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THREE PAPERS ON THE DUFISCHMID
OIL CIRCULATION PROCESS

I

July 25, 1941

CATALYST

The process is based on the use of fused iron catalysts, which was developed by Dr. Linckh in 1927-1936 who also found the best methods of using it. The principal constituent of the catalyst is iron with small amounts of readily available and cheap addition substances. It can be repeatedly regenerated for use in a very simple manner by roasting it in air and re-fusing to form a new catalyst.

SYNTHESIS GAS

The synthesis gas is high in CO and has a proportion of $\text{CO}:\text{H}_2 = 1:0.7-0.85$. This makes the synthesis particularly economical if combined with a water gas producer, e.g., a Winkler generator, in which CO-rich gas is produced directly. All conversion becomes, in this case, unnecessary. The gas must, of course, be purified from sulfur and from organic sulfur, and if the CO_2 contents are high must also be passed through CO_2 scrubbers.

PRESSURE

The synthesis is best carried out at 25 atm pressure and is therefore a middle pressure synthesis.

OIL CIRCULATION PROCESS

The process carried out on a pilot plant scale in 1934-1938, had the liquid products obtained, as well as the synthesis gas, led over a fixed bed of granular catalysts in the reactor. The oil produced is recirculated. The synthesis of motor fuels is done in two stages, without the use of an intermediate CO_2 scrubbing. The fixed bed catalyst overcomes any difficulties in separation of the oil produced from the catalysts, as well as the non-uniform distribution of the catalyst in the oil occurring in the processes with finely divided suspended catalysts.

ADVANTAGES OF THE OIL CIRCUIT

The heat of the reaction in the oil circulation system is carried away from the catalyst by the oil circuit itself. A uniform temperature is produced throughout the whole bed of the catalyst, without overheating even the most active centers. The wetting reduces the formation of the undesirable products which might form as the results of an excessive conversion. The formation of gaseous products is lower than in the gas circulation process.

Unlike the processes with indirect heat removal, the catalyst is not distributed in thin layers. The reactors used have no insets in them. The process may well develop into one involving the construction of large synthesis units, with the resulting constructional advantages.

HYDROCARBON SYNTHESIS

Eighty-seven percent conversion in the two stages were obtained/l cbm synthesis gas with a space/time yield of 0.72 kg

of production/li catalysts, day, and with a total production of 150 g products/cbm gas. The products consisted of:

40% primary gasoline (50-55% olefines, 2% oxygen, o.n. 65)

20% gas oil (40-45% olefines, 0.6-1% oxygen, o.n. 78)

20% hard paraffin wax (m.p. 95°C)

15% gasol (about 75% olefines)

5% alcohols (chiefly ethanol)

ALCOHOL SYNTHESIS

The oil circulation process can be changed over to the synthesis of oxygenated compounds. With a pressure of 180 atm and with only 25-30% conversion of the synthesis gas in a single stage, and with a proportion of $CO:H_2 = 1:1$, 50% and over of alcohols were produced in all the fractions. The high pressure and the higher temperatures used reduce the size of the molecules, and as a result a relatively larger amount of lower and middle alcohols is produced. The oil circulation can, nevertheless, be also adopted to the alcohol synthesis, and one doubtlessly may expect to produce also the higher alcohols when using catalysts treated by the Merseburg method. One may even expect that the above mentioned favorable affect of the catalyst wetting with a corresponding weakening of the active centers of the catalysts will suppress a further conversion to olefines of the alcohols formed as a primary product.

5,000 TE/ANN PROJECT OPPAU

The plant designed for 5,000 te/ann production and laid out to permit enlarging it to 15,000 te/ann, is to be operated

with off gases of the butanol and ammonia synthesis. The products formed are intended to be hydrogenated in the existing units and the gasoline and gasoil used as motor fuels. The paraffin wax will be used as a raw material for the production of detergents, for which it is well suited.

Operating under such conditions, the experimental production will be operated without additional costs.

PATENT SITUATION

The process is protected by the German and foreign patent applications as follows:

J 53,698, 11-18-35 (O.Z. 9,104)

J 57,290, 11-3-36 (O.Z. 9,635)

J 11,461, 3-31-39 (O.Z. 11,461)

In addition, the iron catalyst which so far has been found best, is protected by DRP 708,512, 11-14-35 (O.Z. 9,099).

/s/ Duftschmid

II

October 9, 1942

BRIEF REPORT ON THE HYDROCARBON SYNTHESIS FROM CARBON MONOXIDE AND HYDROGEN BY THE OIL CIRCULATION PROCESS

The data required for the calculation and design have been obtained in the 9 te/mo pilot plant for the development of synthesis of motor fuels and paraffin from water gas by the oil circulation process.

The oil circulation process is characterized by:

(1) The heat of the reaction is absorbed by the cir-

problem of heat removal and the safety of the process of the reaction is therefore solved with the simplest possible reactor construction (towers without insets).

(2) The iron catalyst to be used differs from the ammonia catalyst only by small additions.

(3) From construction standpoint the synthesis plant is similar to the usual pressure water scrubbers. The synthesis is performed at 20-25 atm. Ten thousand te/ann installation will consist of 22 towers, filled with the catalyst without any insets.

(4) The synthesis plant proper has the advantage over the Ruhrchemie-Fischer plants by requiring less than one-half the costs, and about one-third of the requirements for materials (iron and steel).

The cost of a 100,000 te/ann plant (synthesis plant without gas production and without the usual auxiliary units) will amount, according to the estimates of the M.T.A., Ludwigshafen, to RM 4,700,000, with an additional RM 1,020,000 for the catalyst production.

(5) The synthesis requires a CO-rich gas in proportion of: 50:50-56:44, produced directly in the Winkler gas generators. No conversion is necessary.

(6) The primary products are: 40% primary gasoline with an o.n. 62-68 (with 0.1 TEL - 81-85). The 2% oxygen content can be removed by treating with alumina which will increase the o.n. to 70-75 (with 0.1 TEL - 85-87).

20% paraffin, m.p. around 90°C

15% Gasol consisting of	12% propane
	42% propylene
	7% butane
	26% butylene
	5% isobutylene

5% alcohols consisting of	50% ethanol
	25% methanol
	25% higher alcohols, acetaldehyde, acetone, etc.

The proportion of the products can be altered within certain limits.

(7) One hundred and fifty g of the above products/nobm CO + H₂ have been obtained so far in the pilot plant.

Further development possibilities are presumably still present in the process (variation in the catalyst, omission of the final purification of the synthesis gas, etc.).

It is therefore suggested that a production unit for 5,000 - 10,000 te/ann be installed in some already existing or projected plant with an available suitable gas supply. The cost of such a plant, including the cost of the catalysts, will amount to RM 522,000, for the 5,000 te/ann unit, or RM 809,000 for the 10,000 te/ann unit. The construction of a 10,000 te/ann unit would require 350 te iron and 0.8 te copper.

/s/ Duftschmid

III

August 11, 1941

STATE OF EXPERIMENTS ON ALCOHOL SYNTHESIS BY THE OIL CIRCULATION PROCESS

Dr. Muller-Gunradi has ordered in February 1940, to change over the oil circulation process to the production of higher alcohols and to conduct the proper experiments; this was done from February to May 1940, in a 160 li reactor, in which the earlier hydrocarbon synthesis experiments have been run.

In line with the then existing information on the hydrocarbon synthesis obtained in our own experiments, the following operating conditions were supposed to result in the increased formation of oxygenated products:

- (1) The use of hydrogen-rich synthesis gas.
- (2) Use of higher pressures.
- (3) Incomplete conversion.
- (4) The use of special catalysts.

The catalysts favoring the formation of oxygenated compounds had first to be prepared, and moreover the effect of operating conditions had yet to be determined, and the first series of experiments was therefore run with the catalyst 997 previously used for the synthesis of hydrocarbons (reduction temperature 500°C). Experiments were run with hydrogen-rich synthesis gas $\text{CO}:\text{H}_2 = 1:3$, with a conversion of 30-40% instead of the 50% commonly used in the synthesis of hydrocarbons.

The operating pressure was varied during the course of the experiments. The following pressures were used:

100 atm

20 atm

150 atm

180 atm

The pressure of 20 atm was also used because of the advantages of having a process using the same kind of equipment for the synthesis of hydrocarbons and of alcohols. The hydrocarbon synthesis was supposed to operate at 25 atm, and carrying out the alcohol synthesis in the same middle pressure equipment would naturally offer some advantages.

The experiments led to the following results, which agreed with our earlier observations.

The oxygen content of the products increased with increased pressure. The average oxygen content of the total product, including the gasol, calculated from analysis of the different products was as follows:

<u>Pressure</u>	<u>Average Oxygen Content</u>
20 atm	3.5%
100 atm	7.5%
150 atm	11.4%
180 atm	11.5%

The formation of water-soluble alcohols ran parallel with the above:

<u>Pressure</u>	<u>Proportion of C₁-C₆ Alcohols in the Total Product</u>
20 atm	18.4%
100 atm	24.7%
150 atm	40.5%
180 atm	36.1%

The large excess of hydrogen results in a high proportion of the low molecular weight alcohols (chiefly C_2H_5OH , with some C_1 , C_3 and C_4 alcohols).

The increased pressure also results in an additional increase in the proportion of the lower alcohols.*

The above results show that:

The increased hydrogen content of the synthesis gas raises the oxygen content of the total products.** The lower alcohols participate preferentially in this increased production of oxygenated compounds.

The increase in pressure affects the increased total oxygen content as well as the formation of the lower alcohols in the same way as an increased hydrogen content of the synthesis gas.

The following may be stated with regard to the formation of hydrocarbons which proceeds side by side with the production of oxygenated compounds:

* The present results merely confirm the earlier ones previously obtained: thus in experiments with an operating pressure of 100 atm, other conditions remaining the same, 5.5% of water soluble alcohols were obtained when the proportion of $CO:H_2 = 1:1$, and 15.7% of water soluble alcohols were obtained with $CO:H_2 = 1:3$.

An examination of earlier tests for the synthesis of hydrocarbons with the synthesis gas in proportion $CO:H_2 = 1:1$ shows furthermore that the increase in pressure favors the formation of the C_1 - C_2 alcohols:

Oppau 100 atm test, alcohols 6-8% of the total product.
Merseburg 200 atm, alcohols 12-14% of total products.

** We understand in this case by total products all the products with the exception of CH_4 , C_2F_4 , C_2H_4 , CO_2 and H_2O .

The increased hydrogen content lowers the percent of the oxygen-free products in the total products. This is merely another statement of the fact that the oxygen derivatives have increased. It results, however, in a striking lowering of the molecular weight of the hydrocarbons, so that much gasol (C_3 and C_4) and light oils are formed. The rise in pressure affects in this respect the process in the same way as the increase of hydrogen in the synthesis gas.

The experiments were run with the purpose of producing synthetically primarily the higher alcohols, and the above results could not be considered very satisfactory in this respect.

The tendency to produce chiefly low mol. wt. products is affected greatly by the temperature of the synthesis. This viewpoint has, however, been taken into consideration right from the start in this series of experiments, and the catalyst was reduced at as low a temperature as possible ($500^{\circ}C$); no improvements could however be observed with the catalyst 997. A second possibility might have been offered by a change of the $CO:H_2$ ratio, because the CO-rich gas produces more high-boiling oils. This measure was then used as shown below.

The higher alcohols ($C_{12}-C_{20}$) were particularly desired for the production of detergents, and would be contained in the higher fractions of the oils produced.

	<u>100 atm</u>	<u>150 atm</u>	<u>180 atm</u>
Water soluble oil, 150-250°C	9.2%	9.4%	6.7%
Water soluble oil, + 250°C	6.8%	4.6%	2.8%
Vacuum fraction (1mm 100-200°C)	5.4%	4.5%	2%

The above summary shows that the C_{12} - C_{20} alcohols in the 100-200°C fraction (1mm Hg) formed but a small part of the total products, which agreed with the results given above that the hydrogen-rich synthesis gas and high pressure favored the formation of only a very small amount of high boiling oil constituents.

The average molecular weight of the alcohols in this fraction was assumed to be C_{14} , and the alcohol value was obtained from the saponification and hydroxyl numbers.*

The fraction consisted therefore of 30-40% alcohols. One could observe here no clear relationship between this value and pressure, and the important question of whether the higher alcohol content increases with increasing pressure must be still considered unanswered. We cannot evaluate in this respect the test at 20 atm because it failed to fit into the picture and produced hardly any high boiling oil.**

One may notice the relationship between the experimental temperature and the space/time yield.

<u>20</u>	<u>100</u>	<u>150</u>	<u>180</u>
260-286°C	236-278°C	220-270°C	235-260°C
0.43	1.00	0.80	0.95 kg/11, day

We may summarize these tests as follows:

The process may perhaps prove of interest in the production of lower alcohols when operating with a large excess of hydrogen and at high pressures

* This method leads to high alcohol results, as has been shown by more accurate analysis.

** Experience has shown that after catalysts are operated under more extreme conditions, they no longer give normal values when changed over to milder reaction conditions. The order in which the tests were run were - first operating at 100 atm, and only then at 20 atm

(50atm and over). Appreciable amounts of the C_3 and C_4 hydrocarbons are still formed in that way, and the process could be run in connection with the oxo process. In this way additional amounts of butanol, amyl alcohol, also aldehydes and ketones could be obtained.

Experiments with the synthesis gas $CO:H_2 = 1:1$ have been run after completing the tests with hydrogen-rich synthesis gas; the pressure was 120 atm and the conversion 30%.

As expected, the amount of the higher boiling constituents was increased with the higher carbon monoxide content. We obtained

24.0% gasol
21.6% oil - 150°
12.7% oil 150-250°
9% oil + 250°
32.7% lower alcohols

The $C_{12}-C_{20}$ fraction now amounted to 7.2% of the total product. We were, however, surprised to find that the proportion of oxygenated compounds has actually increased in this higher fraction.

<u>Pressure</u>	<u>180</u>	<u>180 atm</u>
$CO:H_2$	1:3	1:1
Hydroxyl number	45-50	60-65
Saponification number	40-50	89-95

The analysis of the products gave the following composition of the liquid fractions:

8.5% methanol
21.0% ethanol
10.0% propanol
6.5% alcohols C_4-C_{11}
2.5% alcohols $C_{12}-C_{20}$
11.5% water soluble fatty acids
5.0% fatty acids C_8-C_{11}
1.5% fatty acids $C_{12}-C_{20}$

26.5% hydrocarbon - 200°C)
 3.5% hydrocarbon 200-300°C) 1/2 of them
 3.5% hydrocarbon + 300°C) olefines

Additional experimental data:

Space/time yield: 1 kg total product/11, h

Yield: 170g/cbm converted CO + H₂

Reactor temperature

Bottom 236°C
 Top 260°C

Conversion 32.5% of CO + H₂

In our later work we retained the following operating conditions:

- (1) Incomplete conversion, with the degree of conversion reduced to 20-30%
- (2) CO-rich synthesis gas, CO:H₂ = 1:1
- (3) Pressure 180 atm

The increased yield of high molecular weight alcohols was to be favored:

- (4) By using oxygen-combining catalysts
- (5) By selection of catalysts operating at lower temperatures

Dr. Linckh has accordingly selected the following catalysts:

Catalyst 1227, especially active in forming O₂

Catalyst 1374, especially active, operates well even at 1 atm

ALCOHOLS

Test number	GV26	GV27
Catalyst number	1227	1374
Degree of conversion, % of CO + H ₂	30.4	21.7
Pressure, atm	180	180
Space/time yield, kg/11, h	1.04	1.10
Yield g/cbm CO + H ₂ conversion	177	226
Cold catchpot oil, % by weight of total production	8.7	27.5

Tail gasoil, % of weight of total production	31.5	21.1
Activated charcoal oils, % of weight by total production	16.5	12.3
Water soluble alcohols, % of weight by total production	11.8	8.9
Gasol, % of weight by total production	31.5	30.2
Reactor temperature, bottom °C	250-260	196-264
Reactor temperature, top °C	270-280	224-274
Percent C ₁₂ -C ₂₀ fraction in total production	20	40
Saponification number of C ₁₂ -C ₂₀ fraction	77	56
Hydroxyl number of C ₁₂ -C ₂₀ fraction	45	58

Date

May 31, 1940 - September 18, 1940

The two tests have not indicated progress in the desired direction.

The catalyst 1227 did not produce the desired increase in alcohol formation.

The catalyst 1374 does begin work at 196-224°, but requires a gradual rise in temperature in order to maintain conversion. It does, however, definitely produce some iron carbonyl at the lower temperatures, which caused us to suspect that the formation of the carbonyl reduced the activity of the catalyst.

We intended to repeat the test with catalyst 1374 at lower pressures to reduce the formation of the carbonyl.

In the meantime, a smaller circulation unit had been completed in July, 1940. The synthesis reactor had a capacity of only 15 li, permitting work with smaller amounts of catalysts, while still accurately maintaining the proper conditions of operations.

A number of catalysts have been studied which have been especially developed by Dr. Linckh for the ethanol synthesis. We selected catalysts which gave the best results under conditions

of ethanol synthesis, with a good alcohol and oil yield. We based our choice on the assumption that the catalysts which give high yields in lower alcohols will produce high molecular weight alcohols under other operating conditions.

These experiments have not, however, brought us much closer to the solution of the problem, because the results obtained with most of these catalysts were very similar to those obtained with the catalyst 997 in the large unit. Catalyst 997 was also used in the new unit for purpose of comparison and proved, in many respects, the best. The hydroxyl numbers of the C_{12} - C_{20} fraction exceeded slightly those obtained previously, and this catalyst excelled especially in the uniformity of operating conditions when compared with the newer catalyst, which gave fluctuations in the course of the synthesis.

The new unit also laid at rest some of the uncertainties about the irregularities in the operation of the larger unit. In the larger unit the preheating of oil was done by direct gas firing, so that any possible small difficulties in the circulation could have resulted in a harmful overheating of the oil, with a splitting of the higher alcohols. No gas firing was used in the new unit where it was replaced with steam heating with a temperature control. The large unit also will later have this source of danger excluded.

The next experiment was run with catalyst 1432 which was recommended by Dr. Müller as being oxygen-active as a conclusion from work in the larger unit. The catalyst operated throughout very uniformly. The circulation oil which contained the higher

fractions was of an exceptional purity, without any trace of rust color. However, the alcohol formation was in general entirely similar to that in the other preliminary experiments. None of these experiments have been successful in increasing the absolute amounts of the higher boiling fractions. No catalysts have been found which permitted lowering the synthesis temperature and thereby overcoming the effect of pressure on reducing the size of molecules.

We learned at that time the results on synol process obtained in Merseburg:

They found that special conditions of reduction of the catalysts (with a large amount of hydrogen) permitted using the fused iron catalyst at 195-220°C. With these catalysts an alcohol concentration at 50% in the middle and upper oil fractions could be obtained at an operating pressure of 20 atm.

Merseburg has found, in this way, a solution for the problem of production of higher alcohols from $\text{CO} + \text{H}_2$ using iron catalysts.

The above work in the oil circulation process should leave no doubt about the applicability of the Merseburg results to work with the oil circuit. Their work permitted changing from the high pressure synthesis field to the middle pressure synthesis.

We are getting ready for runs using catalysts activated by the Merseburg method. The operating conditions will be 25 atm

pressure, at synthesis temperature as close as possible to 195-225°C, the conversion kept low, with a temperature possibly selected somewhat higher if required by the oil phase.

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/s/ Duftschmid