyst, resulting in the true catalyst temperature approximating to that of the liquid medium. The production of methane was therefore small (under some conditions, zero) and the reaction temperature could be regulated easily e.g. by simple cooling coils immersed in the liquid medium, so that larger technical-scale converters could be used than with the conventional process, and they would be comparatively cheap to construct. The main disadvantage of the process was due to the restricted solubility of the reacting gases in the oil which set a limiting factor on the space velocity. Theoretically the solubility ought to increase with pressure but synthesis at 25 atmospheres had been found to give no better results than 10 atmospheres.

Design of reaction vessels. The time of contact is independent of the height of the vessel, but the latter governs the linear gas velocity which must be large enough to ensure a good suspension of the catalyst particles. The smallest reactor used by K  lbel was ca 1.5m. high by ca 7 cm. diameter; he had found the maximum conversion attainable with a tube 0.5 m. high was 8% as against 9% with a tube 1.7m. high. His work had been mainly carried out on pilot plants with reactors 4m. high by 20 cm. diameter. The liquid level in the latter was maintained constant by a ball valve, oil and catalyst being drawn off together; the catalyst was filtered out and returned to the reactor as a concentrated slurry. Cooling was effected by four vertical bayonet tubes filled with water and connected to a pressure steam drum. No trouble was experienced with corrosion, probably owing to the fact that no liquid water was present, nor did crusts of catalyst etc. build up above the liquid surface. The largest reactor built at Rheinpreussen was designed for a gas through-put of 500 - 1000 cu.m. per hour; it was ca. 20 m. high by ca. 130 cm. diameter. This plant was put out of action by bombing before it was operated. No special provision was made in its design to minimise the fire hazard. Subdivision of the gas stream by sinter plates etc. is not necessary, the gas being led in by an ordinary tube.

Catalysts. K  lbel had tried cobalt catalysts in the liquid phase but had found them inferior to iron catalysts. The usual composition of the catalyst was in the range Fe 100; Cu 0.2-0.5; K₂O 1 (2505) and the preparation, etc. were less critical for the liquid phase than for the fixed bed process. The pretreatment of the catalyst could be carried out in the gas or liquid phase with similar conditions of space velocity etc. to those used for fixed bed catalysts. Removal of CO₂ from the pretreatment gas was not so important for liquid phase catalysts. The finer the particle size of the catalyst used in the liquid phase the better was its performance. When asked if he normally used catalysts without a carrier for liquid phase operation, K  lbel said that he did, pointing out that since the catalyst was suspended in oil which performed the functions of a carrier in preventing overheating, sintering etc. addition of a carrier merely diluted the catalyst.

Reaction conditions. The amount of catalyst present is limited by the amount which can be maintained in suspension in the oil: this varies with the catalyst but the best obtainable was about 100 gms Fe per litre of suspension. The space velocity used was ca 75 Vol gas (measured at N.T.P.) per vol. of suspension per hour with a minimum of ca 50, i.e. a space velocity of ca 750 vol. gas per vol. dry catalyst per hour.

Performance. Most of the investigations on the liquid phase had been carried out by K  lbel with a catalyst of the composition: Fe 100 Cu 0.2 K₂CO₃ 1.0 (2505). With this catalyst the Utilisation Ratio of hydrogen to carbon monoxide was 0.5, the reaction following the course $2\text{CO} + \text{H}_2 \rightarrow \text{CH}_2 + \text{CO}_2$ and accordingly a synthesis gas with a H₂:CO ratio of 0.5:1 was used. Recently minor modifications had been made in the catalyst with the result that the Utilisation Ratio had been increased and under suitable operating conditions water-gas or even synthesis gas could be used. K  lbel would give no precise information on the change made in the catalyst but admitted that no carrier had been incorporated. He also admitted that recirculation of the residual gas had been investigated but withheld the results obtained. (The investigations would appear to have been carried out later than June 15th 1947 and K  lbel was therefore entitled to maintain secrecy about them). K  lbel would, however, still prefer to use a gas richer in carbon monoxide than water-gas, especially if a large scale plant were to be built as CO-rich gas gives better conversion and can give products of more varied character. He suggested using a Kopper's generator using coal dust with CO₂ or flue gas to give a CO-rich synthesis gas. Formation of carbon does not appear to take place with the liquid phase technique, but if carbon deposition did occur on the catalyst to a limited extent K  lbel was inclined to think that it would be beneficial in decreasing the catalyst density and so improving the catalyst suspension. K  lbel expressed the opinion that the formation of fatty acids during synthesis might affect the catalyst activity, but he appeared to have made no investigations on this point. Thus he had not tried the addition to the reactor of fatty acids or boric acid or alkalis such as sodium carbonate which have been reported (B.I.C.S. 447.p. 32) to affect the synthesis reaction, particularly the Utilisation Ratio, nor had he investigated the patent claim (International Hydrocarbon Synthesis Co., Italian patent 389201/1941) that removal of fatty acids from the liquid medium by washing with alkali increases the formation of Diesel oil. Increase in the alkali metal in the catalyst decreases the Utilisation Ratio and increases the proportion of wax and oxygenated compounds formed as it does for fixed-bed catalysts, but K  lbel did not know whether the potassium was present as free alkali or in combined form e.g. as iron ferrite.

The observation (2505) made by K  lbel that the Diesel oil used as the liquid medium took part in the reaction and was converted to wax has been confirmed, and the use of a hydrogenated Diesel oil fraction has proved conclusively that paraffin hydrocarbons can react in this way. Experiments designed to measure the rate of incorporation of both low and high-boiling hydrocarbons were cut short by bombing, but K  lbel said that in an experiment when the yield of wax formed by synthesis was 74.4 gm. per cu.m., a further 44.6

gm. per cu.m. was formed by reaction of the Diesel oil.

Kölbel gave some data on performance in the liquid phase; the figures quoted below have been corrected for the increases in yield due to incorporation of the liquid medium.

Using a benzene-forming catalyst at 8-10 atmospheres, 230°C., and a space velocity of 75 vol. gas/vol. reaction space/hr., the synthesis gas having a H₂:CO ratio of 0.5 : 1, a total yield of 168 gm per cu.m. was obtained with a Utilisation Ratio of H₂ : CO of 0.5 : 1. No methane could be detected in the products and the amount of ethane formed was very small. The distribution of the product was:-

Hydrocarbons C ₃ - C ₄	boiling 35-200°C	200-320°C	320°C
19.6%	55%	20.8%	5.6%

The octane number (motor) was 77 for the fraction boiling below 150°C and 68.5 for the fraction boiling below 200°C. The fraction boiling 35-150°C. contained 60% of olefines.

Using samples of catalyst which had a tendency to produce wax, Kölbel had obtained as high a proportion of wax as 67% of the total product (95 gm./m³ of wax when the total yield was 142 gm./m³). It is possible that this wax had an I.B.p of 290°C. but yields of wax bp. 320°C amounting to 74 gm./m³ with a total yield of 140 gm./m³ (i.e. 50% wax) were not uncommon.

Atmospheric Pressure Process. Although Dr. Kölbel had carried out a considerable amount of work on the development of iron catalysts for use at atmospheric pressure, it was considered that this process had little future importance and he was not interrogated on it.

Variation in Product Composition

Dr. Kölbel considered that there was little prospect of directing the synthesis towards the exclusive production of a narrow range of hydrocarbons (other than C₁ to C₄) and knew of no set of conditions which brought about any appreciable increase in the proportion of the Diesel oil fraction. He felt, however, that the limits of the possible modifications in product composition had not yet been reached.

Mechanism of Reaction

On the mechanism of the Fischer reaction Dr. Kölbel had no original observations to make. He expressed the view that carbiding of the catalyst led to the formation of interstitial compounds rather than true individual carbides, formation of which lowered the catalyst activity. Hydrocarbons were formed by the polymerisation of CH₂ groups to form a very large molecule or pseudo-molecule lying parallel to the catalyst surface with the subsequent cracking of this molecule to give the compounds actually obtained as products.