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Dr. Mietzel

Item 65

T.O.M. Microfilm No. 1

Dr. Fritz Winkler

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Discussion of CO-H₂ syntheses in Berlin July 1st, 1941

We are enclosing a report from our Dr. Peters on reports of investigators presented in a discussion on carbon monoxide-hydrogen syntheses July 1st, 1941. We are also attaching a table in which the more significant data of the various processes are compared. To the process of Dr. Michael we have made a few additions. Should you wish more complete or corrected data, please advise.

Sgd. Horing
Pier

Report (Data for Dr. Pier)Re: Hydrocarbon syntheses with iron catalysts.Paraffins:

We have operated with activated iron catalysts of various compositions. Our intention in the first place was to obtain a straight chain paraffin as raw material for the oxidation of paraffin. By using a synthesis gas $\text{CO:H}_2 = 1:2$ at temperatures of 205-225°C it is now possible to obtain a product boiling to the extent of 70% above 320°C while the remainder is divided in about equal parts in fractions up to 200° and 200-320°. The portion of the primary product boiling above 320° consists to the extent of about 90% of straight chain paraffins. Of the 70% mentioned about 1/3 is within the boiling range of 320-450°, the remainder is above that range. This high boiling portion can be cracked to paraffins having a boiling point of 320-450° to the extent of 65-70% so that in total about 50% of the entire primary product becomes available for oxidation.

Operation on a large scale may be embodied as a recycle process or be operated in a number of stages, with the carbon dioxide being washed out and the product separated. The calculated yield on converted gas is 180 g/Nm³ so that if 80% of this amount can be actually obtainable, 145 g of liquid + solid products/Nm³ would be obtained.

Olefins:

Using a synthesis gas mixture $\text{CO:H}_2 = 1:1$ the preferred formation of olefins can be obtained with the same precipitated catalysts. With a CO consumption of about 30% in one single throughput and at temperatures of 210-230°C a product is obtained the higher fraction of which (above 200°) consists of olefins to the extent of about 50% without the distribution of the product being substantially changed within the individual boiling range. The product consists of straight chain compounds

to the extent of at least 80%. The conversion of CO:H_2 takes place in the ratio 1:1, consequently in the same ratio as it occurs in the initial gas. This procedure makes it possible to utilize the middle fraction for the oxo-reaction while the higher boiling portion can be used for paraffin oxidation after previous hydrogenation.

The use of fused iron catalysts for producing olefins requires higher operating temperatures and a higher (twice as high) load/liter cats./hr. The olefin percent age in the middle and higher boiling fractions is about 75 and 60%, respectively. The catalysts have the disadvantage of converting the gas mixture in the ratio 1:1 even when a synthesis gas of 1:1 is used; if such a gas ($\text{CO:H}_2 = 1:1$) is passed over the catalyst from the start it is consumed in the ratio of $\text{CO:H}_2 = 1:0.6$, an observation which has frequently been made in the use of precipitated catalysts of other composition than the one presently used. The olefins which are obtained are straight chained compounds to the extent of 65% for the boiling range of 200-320° and to the extent of 75% for the higher fraction.

The higher synthesis temperature and the use of the synthesis gas in some other ratio than the one specified makes it appear that the precipitated catalysts will be found advantageous in the future for the synthesis of olefins.

Alcohols:

The production of alcohols from CO and H_2 have been attempted at average and higher pressures both with fused iron, roasted iron and precipitated iron catalysts without it being possible to present a conclusive result.

The qualitatively different results, however, are evident in the use of the above catalysts. There are sound reasons to believe that the precipitated catalysts will yield higher alcohols which can be used for the production of fatty acids when used at higher pressure (above 50 atm.), and without any noticeable

formation of carbonyl. For example, 20% a total yield of 70 g is obtained in a single throughput, or 180 g/Nm³ of converted gas.

Boiling Point	%	% Alcohols
- 200°	60	35
200 - 320°	20	40
320 - 450°	13	43
above 450°	7	55

Operating Conditions: 200 atm., catalyst load 500:1.

When roasted catalysts are used, lower C₁-C₅ alcohols are preferably obtained under the same operating conditions, in about equal proportions.

The work with fused iron catalysts has been temporarily discontinued because of the poor yields obtained with this type of catalysts under our operating conditions.

Sgd. A. Scheuermann

G. Wietzel

DISCUSSION ON CARBON MONOXIDE-HYDROGEN SYNTHESIS

Reports of Investigation

The investigators Dr. Michael, Dr. Duftschmidt, Dr. Scheuermann and Dr. Wenzel report on the progress of their work:

1. Gas Recycling and Foam Method

Dr. Michael, Ludwigshafen

Originally the work was designed to produce naphthas (benzines) with iron catalysts. Iron catalysts requiring temperatures in excess of 300°C can not be used in tube furnaces. Within the range of 300-350°C there is always a danger of carbon separation.

The gas recycling method was developed, in which a much smaller cooling surface is sufficient than in a tube furnace since the heat of reaction is conducted away through a waste heat boiler outside of the reaction chamber by means of which the operation can be conducted with a temperature gradient up to 50°C while only a few degrees are permissible in the tube furnace. At reaction temperatures in excess of 300°C the liquid product consists of 2/3 up to 3/4 of naphtha. This naphtha, after removal of oxygen with clay (alumina) has a research octane number of 84-85, contains much olefins and, after refining with clay (bleaching earth) and addition of alphasaphthol, is stable on storage and satisfactory on testing. 1/6 of the product consists of Diesel oil. This oil contains about 1.5% of oxygen and has a cetene number of 50-55. In addition, 1% of paraffin is obtained. The gas formed in the gas recycling process in addition to liquid products (about 30% of the total yield) contains much ethylene, propylene and butylene.

In experiments in a recycle furnace of 800-1000 Jato (metric tons per year), which was otherwise satisfactory, it was found that on transition from the relatively narrow recycle lines into the wide contact chamber a turbulence was produced and easily gave trouble when this transition did not coincide with a change in the direction of the gas flow. In later constructions this trouble has been taken into account.

Very solid sintered iron catalysts are used in the gas recycling process. Precipitated catalysts have not been found satisfactory because of their crumbling.

When the problem came up of producing middle oils, the foam process was adopted with a "red iron" (Eisenrot) prepared from iron carbonyl as catalyst, ground up in oil. A better middle oil is obtained in good yield at 240-250°C than in the gas recycling process. The feed used is a product containing as much olefins as possible. The Diesel oil has a cetene number of 60-70.

The foam method has the advantage that very little gas is formed. According to the operating temperatures, 3-8% is produced against 18-20% in the gas recycling process.

The process can be worked in furnaces provided with stirrers in which case stuffing box trouble develops. It is simpler to operate with a foam plate in which case additional circulation of oil prevents sinking of the catalyst. The portion of the oil circulation outside of the reaction chamber can be used for conducting away heat and for heating at the start of an operation.

In the foam process there was obtained, for example:

30 parts of naphtha (benzine), 30 parts of middle oil and 40 parts of paraffin which can be cracked to the extent of 70% to middle oils. Under somewhat modified conditions there may be obtained; 60% of naphtha, 30% of oil boiling to 350°C and 10% higher boiling oils. The naphtha obtained at 310° has a research O.N. of 90.

For the gas recycling process the following figures are characteristic:

Reaction temperature	325°C
Output	0.8 kg prod./liter cat./day
Conversion	91.5% in two stages
Yield of total products from 1 Nm ³ ideal gas	160 g

Of this product 70% = 112 g is liquid, thereof

30% = 48 g gases, thereof

7% alcohols + acids

15% Diesel oil 200-350°C

48% naphtha up to 200°

8% ethylene

9% propylene

3% propane

8% butylene

2% butane

= 100%

Of the C_4 compounds 60-65% are iso compounds. Including polymerization the yield is 112 g instead of 112 g. The 48% of naphtha can be made free of acid and odorless by clay refining. In that case the yield drops from 48 to 45.

The following figures may be given for the foam process on the middle oil.

Reaction temperature	240-250°C
Output	0.2 kg/liter foam vol./day.
Conversion	90% (in 3 stages).

Yield of 170 g of liquid and solid products from 1 kg/ m^3 ideal gas.

4-5% of alcohols are contained in the product water.

The oily product consists of

30% naphtha

30% middle oil

40% paraffin

To this should be added:

4-5% gasol

3% gas (gasification)

When naphtha is to be produced by the foam process with a high octane number, a reaction temperature of 310°C or somewhat less is necessary. The yield in that case is 160 g.

Dr. Wenzel gives the following figures on the inspection of products which Dr. Michael prepared with his own catalysts and with Leuna catalyst and which had been tested for alcohol content in Merseburg:

	Foam Process Sump Phase	Gas Recycling Process Gas Phase
Reaction Temp.	250°C	195°C
Catalyst	Michael Sintered Iron Cat.	Merseburg Fused Iron Cats. Reduced in Me-
Alcohols	Maximum at 160°C	Max. 36% in 1 fraction
In the Washing Agent Fraction C ₈ to C ₁₈	Not above 12%	26-28%
Olefins in C ₈ to C ₁₈	60-65%	40-50%

The rule seems to apply that the sum of alcohols plus olefins is about constant.

Dr. Wenzel reports that Leuna recently received a product from the Ruhr-Chemie which contained 80% of olefins in the C₈-C₁₈ fraction.

Dr. Michael gives a brief report on experiments with the Merseburg Synol catalyst in the foam process at 20 atm. and 210°C. For an output of 0.15 a product was obtained having the following properties:

In Fraction	220 - 250°	250 - 300°	300 - 350°
Alcohol	23%	24%	15%
Olefin	36%	30%	27%

II OIL CIRCULATION PROCESS

Dr. Duftschmidt, Oppau

In 1927-1928 Dr. Linck developed fused iron catalysts. In operation in the gaseous phase under high pressure trouble developed due to difficulties caused by carbon deposits.

In 1934 experiments were made in liquid phase and an oil circulation process was developed in which oil and gas were passed in parallel flow over fixed catalysts. It is important to operate in a boiling phase which can easily be accomplished by returning relatively low boiling oil constituents. At first the operation was conducted at 100 atm. and later under average pressure in 2 stages.

for an inlet temperature of 240°C to the furnace and 290°C outlet temperature 150 g of primary product (liquid + gasol) of the following composition was obtained in a 50% conversion in one stage from one Nm³ ideal gas:

40% primary naphtha	O.N. 62-68, O.N. + 0.1 lead, 85 2% oxygen content, removable by washing with water.
20% middle oil	Cetene number 78
20% hard paraffin	M.P. 95°C
15% gasol (without C ₂)	85% olefins
5% alcohols with	25% methanol 50% ethanol 25% higher alcohols, acetaldehyde, acetone, etc.

The yield is 30 g/lit.cat./hr. = 0.76/lit.cat./day.

With increasing pressure--experiments were made at 25, 100, 150 after 180 atm. the oxygen content of the products increases; at 180 atm., however, a large quantity of low boiling products is obtained and only a small amount of higher alcohols.

In order to direct the process toward the production of alcohol it is necessary to operate with a small throughput and a synthesis gas richer in hydrogen

With a $\text{CO}:\text{H}_2$ ratio of 1:1, 180 atm. and 280-290°C, 48.5% of alcohols were obtained in the total liquid produced for a 20-30% conversion:

- 8.5% methanol
- 21 % ethanol
- 10 % propanol
- 6.5% $\text{C}_4\text{-C}_{11}$ alcohols
- 2.5% $\text{C}_{12}\text{-C}_{20}$ "

The 33.5% hydrocarbons contained

- 25.5% naphtha (benzine)
- 3.5% middle oil
- 3.5% above 300°C

Of the 18% fatty acids

- 11 % were water soluble
- 5 % were $\text{C}_5\text{-C}_{11}$ acids
- 2 % $\text{C}_{12}\text{-C}_{20}$ "

The alcohols in the product disappeared

- a) for a high conversion
- b) When carbon is deposited on the catalysts.

III PARAFFIN SYNTHESSES

Dr. Scheuermann, Ammonia Laboratory, Oppau

The operation was conducted with the Ruhr-Chemie apparatus and cobalt catalysts were developed which gave high yields in paraffin, as previously reported.

The $\text{CO}:\text{H}_2$ ratio was 1:2, the pressure was 12 atm.

Later, precipitated iron catalysts were developed which operated as low as below 230°C. At present iron catalysts are available which operate as low as 195°C.

In one stage 70-75 g of product was obtained from one Nm³ ideal gas consisting of:

10% paraffin

15% middle oil

15% naphtha (benzine) with 3-5% of alcohols and 6-10% of unsat.

The calculated yield (on 100% conversion) is 130 to 140 g per Nm³.

At 260°, 75-80% olefins are obtained with a fused iron catalyst, of which 15-20% are suitable for the oxo-reaction. They contain to the extent of 30-95% straight chains. From the higher paraffins 70% of middle oil may be obtained by cracking.

IV. PARAFFIN AND SYNOL SYNTHESES

Dr. Wenzel, Merseburg

An attempt was made in 1938 to improve the Ruhr-Chemie process. Calculations indicated, however, that the process is still rather expensive.

It was therefore planned to work up special products.

1.) Hard Paraffin

A cobalt-aluminum oxide-zinc oxide catalyst was developed which at 180-185°C and 10 atm. gave in the tube furnace 140 g of product in one stage from 1 Nm³ synthesis gas, containing 70% of hard paraffin of 95°C m.p.

3.) A product was obtained in the tube furnace with fused iron catalyst (ammonia catalyst) which in its individual fraction contained, on the average:

	% Alcohol	% Olefins
100 - 200°	60	38 - 20
- 380°	65	30 - 20
- 440°	32	35 - 40

The product must be neutralized in order to prevent formation of esters during the distillation.

The alcohols and olefins are straight chained compounds to the extent of 80-85%

For the plant in Auschwitz the method has the advantage of being more easily changed from the production of naphtha + Diesel oil during the war to alcohol (synol) in peace time.

	Naphtha + Diesel Oil	Alcohol (Synol)
	3 stages	4 stages
CO ₂ Absorption	2 times	3 times
Gas Load	1:250	1:150
Yield ton/liq. prod./m ³ /day	0.92	0.64
g liq. prod. per m ³ ideal gas	140	160
g gas oil per m ³ ideal gas	14	16
g total/m ³ ideal gas	154	176
g ideal yield calculated from methane balance	181	190
% gas loss from gas use	8	5

Composition of product	%	Alcohols	%	Alcohols
to 200	64 - 40	5 - 10	44	38
200 to 300	18 - 30	3 - 8	18	56
300 to 400	6 - 15	2 - 5	15	50 - 60
above 400	12 - 15	2 - 5	23	37

The process can be carried out in the Ruhr-Chemie Mannesmann Plate furnace which has been tried out industrially and found to be satisfactory. A great advantage is that a stationary catalyst is used and no heated moving parts are needed in the apparatus.

The fused catalyst is easy to make, is very hard and unchangeable and may be readily regenerated by fusion.

Moreover, the plate furnace allows a change of catalyst at any time, such as the use of Oppau or Kersburg catalysts for producing paraffin or, especially, hard paraffin.

In order to obtain high yields in alcohol it is necessary:

- 1) To use low temperatures and to flush the catalyst with hydrogen.
- 2) To have a low conversion rate (the alcohols are again destroyed at higher temperature).
- 3) To allow a short contact time. (The alcohols are decomposed on iron catalysts. A catalyst layer longer than 2 meters should therefore not be used).

The CO₂ wash between the individual stages is done with water under pressure, causing the CO₂ content of the gas to drop from 15 to 3%. Low boiling products are additionally recovered with charcoal (A-carbon) from the CO₂ that has been washed out.

In conclusion Dr. Michael pointed to differences occurring in the different determinations for alcohol, rendering a direct comparison of the different processes difficult.

The alcohol contents of the Ludwigshafen products with Synol catalyst according to the foam process attain 75-80% of the alcohol contents of products produced in Leuna in tube furnaces, provided the analysis is made by the same method.

Dr. Wenzel pointed out that the alcohols break down during the distillation and that differences may be caused by this fact.

Dr. Michael believes that a decomposition of the alcohol in the distillation of his products is improbable inasmuch as the distillation is performed under a 2 mm vacuum. The reasons for the differences in the determinations is to be cleared up as soon as possible.

The patent situation was discussed.

After completed discussion the results were tabulated on the suggestion of Dr. Fier (See attached table.).

Note:- This table appears on T.O.M. Reel No. 1
at the ends - 9 -
of Item 65 in German. Copy follows this page

Fahrweise	Hochdruckversuche Ludwigshafen					Oppau		Hersberg		Annonlabor Op.	
	Michael					Duftschmidt		Wenzel		Scheuermann	
	Benzin	Synol	Dieselmil	Benzin	Synol	KV-Synthese	Alkohol Sy	M-Dieselmil	Synol	Paraffin	Olefin
Druck	20 atü	20 atü	20 atü	20 atü	20 atü	25 atü	180 atü	19-25 atü	19-25 atü	12 atü	12 atü
CO + H ₂	1 : 1,2	1 : 0,7	1 : 0,8	1 : 0,8	1 : 0,7	1 : 0,82	1 : 0,82	1 : 0,72	1 : 0,72	1 : 2	1 : 2
Temperatur °C	325	195	240-250	500-510	210	240-250	255-280	220-245	190-220	195-215	260
Verfahren	Gaswäscher		Schmelzverfahren			Alkoholampf		Gasphase		Zemphase	
Kontakt	Eisensinter	Synol-Kontakt 3-5 mm	Nickoxyd-Kontakt dünnschicht und gemahlen	ca. 90	Synolkontakt; fein	Eisenschmelzkontakt	Eisenschmelzkontakt	Eisenschmelzkontakt		akt. FeCoK Fällfugekontakt	Eisenschmelzkontakt
Zahl der Stufen	2	4	3	3	4	2	3-4	3	4	1 (Labor- ca. 8 Stab)	1 (Labor)
CO ₂ -Wäsche	1 x	3 x	2 x	2 x	3 x	keine	2 bis 3 x	2 x	3 x	techn. ja	techn. ja
% Umsetz	91-92	90	ca. 90	ca. 90	90	87	ca. 90	90 bis 95	90 bis 95	48 (1 Stufe)	60 (1 Stufe)
Frühprodukt 10 H ₂ O + CO + H ₂ g flüssig	112	160	170	170	165	120	ca. 140	140	160	75	60
g C ₂ O ₄ (% Olefine)	35 (80%)	25	5	5	12	22	ca. 50 (65%)	14 (75%)	16 (75%)	-	-
g C ₂ (% Olefine)	13								ca. 4 (100%)	-	-
g C ₁	35	10	6	10	6					ca. 10	ca. 15
Gasol + flüssig ber.					?			181 g	190 g	ca. 170 g	ca. 130 g
Flüssig-Produkt % bis 200 °C (% Alkohole)	78 (30 %)		34	63	52	59 (8%)	? (ca. 45%)	64-40 (5-10%)	44 (38%)	15 (-)	50 (?% Olef.)
% 200-300 °C					17	12 (ca. 2-3%)	? (ca. 45%)	18-30 (3-8%)	18 (56%)	15	15 (75% Olef. + ca. 10% Alk.)
% 300-350 °C	20		28	28	19			6-15 (2-5%)	15 (50-60%)		
% 350-400 °C			38	9	12	29				70 davon	35 (ca. 60% Olef. + ca. 10% Alk.)
% über 400 °C	2							12-15 (2-3%)	23 (37 %)	47 U. 450°	
Leistung kg/Liter-Raum/Tag	0,8	0,5	0,2	0,4	0,15	0,72	ca. 0,8	0,92	0,64	0,35-0,45	0,7
Gas-Durchsatz m ³ Gas/m ² Kat./Std.	1 : 250	1 : 120	1 : 100	1 : 200	1 : 40			1 : 250	1 : 250	1 : 180 bis 240	1 : 460