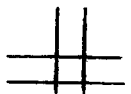# I. FISCHER TROPSCH SYNTHESIS.

A. Catalyst development.

1. Cobalt catalysts.

I.G. FARBENINDUSTRIE A.G.,
Ludwigshafen-Oppau,
May 23rd, 1947.

Dr. Schiller   )
Dr. Scheuermann) Oppau ——— 140

Dr. Scheuermann has studied several types of cobalt catalysts but was at present more interested in iron catalysts suitable for the preparation of high proportions of paraffin wax. The following information was obtained on previous work with cobalt.

It is possible to prepare catalysts consisting solely of Co. If such a catalyst is obtained by precipitation followed by drying at $100^{\circ}C$ and reduction at $350^{\circ}C$, the cobalt undergoes severe sintering and therefore the final catalyst is inactive. If the product is reduced at $200^{\circ}C$ the catalyst is definitely active, but deteriorates rapidly due to sintering. It is, however, possible to avoid this collapse of structure by drying the precipitated cobalt carbonate slowly in a moist atmosphere for 24 hours at $110^{\circ}C$. The final product obtained in this way contains hexagonal Co_3O_4 next to basic cobalt carbonate and the oxide obviously is a stabilizer for lattice disturbancies in the reduced catalyst.

According to Dr. Scheuermann these disturbancies are generally favoured by slow precipitation and application of a low temperature of precipitation ($20^{\circ}C$) ').

The function of thoria on the one hand is also that of a stabilizer of disturbancies, on the other hand that of a promoter.

') Difference in opinion from Ruhrchemie

Catalysts prepared by the application of the above knowledge consisting of 100 Co, 28 ThO$_2$ and 200 kieselguhr, which have been reduced at 250°C during 5 - 10 hours, were active at 160°C and yielded a product with 35% of wax (320°C $^+$) if the conventional synthesis gas (2 H$_2$:1 CO) and atmospheric pressure were used, whereas with water gas under 12 ats pressure more olefines and branched hydrocarbons were obtained with a total product distribution of

> 15% gasoline
> 15% middle oil
> 20% Gatsch
> 50% paraffin wax.

This type of catalyst had been operated for as long as 4 months without intermediate regeneration.

Dr. Scheuermann had also investigated the possibility of applying kaolin, alumina and silicagel as a carrier for cobalt catalysts. Although no outstanding results could be obtained with these materials, he had succeeded in preparing fairly active catalysts. To this end it had been necessary to give the carrier materials a high temperature pre-treatment in order to make them less reactive towards the cobalt; it serves to modify the pore size distribution, only silica gel with narrow pores proving suitable for the purpose.

X-ray studies of cobalt catalysts had revealed the presence of hexagonal Co. and of cubic Co in case alkali was present, no Co-carbides or Co-silicates having ever been found in these X-ray studies.

2. Iron catalysts

d) I.G. FARBENINDUSTRIE A.G., Oppau,
May 23rd, 1947

<div align="right">

Dr. Schiller) Oppau ‡ 140
Dr. Scheuermann)

</div>

Four types of iron catalysts had been investigated in the Oppau laboratory:

a. Fused oxide catalyst ("Schmelzkontakt")
b. Knead catalyst ("Kneukontakt")
c. Sinter catalyst ("Sinterkontakt")
d. Prepcipitation catalyst ("Fällungskontakt").

a. <u>Fused oxide catalyst.</u>

This type of catalyst had been derived from the type conventionally used in the ammonia synthesis, substituting, however, MgO for Al_2O_3. .The catalyst is prepared by blowing oxygen in an iron vessel filled with iron powder, mixed with MgO and an appropriate amount of alkali; the mixture is ignited, melts and finally solidifies. As soon as solidification starts the pot is tipped over and the obtained product is cooled and subsequently broken into pieces of appropriate size. Usually 3-4% of MgO was used, this amount being limited by the solubility of MgO in the molten mixture. The quantity of alkali is partly determinant for the olefinicity of the final product as shown by the following graph:
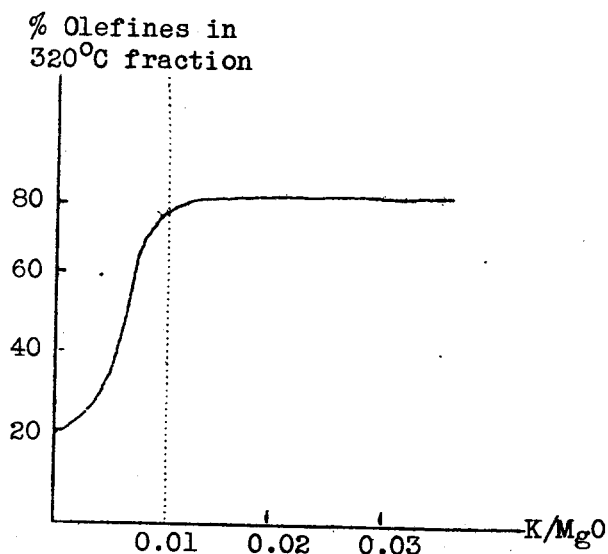
<u>Representative results.</u>

Catalyst	3% MgO, 0.03% K
Bulk density	2.7 kg/l
Reduction temperature	500°C
Synthesis temperature	240°C
Synthesis pressure	12 ats.
Space velocity	200 v/v.h.
Product yield	100 g/cub.m.
Product distribution	50% gasoline
	20% middle oil
	18-20% Gatsch
	12-10% paraffin wax

It should be noted that in the Ruhrland-Schwarzheide Reichsamt Comparison tests I.G. had participated with this type of catalyst containing some CaF_2, the results of which were not favourable '').

A serious disadvantage of the fused oxide catalyst is its high bulk density. Since also its preparation is rather elaborate and would require development of the procedure on a large scale, I.G. had abandoned this type.

b. **The knead catalyst**

For some time Dr. Scheuermann had worked on a catalyst prepared by combustion of finely divided iron (obtained through decomposition of iron carbonyl) with oxygen and kneading the iron oxide with a dilute solution of alkali, at the same time adding copper and magnesia and also kieselguhr, if desired. After drying, the mixture could be shaped by applying grooved mills (compare the device considered by Ruhrchemie for preparing their "Schiffchen-kontakt").

The representative composition of this type of catalyst was:

$$400 \ Fe$$
$$4\text{--}5 \ MgO$$
$$10 \ Cu$$
$$6 \ K$$

c. **Sinter catalyst.**

If the dried knead catalyst is subjected to igniting at 800°C a denser form of granules is obtained (bulk density 1.5 kg/l).

d. **Precipitation catalyst.**

Dr. Scheuermann at present was studying iron catalysts containing various admixtures. These

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') Compare F.I.A.T. F.R. 276 "Kaiser Wilhelm Institut für Kohlenforschung, Mülheim, Ruhr. Interrogation of Dr. Helmuth Pichler and Prof. Karl Ziegler, page 11.

products were obtained by slow precipitation with K_2CO_3. A high activity is obtained by a low temperature of reduction. Cu is always added in order to make reduction easier and the presence of MgO or Al_2O_3 improves the stability of the structure (maintaining the presence of lattice disturbances).

Representative data:

Composition of catalyst	100 Fe
	10 MgO
	25 Cu
	8 K
	100 Kieselguhr

Bulk density   0.5 - 0.8 kg/l

Reduction in the Fischer-Tropsch reactor:

temperature	$200^{\circ}C$
hydrogen rate	2000 v/v.h.
duration	15 hours
Synthesis temperature	$210-220^{\circ}C$
Synthesis pressure	12 ats.
Synthesis gas	water gas
Product yield	145-150 g/cub.m.
Product distribution	15% gasoline
	20% middle oil
	65% wax

The synthesis is carried out with 4 reactors in series, 5 m x 15 mm $\varnothing$, each with the gas in down-flow and with intermediate separation of wax between each 2 reactors. The total space velocity is 400 v/v.h. to the first oven, i.e. 100 v/v.h to the total system. The total CO-conversion in the system amounts to abt. 70%. CO and H_2 are used in the ratio 1.0 CO : 0.9 H_2 according to the approximate equation

$$3\ CO + 3\ H_2 \longrightarrow 2\ CH_2 + CO_2 + H_2O$$
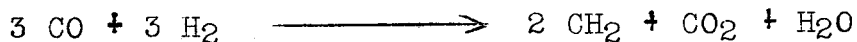
Another modification of this catalyst type consists of Fe, Cu, K and Al_2O_3, in which case no carrier is used. The catalyst is active at abt. $200^{\circ}C$ yielding somewhat less paraffin wax with a

relatively low olefine content; the paraffins, however, are very little branched.

X-Ray investigation of these iron catalysts has shown that – after use – they always contain iron carbides. If Cu is present the carbide is definitely stabilized and it was found to be present in a new hexagonal form different from the hexagonal Fe_2C of Hägg. The formation of this new carbide is connected with the high catalyst activity and it was found that a low reduction temperature (200^oC) favours its formation.

2. Iron catalysts

β) KAISER WILHELM INSTITUT FÜR KOHLENFORSCHUNG, Mülheim Ruhr, June 3rd, 1947.

Dr. H. Pichler)
Dr. H. Koch) [1]

The Kaiser Wilhelm Institut has been working with an iron type precipitation catalyst, obtained from a 1 : 1 $FeCl_3$ – $FeCl_2$ solution via carbonate-precipitation at $60-70^oC$, the final composition being 100 Fe
    10 Cu
    1-2 K_2CO_3
    no carrier.

Magneto-chemical studies had shown that in the used catalyst two modifications of the Fe_2C-carbide must be present, the respective Curie-points being 260^oC and 380^oC. The Fe_3C-carbide, Curie-point 210^oC, certainly has no significance in connection with the synthesis reaction, and it was even considered doubtful whether any role as an intermediate compound should be assigned to the Fe_2C-carbides; the rate of formation of the carbides is considerably less than that of the synthesis reaction.

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[1] Cf.CIOS XXV-1 "Kaiser Wilhelm Institut für Kohlenforschung, Mülheim".

Putting together the information as from I.G.'s
X-ray work and KWI's magneto-chemical and re-action
velocity studies one would be inclined to conclude
that preparation of iron type synthesis catalysts by
precipitation with carbonate, ensuring the reduction
at a relatively low temperature through the presence
of copper, yields active catalysts. The special
structure to which high activity must be ascribed
also seems to favour the formation of two different
modifications of the Fe_2C-carbide.

2. Iron catalysts

Y) Metallgesellschaft LURGI, Frankfort a/M,
    May 30th 1947.

Dr. Royen ').

Lurgi have devoted their attention mainly to
the precipitation-type of iron catalyst, to which
copper and alkali are added for the reasons stated
before, whereas Al_2O_3 or ZnO are added in order to
improve the stability of the catalyst structure
possibly through partial formation of spinels.

They have shown that the presence of kiesel-
guhr as a carrier yields active catalysts with less
of the active material, iron, per unit volume;
however, the operational temperature of the carrier-
catalyst is somewhat higher. The effect of copper
is to cause the reduction to proceed more smoothly
and to yield a slightly more active catalyst.

The final catalyst is shaped through extrusion.
The following table will show some illustrative
figures.

') Cf CIOS XXXII-91 "Lurgi Gesellschaft für
                    Wärme-technik, Frankfurt am
                    Main, page 11

CIOS XXXI -23 "Metallgesellschaft Lurgi,
                    Frankfurt am Main", page 6

Type No. 1; precipitation with K_2CO_3:

100 Fe	100 Fe	100 Fe
5 Cu	0 Cu	5 Cu
9 Al_2O_3	9 Al_2O_3	9 Al_2O_3
5-9 K_2O	5-9 K_2O	5-9 K_2O
120 Kieselguhr	120 Kieselguhr	0 Kieselguhr

reduction during $\frac{1}{2}$ h at 280°C with 1000 v/v.h H_2

15% free Fe	5% free Fe	
	rest FeO, Fe_2O_3, Fe_3O_4	

operational temp.	op. temp.	op. temp.
240°C	250°C	220°C

Kieselguhr may be replaced by active charcoal, in which case, however, the mechanical stability of the obtained catalyst granules is very insufficient.

The proportion of Al_2O_3 should not be increased over 9 Al_2O_3 per 100 Fe in order to prevent the formation of non-reducible Fe-Al_2O_3 compounds. With 100 Al_2O_3 per 100 Fe e.g. no reduction of the iron could be effected and the final catalyst showed no activity whatever.

As to the quantity of K_2O in the finished catalyst it should be noted that this compound must not be present in a concentration of over 10 K_2O per 100 Fe. If this should be the case, due to insufficient washing out of the material, under medium-pressure conditions (20 ats. operating pressure) so much fatty acid is found that the catalyst is attacked chemically, the iron being converted into a solution of iron fatty acid salts dripping out of the catalyst space ("bleeding" of the catalyst).

This phenomenon can be prevented by including K_2SiO_3 in the catalyst, which may be done by boiling the kieselguhr for some time with KOH prior to its use, or by impregnating the final catalyst with K_2SiO_3 as such.

This was the reason for the development of a second type of iron catalysts, in which rather high

proportions of alkali may be used:

Type II; precipitation with KOH and subsequent
addition of K_2SiO_3:

100 Fe		100 Fe
5-10 Cu		25 Cu
9 Al_2O_3		18 ZnO
9 K_2O	)added as water-	9 K_2O
	)glass (10 K_2O, 22	
24 SiO_2	)SiO_2), moreover	24 SiO_2
	)some 1-3 K_2O may	
	)be present from	
	)the KOH used in	
	)the precipitation	

120 Kieselguhr or no carrier at all	120 Kieselguhr or no carrier at all.

In this catalyst-type SiO_2 is set free from
K_2SiO_3 and CO_2 as formed in the synthesis, Some
Fe-SiO_2 structure will form during operation, but
this will not hamper the synthesis under medium-
pressure conditions.

This type is active at 220°C operation temper-
ature, a pressure of 10-20 ats. and a free iron
content 5-20%.

No major differences were found between the
Al_2O_3 and the ZnO containing catalysts; they both
yield, if tested in one reaction stage with water
gas:

abt. 135 g/ m^3 C_3^+ on entry gas

abt. 70-75%   CO + H_2 converted

abt. 10-16%   CO converted into CH_4 + C_2H_6
(6-10%) and C_2H_4 (4-6%)

The product distribution is:

abt.　8% wt.　C_3 - C_4
　　　16%　"　gasoline - 200°C　　60% olefine
　　　16%　"　diesel oil 200 -.　　45% olefine
　　　　　　　　　　320°C
　　　15%　"　Gatsch 320 - 450°C
　　　45%　"　wax 450°C +

As described previously Lurgi have developed a gas circulation process, applying recirculation of rest gas at a relatively low rate (2 : 1 or 3 : 1 cycle gas to fresh water gas). As the CO_2 formed in the synthesis step is in this way partly fed back to the reaction space, this tends to shift the water gas - equilibrium - occurring by the side of the synthesis proper - to the CO-side:

$$H_2 + \cancel{CO_2} \longrightarrow H_2O + CO$$
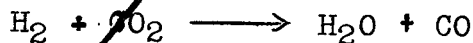
This ensures that the gas fed to the catalyst is <u>potentially</u> of the appropriate composition as required by iron type catalysts:

$$2\ CO + H_2 \longrightarrow (CH_2) + CO_2$$
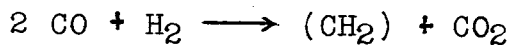
even though ordinary water gas of abt. 1 CO + 1.3 H_2 is used as fresh gas.

B. Processing

I.G. FARBENINDUSTRIE A.G., Oppau,
    May 29th, 1947.

Dr. Duftschmid, Oppau ─H─299.

  Whereas all commercial Fischer-Tropsch synthesis
plants in Germany have been built according to the
conventional Ruhrchemie-type design, the I.G.
laboratories have tackled the problem of finding a
better way of carrying out the reaction from various
angles. None of the possibilities studied, viz.

  a. Michael fixed-bed gas circulation process
  b. Michael liquid-phase catalyst-foam process
  c. Duftschmid (Winkler) fixed-bed oil circulat-
   ion process, has, however, found its way
   into commercial praxis.

  Since an outline of these studies has been given
before ') reference is made to the relative reports
and only some additional information as obtained from
Dr. Duftschmid will be reported here. Moreover,
attention is drawn to Dr. Duftschmid's survey of his
own work in Addendum No. I.

  In Dr. Duftschmid's "oil circulation process"
the Fischer-Tropsch reaction is carried out over a
fixed bed of catalyst, the synthesis gas passing up-
flow through the reaction space together with a
relatively large amount of recycled liquid reaction
product. The main aim of this development was to
remove the heat of reaction in large-size catalyst
beds, thereby making the use of big single catalyst-
space reactors (without any cooling tubes or similar
devices) possible.

  The work was started with fused iron catalysts
at 270°C and 100 ats. pressure, but although relatively
high space time yields were reached this operation was
not considered to be a paying proposition in view of

') FIAT F.R. No. 426 "Interrogation of Dr. Pier and
  staff, I.G. Farbenindustrie, A.G. Ludwigshafen/
  Oppau", page 7.   CIOS XXX-103 "I.G. Farben-
  industrie, A.G., Works Ludwigshafen and Oppau".

the high costs of the high pressure equipment. When iron catalysts were found to be active at lower temperatures and pressures, the operating pressure was reduced to abt. 20 ats., the same catalyst being used as by Dr. Michael (prepared through de-composition of iron carbonyl).

The pilot plant used in the later stages of this work consisted of a reactor 6 m x 500 mm $\emptyset$, provided with a hot separator for wax and an intermediate separator for middle oil, the latter product being recycled to the entrance of the reactor (Fig. I-1) ').

The temperature distribution in the reactor naturally depends on the amount of cold cycle oil. It may, however, also be affected by the way of injecting: if the total amount of cycle oil is introduced at the bottom a temperature distribution curve is obtained as indicated in Fig. I-2, showing a rather steep rise towards the end; if, on the other hand, part of the oil is injected near the top of the catalyst bed a much flatter temperature curve and a smaller total rise in temperature can be reached. Dr. Duftschmid had actually reduced the temperature rise from $50^\circ C$ to $20^\circ C$ at 65% CO conversion by running his plant in the latter way.

The nature of the cycle oil will also play an important role in the picture: heavy oil, B.P. $> 400^\circ C$, will not evaporate and will wherefore act according to its specific heat; light oil, B.P. $> 200^\circ C$, will partly evaporate in the reactor and consequently much heat will be removed as heat of evaporation.

Dr. Duftschmid would suggest making use of both faculties when designing a large-scale plant and would introduce heavy cycle oil at the bottom of the reactor and inject light oil at various spaces in the catalyst bed as indicated in Fig. I-3.

In order to keep the temperature well in hand at least 60-70 1 of middle oil $(200^\circ C$ $^+)$ of room temperature must be recycled to the reactor per kg of

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') It should be noted that the pilot plant had been damaged during the war and that Dr. Duftschmid was not working on the problem at the time of this visit.

reaction product formed and if a heavier oil ($400°C+$) is used this quantity would rise to a much higher value (150-200 l/kg).

Whereas in the "Hauptlaboratorium" at Ludwigshafen the "Rieselverfahren" (trickle operation) as developed by Dr. Reppe was generally used for carrying out fixed catalyst bed gas-liquid reactions with a large heat of reaction, this system had not been investigated by Dr. Duftschmid. Model experiments in glass equipment had convinced Dr. Duftschmid that turbulency is so intesive in the reactor as to ensure a very good contact between catalyst, gas and liquid and he therefore did not expect improvement from reversing the flow through the reactor.

The following figures were given for the Foam process and the oil circulation procedure:

In the oil circulation process in one stage 50-65% CO may be converted, whereas in two stages (the second being run at a $10-20°C$ higher temperature) abt. 90% CO-conversion is reached. The exit gas is composed of 55% CO_2
6-12% CH_4
20-23% H_2
13-18% CO

About the same applies to the Foam process.

	Oil circulation process:		Foam process:
Entry temp., $°C$	240		260
Pressure, ats.	15-30	100	15-30
Synthesis gas	CO/H_2 55/45		CO/H_2 45/55
Product yield, on synthesis gas $C_3 + g/m^3$	150-155		
Gaseous products ($C_1 + C_2$) on synthesis gas g/m^3	19		
Space time yield $C_3 +$, g/l, h	20-25	155	15-20

Product distribution and olefinicity (% wt.)	Oil circulation process:	Foam process
C_3-C_4	15 (85)	15 (80)
Gasoline 20-200°C	40 (50)	35 (70)
Middle oil 200-400°C	20-25 (25-40)	30 (70)
Heavy oil 400°C +	20-25 (20)	15 (65)
Alcohols	5	5

The gasoline must be subjected to a water treatment and further conventional refining; its octane number amounts to 65.

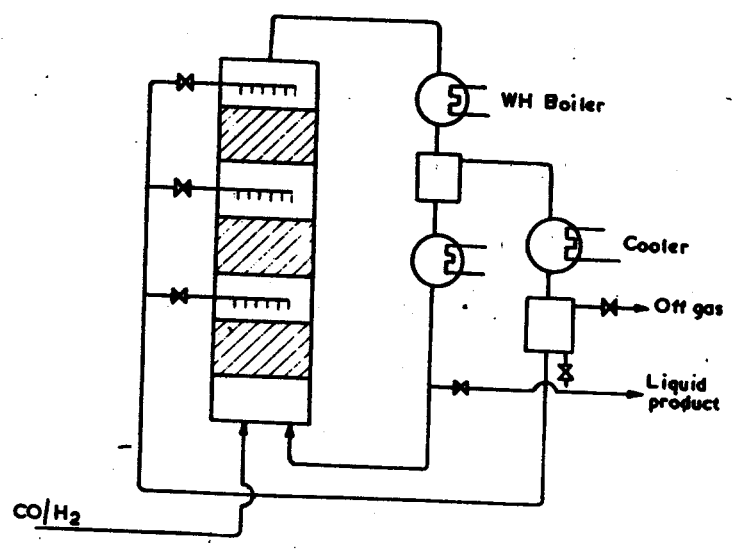The middle oil is very suitable for use as a diesel fuel; cetane number 75-80.

FIG. I⁻¹

Das Ölkreislaufverfahren zur Herstellung von Kohlenwasserstoffen
aus Kohlenoxyd und Wasserstoff

No 25812_A₄

FIG. I - 2

CO/H₂   cycle oil

temperature °C

290°C

no oil spray

260°C

240   with oil spray

length of oven
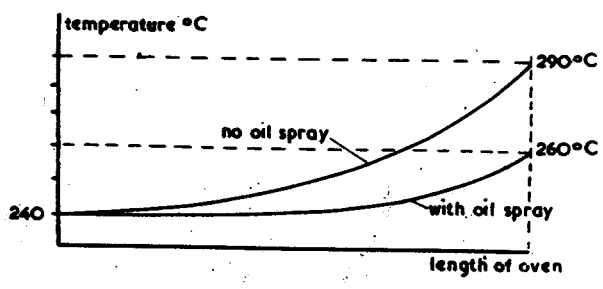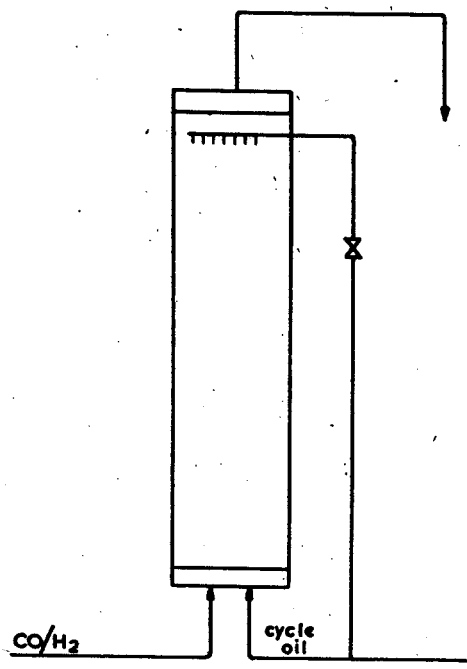
TEMPERATURE DISTRIBUTION IN REACTOR FOR FISCHER TROPSCH OIL CIRCULATION PROCESS   No.25813_A₄

FIG. I - 3

WH Boiler

Cooler

Off gas

Liquid product

CO/H$_2$