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CARBON MONOXIDE - HYDROGEN SYNTHESIS
Discussions in Berlin , July 1, 1941

Dr. Butefisch gave a review of the methods of synthesis in his introduction, and later in his summary of the reports of the other participants.

At present much work is done in many places on the CO/H_2 synthesis. Very few of the results are being published, except those by Fischer and the Ruhrchemie and some other synthesis plants, such as Brabagg, but there is no doubt that much progress has been made in many places.

The Ruhr-Chemie is here a pioneer. By agreement with the I. G. and a number of foreign concerns (e.g. USAC), the Ruhr-Chemie works in cooperation with the I. G. on the hydrocarbon synthesis. Ruhr-Chemie has in addition agreements with their licensees without apparently a clear understanding on the scope of the license and an exchange of experiences. There are or were agreements also between the Ruhr-Chemie and Lurgi (on syntheses and products), as well as between Ruhr-Chemie and the Gute-Hoffnung-Hütte. Certain difficulties may be expected in the days to come between ourselves and the IHS about the extensions of the areas of agreement after the changes in boundaries of Europe.

The synthesis of fuels is not to-day as economical as the hydrogenation. All installations are trying therefore to change their mineral oil processes to processes for chemicals, i.e. the production of products which bring higher profits than fuels.

1. Mineral Oil Section.

When the Fischer synthesis is used one may count on a production of 135 g. liquid products, including gasol. An improvement in the production by 20%, to 150 - 160 g would be of deciding importance in permitting it to compete with hydrogenation.

The installation costs of hydrogenation plants (from coal to gasoline) are about the same as for synthesis plants (from synthesis gas to gasoline.

2. Chemical Section

The first product made by the synthesis plants to be used for the production of chemicals was paraffin for the paraffin oxidation. The economy of the paraffin production has been changed many times, when the price of paraffin changed from 50 pfg/kg to 18 pfg, and was then artificially raised to 27 - 30 pfg.

The production of hard paraffin which was sold for over RM 60 (up to 85 - 90 RM /100 kg) resulted in some improvement in proceeds. The field of application is emulsifying agents. One may assume that an over-production will also be observed in the production of hard paraffin.

The Ruhr-Chemie has then developed in the chemical section the oxo process, which produces raw materials for detergents. There is an agreement in this field between the Ruhr-Chemie, I. G. and Henkel.

Organic chemistry requires alcohols in a high concentration .

The Auschwitz Company is supposed to have spread its activities over the whole field of chemistry. It is supposed to possess a fuel production department as well as an artificial rubber synthesis plant. The concern is supposed to furnish on a large scale the raw materials for the lacquer manufacture. The utilization of gases for valuable products in particular is supposed to be highly developed there.

Dr. Butefisch recommends the field of utilization of gases as particularly valuable for the production of chemicals.

Dr. v. Staden gave particulars about the Auschwitz installation. The Buna plant has a capacity of 30,000 te/year (?). In addition three experimental units are supposed to be erected there, namely

1) for the three stage process,
2) using the Reppe process (acetylene plus formaldehyde)
3) the propanol process.

They are supposed to have

1) carbide furnaces
2) a high pressure CO/H_2 synthesis, producing 5% propanol and 30% ethanol
3) an intermediate pressure synthesis

In addition, Auschwitz is supposed to produce also lubricants, i.e. esters of poly acids with alcohols and esters of polyalcohols with acids.

The lacquer plant produces in particular acetic acid esters with higher alcohols (chiefly to be used as thinners).

The acetic acid is produced catalytically by the addition of carbon dioxide to methanol.

Research directors Dr. Michael, Dr. Duftschmidt, Dr. Scheuermann and Dr. Wenzel report on the stage of their research.

1. Gas Circulation and the Foam Process.
Dr. Michael, Leuna

The original aim of the work was the production of gasoline with iron catalysts. Iron catalysts requiring temperatures in excess of 300° C can not be used in tubular reactors. There is always danger of deposition in the range between 300 and 350°C.

The gas circulation process has been developed, in which operations could be conducted with much smaller cooling surfaces, because the heat of the reaction was absorbed in a cooler outside the reaction space, which permitted operations with a temperature drop of 50°, while only a few degrees drop was possible with the tubular converters. With reaction temperatures in excess of 300°, the liquid components will contain 2/3 to 3/4 gasoline. After oxygenated compounds had been removed with alumina, an octane number 84 - 85 (research) had been obtained, with the gasoline high in olefines and stable in storage after refining with bleaching earth and the addition of α - naphtol as a stabilizer, and perfect in all the tests. 1/6 of the production consisted of Diesel oil. It contains 1 1/2% oxygen and has a cetane number 50 - 55. In addition about 1% paraffin is obtained. The gas formed with gas circulation, including the gaseous products (about 30% of the total production) contains much ethylene, propylene and butylene.

Tests with a recirculation reactor of 800 - 1000 te/year capacity, which operated in general satisfactorily, showed, that when passing from the relatively small circulation tubes to the wide catalysts space, there formed readily some disturbing gas eddies, if it coincided with changes in the gas direction. This must be taken into consideration in the new installations.

Very strong sintered iron catalysts are required for the gas circulation process. Precipitation catalysts have not been found satisfactory because they are readily abraded.

The foam process was taken up when the middle oil production came up for discussion. With a catalyst composed from "iron red" from iron carbonyl, reground in the oil, a better grade of middle oil is obtained by the foam process at 240 - 250°C, and with a better yield, than in the gas circulation process. Operations are conducted for the production of a maximum olefine concentration. The cetane number of the diesel oil is 60 - 70.

The foam process has the advantage of a very low gasification. It amounts to but 3 - 8%, depending on the temperature, against the 18 - 20% in the gas circulation process.

The process can be carried out in mixer reactors, but stuffing box troubles in that case will have to be overcome. It is technically more simple to operate with a foam plate, preventing any settling of the catalyst by an additional oil circuit. The part of the oil circuit outside the reaction space may be utilized for heat removal, or for heating up when starting operations.

An example of results obtained in the foam process:

30 parts gasoline, 30 parts middle oil and 40 parts paraffin, which could be split to 70% middle oil. By changing conditions, one could get 60% gasoline, 30% below 350°C and 10% higher boiling. The research octane number of gasoline obtained below 310° was 90.

The characteristic factors of the gas circulation process are:

Reaction temperature	325°C
Yield	0.8 kg prod/li catalyst/day
Conversion	91.5% in two stages.

Total yield of products 160 g/nm^3 ideal gas

of which 70% or 112 g are liquids containing	7%	alcohols and acids
	15%	Diesel oil 200 - 350°
	48%	gasoline, to 200° C
30%, or 48g are gases, containing	8%	ethylene
	9%	propylene
	3%	propane
	8%	butylene
	2%	butane
	100%	

60 - 65% of the C_4 are iso compounds. If polymerization be included, the yield amounts to 142 g, instead of 112. The 48% gasoline can be neutralized and made odorless by refining with alumina. This will reduce the yield from 48 to 45%.

The following characteristic production factors were quoted for the foam process for the production of middle oil:

Reaction temperature	240 - 250°C
Production	0.2 kb/li of foam volume/day
Conversion	90% (in three stages)

Yield in liquids and solids - 170 g/nm^3 of ideal gas
Of these, 4-5% alcohol in the reaction water.

The oil fraction consists of

Gasoline	30%
Middle Oil	30%
Paraffin	40%

There is, in addition, Gasol 4-5%
Gasification 3%

If the foam process is conducted for the production of gasoline, a reaction temperature of 310°C or lower must be maintained for the production of high octane number. The yield in that case is 160 g.

Dr. Michael studied the products obtained with his own and the Leuna catalysts, and had them tested for alcohols in Merseburg, and Dr. Wenzel reports the following values for them:

	Foam process. Sump Phase	Gas circulation process Vapor Phase
Reaction temperature	250°C	195°C
Catalyst	Michael sintered iron catalysts	Merseburg fused iron catalyst, reduced in Merseburg.
Alcohols	Maximum at 160°C	Maximum 36% in a single fraction
C_8 - C_{18} in the scrubber agent	Not over 12%	26-28%
Olefines in C_8 - C_{18} fraction.	60 - 65%	40 - 50%

The rule holds, that the sum of alcohols and olefines is nearly constant.

Dr. Wenzel says that Leuna has recently obtained from the Ruhr-Chemie a product consisting of 80% olefines in the C_8 - C_{18} fraction.

Dr. Michael has made a short communication on tests with the Merseburg Synol catalyst using the foam process at 20 atm. and 210°C. The following product was obtained with a 0.15 yield:

In the fractions:	220 - 250°	250 - 300°	300 - 350°
Alcohols	23%	24%	15%
Olefines	36%	30%	27%

3. Oil Circulation Process
Dr. Duftschmidt, Oppau

Dr. Link has first developed the fused iron catalysts in 1927 1928. When working in the gas phase under high pressures, difficulties were met, resulting from the deposition of carbon.

Experiments in a liquid phase were begun in 1934, and the oil circuit process then developed, in which oil and gas are led concurrently over a fixed bed catalyst. It is important that operations be conducted in a boiling phase, produced by the return of the relatively low boiling oil fractions. Operations were first conducted at 100 atm., later at medium pressures in two stages.

At the reactor inlet temperature of 240° and outlet at 290°, 150 g yields were obtained/nm^3 of gas in each stage (liquid and gasol), of the following composition:

40% primary gasoline, octane number 62 - 68, with 0.1 lead o.n. 85
oxygen contents 2%, can be removed by water washing;
20% middle oil cetane number 78
20% hard paraffin melting point 35°C.
15% Gasol (Not counting C_3) with 85% olefines
5% Alcohols consisting of 25% methanol
50% ethanol,
25% higher alcohols, acetaldehyde, acetone, etc.

The yield is 30g/li cat./ hour - 0.76/li.cat./day

Tests were run at 25, 100, 150 and 180 atm., and with increasing pressure the oxygen content of the product is raised, but at 180 atm. very much lower boiling and only very little of the higher alcohols is obtained.

The process can be converted to alcohol production, the conversion of a hydrogen-rich gas must be kept low.

With a $CO:H_2$ ratio of 1:1.180 and at 280-290°C, with a 28 - 30% conversion, 48.5% alcohols were obtained, namely:

8.5% methanol
21% ethanol
10% propanol
6.5% C_4 to C_{11} alcohols
2.5% C_{12} to C_{20} alcohols

The 33.5% hydrocarbons contained

26.5% gasoline
3.5% middle oil
3.5% over 300°C

The 18% fatty acids were

11% water soluble
5% C_5 to C_{11}
2% C_{12} to C_{20}

The alcohols in the product disappear

a) with high conversion
b) with carbon deposition upon the catalyst.

III Paraffin Synthesis
Dr. Scheuermann, Ammonia Laboratory, Oppau

Operations were performed with the Ruhr-Chemie equipment and Co catalysts have been developed which produced high paraffin yields, as already reported previously.

The $CO:H_2$ ratio is here 1:2, the pressure 12 atm.

At a later date, precipitated iron catalysts were developed, which were already active at below 230°C. At present we have iron catalysts which operate already at 195°C.

With one stage operation 70 - 75 g products / nm^3 ideal gas were obtained, consisting of:

10% paraffin
15% middle oil
15% gasoline with 3 - 5% alcohols and 8 - 10% unsaturated.

The calculated yield (to 100% conversion) was 130 - 140 g/nm^3.

At 260°C, using a fused iron catalyst, 75 - 80% olefines were obtained, 15 - 20% of which are suited to the oxo reactions. They contain 90 - 95% of straight chains. 70% middle oil can be obtained by splitting the higher paraffins.

IV. Paraffin and Synol Synthesis
Dr. Wenzel, Merseburg

Efforts have been made in 1938 to improve the Ruhr-Chemie processes. Calculations showed however that the process was becoming steadily more costly.

The work was therefore changed over to producing special products:

1) Hard Paraffin

A cobalt-aluminum oxide-zinc oxide catalyst was developed which produced 140 g. product/nm^3 of gas at 180 - 185°C and 10 atm. pressure, operating in one stage tubular furnaces, and containing 70% hard paraffin, m.p. 95°C.

2) Alcohols (notice: No. 2 in the original).

Products were obtained with fused iron catalysts (Ammonia catalysts) the different fractions of which contained on the average

	% alcohols	% olefines
100 - 200°	60	38 - 20
- 380°	65	30 - 20
- 440°	32	35 - 40

The product had to be acidified to prevent ester formation during the distillation.

The alcohols and olefines are 80 - 85% straight chain.

This installation offers advantages over the Auschwitz installation of being more readily changed over during the war to a gasoline plus Diesel oil process, and during peace to the alcohol (synol) process.

Details of the two processes are:

	Gasoline - diesel oil	alcohol (synol)
CO_2 absorption	3 stages twice	4 stages three times
Gas load	1 : 250	1 : 150
Yield to/fl.prod./m^3/day	0.92	0.64
Temperature, °C	220 - 245	190 - 220
g liq. prod/m^3 ideal gas	140	160
g gasol/m^3 ideal gas	14	16
Total g/m^3 ideal gas	154	176
g ideal yield computed from methane balance	181	190
% gasification of the gases used	8	5

Composition of products	%	alcohols	%	alcohols
to 200	64-40	5-10	44	38
200 - 300	18-30	3-8	18	56
300 - 400	8-15	2-5	15	50-60
over 400	12-15	2-5	23	37

The process can be carried out in Ruhrchemie Mannesmann-plate reactors, which have been tested on a large scale and gave good satisfaction. It has the advantage of a fixed bed catalyst and no hot movable parts in the equipment.

The fused catalyst can be easily made, is very hard and strong, and can be readily regenerated by fusion.

The plate reactors permit a ready change-over to other catalysts, e. g. the Oppau or Merseburg catalysts for the paraffin or the hard paraffin production.

It is important for the production of high alcohols to

1) operate at lower temperatures, and after a previous flushing of the catalyst with hydrogen.
2) low conversion (alcohols are again destroyed at high temperatures).
3) short time of contact with the catalyst (alcohols are destroyed by contact with iron catalysts. One should not therefore exceed in practice a 2 m layer of the catalysts).

The CO_2 scrubbing between the individual stages is done with water under pressure, which reduces the CO_2 content of the gas from 15 to 3%. Low boiling fraction are recovered from the washed CO_2 by a subsequent absorption on activated charcoal.

Dr. Michael pointed out in conclusion the difference found in the different alcohol determinations which made direct comparison of the different processes more difficult.

The alcohol content of the Ludwigshafen product of the synol process, run by the foam method reach 70 - 80% of the alcohol content of the product made in Leuna in the tubular furnaces, when the analytical methods are the same.

Dr. Wenzel pointed out the decomposition of the alcohols during the distillation which might have accounted for the difference in results.

Dr. Michael considered the decomposition of the alcohols during the distillation as being improbable, because the distillation is carried out in a vacuum of 2 mm. The reason for the difference in results will be studied in the near future.

In conclusion, the patent situation has been discussed in detail.

	High Pressure Experiment, Ludwigshafen Michael				
Method	Gasoline	Synol	Diesel Oil	Gasoline	Synol
Pressure	20 atm.	20 atm.	20 atm.	20 atm.	20 atm.
CO : H_2	1 : 1.2	1 : 0.7	1 : 0.8	1 : 0.8	1 : 0.7
Temperature °C	325	195	240-250	300-310	210
Process	Gas Circulation			Foam Process	
Catalyst	Sintered Iron	Synol-Catalyst 3-5 mm	Reduced and ground iron oxide catalyst.		Synol-Catalyst finely ground
Number of stages	2	4	3	3	4
CO_2 - Scrubbing	1 x	3 x	2 x	2 x	3 x
% Conversion	91-92	90	about 90	about 90	90
Primary product per Nm^3 CO + H_2 g liquid	112	160	170	170	165
g C_3C_4 (% Olefins)	35 (80%)	15	5	5	12
g C_2 (% Olefins)	13				
g C_1	35	10	6	10	6
Gasol + Liquid					?
Liquid Product % to 200 (% Alcohols)	78 (30%)		34	63	52
% 200 - 300°C	20		28	28	17
% 300 - 350°C					19
% 350 - 400°C			38	9	12
% over 400°C	2				
Capacity kg/Liter-space/day	0.8	0.5	0.2	0.4	0.15
Gas-Thruput m^3 Gas/m^3 Cat/hr	1 : 250	1 : 130	1 : 100	1 : 200	1 : 40

	Oppau Duftschmidt		Merseburg Wenzel	
Method	Hydrocarbon - Synthesis	Alcohol Synthesis	Gasoline + Diesel Oil	Synol
Pressure	25 atm.	180 atm.	19-25 atm.	19-25 atm.
CO : H_2	1 : 0.82	1 : 0.82	1 : 0.72	1 : 0.72
Temperature °C	240 - 290	235 - 280	220 - 245	190 - 220
Process	Circuit		Gas Phase	
Catalyst	Fused iron Catalyst	Fused iron Catalyst	Fused iron catalyst	
Number of stages	2	3-4	3	4
CO_2 - Scrubbing	None	2 to 3 x	2 x	3 x
% Conversion	87	about 90	90 to 95	90 to 95
Primary Product per Nm^3 CO + H_2 g liquid	128	about 140	140	160
g C_3C_4 (% Olefins)	22	abt. 50 (65%)	14 (75%)	16 (75%)
g C_2 (% Olefins)			-	abt. 4 (100%)
g C_1				
Gasol + Liquid			181 g	190 g
Liquid Product % to 200 (% Alcohols)	59 (8%)	?=(abt. 45%)	64-40 (5-10%)	44 (38%)
% 200 - 300°C	12 (abt. 2-3%)	?=(abt. 45%)	18-30 (3-8%)	18 (56%)
% 300 - 350°C	29	? =	6-15(2-5%)	15 (50-60%)
% 350 - 400°C				
% over 400°C			12-15(2-5%)	23 (37%)
Capacity kg/ Liter-space/day	0.72	abt. 0.8	0.92	0.64
Gas-thruput m^3 Gas/m^3 Cat/hr.			1 : 250	1 : 250

	Ammonia Laboratory - Oppau Schsuermann	
Method	Paraffin	Olefin
Pressure	12 Atm.	12 Atm.
CO : H_2	1 : 2	1 : 2
Temperature °C	195 - 215	260
Process	Gas Phase	
Catalyst	act. FeCuK precipitation Catalyst	Fused iron Catalyst
Number of stages	1 (Laboratory Scale)	1 (Laboratory Scale)
CO_2 - Scrubbing	Yes, on Industrial Scale	
% Conversion	48 (1 Stage)	60 (1 Stage)
Primary Product per Nm^3 CO + H_2 g liquid	75	60
g C_2C_4 (% Olefins)	-	-
g C_3 (% Olefins)	-	-
G C_1	abt. 10	abt. 15
Gasol + Liquid	abt. 170 g	abt. 130 g
Liquid Product % to 200 (% Alcohols)	15 (-)	50 (?% Olefins)
% 200 - 300°C	15	15 (75% Olef.) + 15% Alc.)
% 300 - 350°C	70 of this	35 (abt. 60% Olef. + abt. 10% Alc.)
% 350 - 400°C		
% over 400°C	47 over450°	
Capacity kg/Liter space/day	0.35-0.45	0.7
Gas-thruput m^3 Gas/m^3 cat./hr.	1:180 to 240	1 : 480