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PROCESSES OF SYNTHETIC OIL PRODUCTION

Discussions in February, 1949

Gas Circulation Process

Mr. Michael has supplied the following data:

The optimal temperature range of the synthesis	about 10°
Permissible temperature range	about 50°

An additional cold circuit permits the separation of the high boiling fractions of the hot circuit in any desirable concentration. More CO₂ is formed during synthesis when no cold circuit is used. The partial pressure of carbon dioxide at 50 atm total pressure is for instance only 2-3 atm. Operations are conducted to produce satisfactory conditions with a 70-80% conversion.

The proportion of CO₂ in the make-up gas is 4:5. 92% conversion can be obtained in 2 stages with this gas; a 95% conversion is possible with a 3:7 ratio of 4.2:4.8. The proportion of the gas consumed in the synthesis is CO₂ = 4.2:4.8. With such a starting gas composition the amount of gas required is constant.

The following data are given on the gas conversion

	Gas after the 1st stage with a 78% conversion	Gas after the 2nd stage with 13.8% conversion, with CO ₂ scrubbing between the stages
CO ₂	25-30	20-25
C ₂ H ₄ + C ₂ H ₆	1-2	15
C ₃ H ₈ + C ₃ H ₆	2-3	5-6
H ₂		Up to 60%

Water + oil + gasoline are separated with water cooling, LPG + light gasoline with an ammonia cooler.

The following data are given on the yield and the composition of the products

Liquid constituents:

- 62% oil
- 8% alcohol in the water of the reaction
- 30% (C₂ with 25% alcohols, 2/3 iso-C₂, (C₃ with 61% alcohols)

Energy is calculated as 12 1/2% of the reaction

The oil consists of:

- 1/4 alcohol oil (with 10% weight of oxygen)
- 3/4 gasoline with 1/3 by weight of oxygen, with 70% of alcohols in both fractions.

The 62% of oil produced consist of 25% gasoline, 15% diesel oil and 22% paraffin.

The alcohol are composed of:

- 53% iso-1 alcohol
- 25% propyl alcohol
- 5% ethyl alcohol
- 17% n-butyl

Energy is calculated as 12 1/2% of the reaction

The 15% of diesel oil is composed of 10% diesel oil

The 22% of paraffin is composed of 10% paraffin

The octane number of the refined gasoline is 64-68, with 70-80% of unsaturated, and 50-60% fraction boiling below 100°C. The specific gravity of the unrefined gasoline is 0.730, after removing the oxygenated compounds, 0.730-0.710 with the end point of distillation at 190°C; approximately 1% of the alcohol production (etc).

The diesel oil boils at 230-250°C, with a cetane number of 56 (without elimination of oxygen) and a pour point of -25 to -23°C. Catalytic polymerization of the unreacted C₂, C₃, and C₄ fraction results in the production of the polymerization gasoline with an octane number of 87 by the research method and with 20% boiling below 100°C. The blended octane number is 100%. The polymerization of ethylene gives a gasoline with an octane number of 85 and with 15% boiling below 100°C.

Catalytic cracking of the diesel oil produces a gasoline with an octane number 68-69 research, 40-45 motor method. The melting point of paraffin is 30°C, with a high melting paraffin present and small amounts of triglycerides.

The space/time yield of the gas circulation process is 0.35 kg of valuable products per liter of catalyst and per day. The space/time yield is 2.3 with a gas containing a higher percentage of inerts.

The pressure drop of the catalyst bed at 100% total pressure amounts to only 1.5 meters water. The bed has 30 pores per ton of product in parallel with the catalyst bed, with the thickness of the catalyst bed of 1 m.

The reactor for the steam-catalyzed isomerization in a stainless steel container 400 mm diameter and 1.5 m high produces 500 kg of raw product

(oil + utilizable gases) per day, corresponding to 365 kg of finished products, with a gasification of 70 kg.

A total gas conversion of 91.5% was obtained per volume gas at 0° and 760 mm when operating in two stages (first stage 75%, second stage 15.5%) with

	$CH_4 + C_2H_6$	35 gm
Utilizable products, including oxygen		160 gm
		195 gm.

The utilizable products were defined as follows:

160 gm		
14 gm alcohols:	105 gm oil, with	41 gm gases, with:
8 gm C_2H_5OH	2 gm crude paraffin	10 gm C_2H_4
3-4 gm propanol	22 gm crude diesel oil	17 gm C_3
2 gm acetone	32 gm crude gasoline	14 gm C_4
1 gm acetaldehyde		
0.5 gm higher alcohols		

Refining of 32 gm crude gasoline gave	27 gm refined gasoline
Polymerization of the unsaturated compounds gave	20 gm polymerization gasoline
1 gm polymerization diesel oil	
	107 gm total gasoline

Dr. Hier and Dr. Michael have given the following information on different problems of the Birchokite which came up during discussions:

The effective gas velocity during gas circulation amounts to over 1 m/second for 1 m height of the catalyst.

The rate number of the product obtained with recirculation of the gas was about 10 times higher than when operating with a straight path of the gas. The effect of the temperature manifests itself in that a larger proportion of gas can be obtained at lower temperature. The catalyst however begins operating only at 530°C. The extraordinarily

strong sintered iron catalyst are very stable; not a trace of carbon is deposited during synthesis. A very large number of experiments have been made with catalysts; the catalysts however have a smaller effect upon the composition of the product than does the temperature. No methanol is formed during synthesis.

Gas can be used without final purification; it contains 7 mg organic sulfur/ton. Reused catalysts are very readily spontaneously reactivated with pure gas. The reactivation of the used catalyst may be brought about by oxidation outside the reactors, followed by a reduction. In one test with strong temperature fluctuations, the life of a catalyst was 10 weeks. After that time the catalyst began to disintegrate. No corrosion has so far been observed; no attack of hydrogen upon the reactor material is to be feared at the low partial pressure (10-12 atm of hydrogen and 2-3 atm of CO). The formation of iron carbonyl has not been observed.

The optimum pressure is 20 atm; with higher pressures the product contains more oxygen. The cracking of diesel oil proceeds particularly readily, more readily even than of kerosine.

Industrial units with reaction space of 20 cm each with one recirculation reactor are being considered, with the catalyst distributed in six layers of 1 m height each and 2 m diameter.

Dr. Pier pointed out several possibilities offered by the gas circulation processes for the synthesis of hydrocarbons from water gas, and also to the possibility of making gas circulation tests with catalysts obtained from the Edmunds.

Dr. Pier has presented a number of data on the properties of the products which were collected by Dr. Michael in December 1953.

Dr. Bützfisch pointed to the general connection between the demands made today on gasoline and the requirements of the motor industry on the one hand, and the gasoline industry on the other hand. There still remain several problems to solve regarding the refining of the product and polymerization, but the work of the I.G. has added much to widen the total picture of synthesis starting with CO mixtures, and as a result the cooperation of the Essochemie and the I.G. is expected to produce valuable mutual incentives and complement each other.

The high percentage of iso-compounds in the T_{10} fraction of the Michael process is at present particularly important, and it remains yet to be proved whether the proportion of iso-butane could not be further increased to meet the demands of the iso-octane manufacture. Dr. Bützfisch considered it incorrect to increase the iso-octane production by way of alcohols.

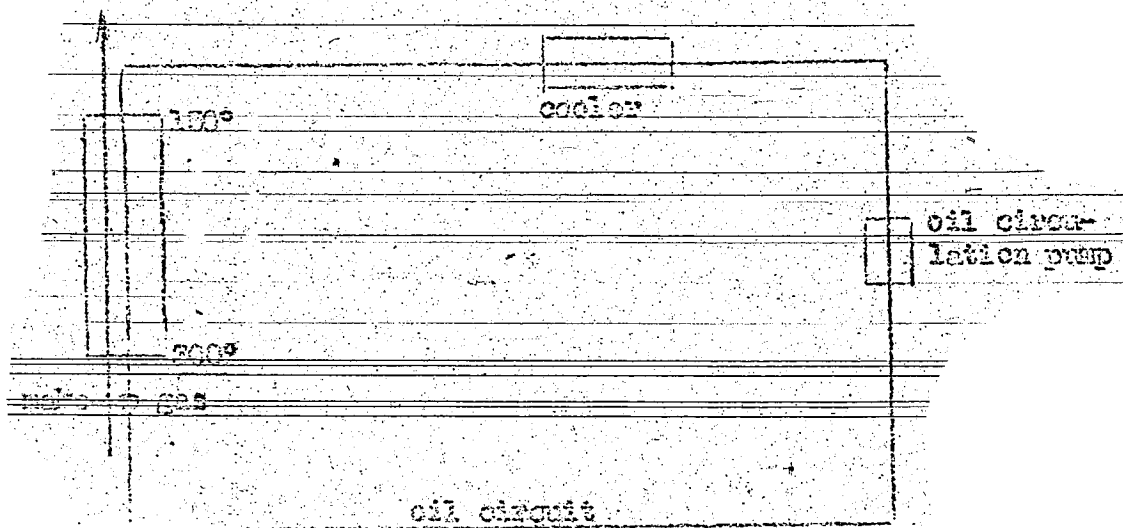
II. Manuscript by Dr. Luftschmid The Oil Circulation Process

The carbon monoxide-hydrogen oxidation is carried out in the liquid medium, using one of the oil circulations. A fixed bed granular catalyst is used in the reaction space.

The figure below shows the general scheme of the process.

The oil produced in the synthesis is recycled. The synthesis gas enters the reactor either concurrently with the oil or counter-currently. The oil carries out the heat of the reaction, in

part as sensible heat, in part as heat of vaporization. If a cooling system be inserted into the circuit to lead out the heat of the reaction in usable form and to cool the oil to the original temperature, condensing the vaporized constituents, this would solve not merely the problem of heat recovery, but an additional advantage will be obtained:



The wetting of the catalyst with oil does not merely result in maintaining definite reaction temperature, but also helps later to a great extent the activity of the catalyst. The most active centers of the catalyst will have their activity reduced, which will

depress the undesired progress of reaction to a gaseous final product, even with a large load.

The construction of the reactor is very greatly simplified by the omission of indirect cooling, and it becomes no longer necessary to distribute the catalyst in thin layers.

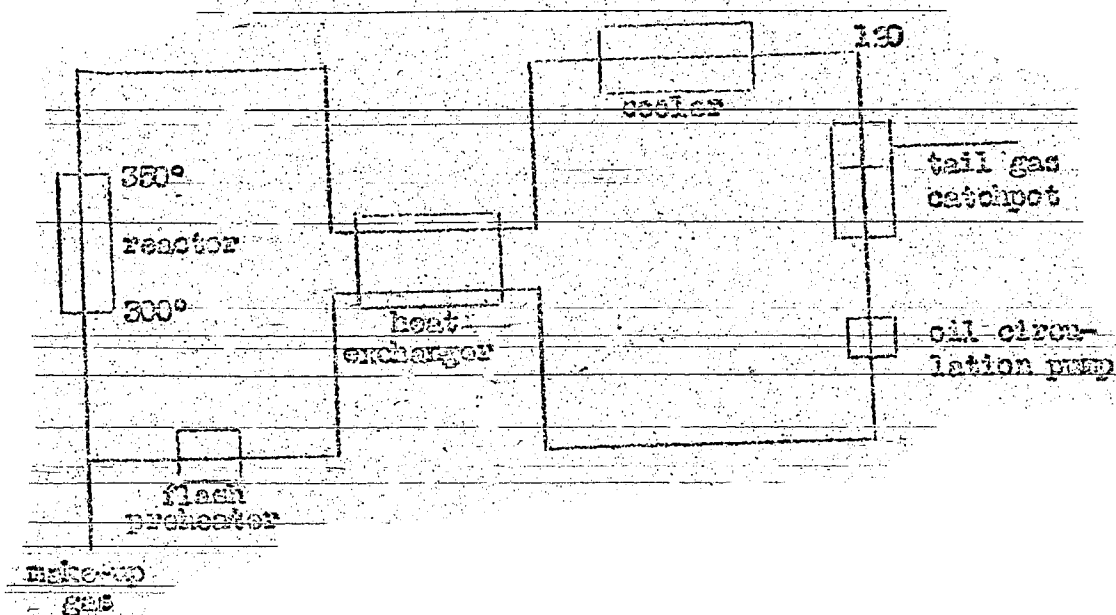
The process operates particularly well when working with the sensitive iron catalyst and especially at elevated temperatures and with greater loads.

The process has been used in a pilot plant for a wide variety of pressures from 20 to 200 atm, and is still so used, occasionally modifying details of the operations. We will illustrate below the process by a typical example of operations under 100 atm pressure.

The oil in circuit was cooled not merely to the reaction temperature, but much below it (e.g. 200°). This condensed the lighter boiling oil constituents and returned them to the oil circuit.

In this way an advantage was obtained of having the conversion proceed not in the slowly moving viscous liquid, but under active boiling action. Bubbling vapor bubbles produce a good contact of the gases to be acted upon by the catalyst, offering all the advantages of the liquid wetting of the surface mentioned above.

The schematic flow sheet of the process is given below. The gas is lead in concurrently with the oil. The cooling oil is extracted in a heat exchanger in the circuit. The rapid separator is used for the separating and as separator of the oil gas free oil.



Depending on the temperature in the catchpot, the tail gas will carry some of the lighter boiling constituents, which can be returned into the oil circuit at any desired place, depending on the details of the process. The circulation oil can be set for a selected boiling range by suitable measures, in particular by the catchpot temperature.

The regulation of the circulation oil permits during the reaction for the required degree of conversion, and to maintain it at the desired temperature.

The amount of circulation oil is kept in a certain proportion to the reactor load. With a space/time yield of 240 kg total product per day in 60 li reactors, 450-750 li of oil are pumped per hour.

The synthesis temperatures depend on the load of the reactors, the degree of conversion, and the activity of the catalyst. The synthesis may be conducted within a relatively wide temperature range without affecting the output.

The upper temperature is about 400°, above noticeable gasification losses will be observed resulting from the cracking of oil, and the yield of the liquid products will drop.

As a rule the temperature differences in the reactors amounted to 30-70°C, an average around 50°C. The heat removed from the oil was distributed with 1/2 of it as sensible heat, 1/2 as heat of vaporization.

The work with iron catalyst was carried out in the temperature ranges of 240-300°C and at 300-360°C. The data below were obtained in operations at 300-350°C.

Catalysts

The catalyst must meet the minimum requirements of mechanical strength and abrasion in order to withstand the mechanical stresses of the oil circuit. The catalyst consisted principally of iron with small additions of various activators.

An insufficient reduction of the catalyst lumps must be avoided, because it results in the blocking up of the catalyst caused by deposition of carbon upon the cyclic nucleus.

The size of the catalyst pieces varied between 8 and 15 mm in diameter.

Conversion

The reduction of carbon monoxide proceeds primarily with formation of carbon dioxide, and a make-up gas with a CO:H₂ ratio of 15:85 to 50:50 is used in the conversion.

When operating with a make-up gas having a ratio of CO:H₂ = 55:45, the tail gas contains the unconverted CO + H₂ in the same proportion as the fresh make-up gas.

The conversion was preferably so conducted that 50% of the CO + H₂ in the make-up gas was converted in one pass through the reactor.

The tail gas leaving the first stage must therefore be fully converted in subsequent stage or stages, or else may be re-introduced after an intermediate scrubbing out of the CO₂. The ^{synthetic} gas after a 50% conversion of 3 cbm make-up gas (CO + H₂) gave 1.25 cbm tail gas after the first stage, having the composition

16% CO₂
3% H₂
81% CO + H₂

As an example, 1 cbm of the converted CO + H₂ produced:

	gm per cbm (15°C, 755 mm)	gm per cbm (0° 760 mm)	Per Cent
Water	63	74	---
CO ₂	375	402	---
C. (C ₂)	55	28	---
Gasol (C ₃ , C ₄ , C ₅)	23	23	17
Gasoline, -200°	34	31	41
Oil and solid hydro-			
Carbon	40	32	53
Alcohols	18	9	6

Properties of the Products

	Per Cent Olefines	Per Cent O	
Gasol	55-70	---	
Gasoline	35-45	1.0-2.0	c.n. 55
Gas Oil	10-20	0.5-1.0	cat. No. 70
Higher boiling and solid hydrocarbons	---	0.2-0.6	

The alcohols consist of 55-65% of ethanol, 25-35% of methanol, and the balance of higher alcohols, acetone and acetaldehyde.

A space/time yield of 240 lb total products (gasol + gasoline + oil + paraffin + alcohols) were obtained in a 60 in high pressure reactor (i.d. 120, 6 in high) with an operating pressure of 100 atm. This figure is a space/time yield of 120 gm per lb reactor space-catalyst space and per hour.

Signal-Refined

In the subsequent discussions of the question raised by the application of the Refined to the Refined gave the following additional information: The oil calculation amounted to 400 lb per hour. For this reason the proper collection of the product and the absence of any other material is important, because the Refined is a catalyst separator. The Refined is a product of the Refined and is separated by the gas separator of the Refined.

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Dr. Pier is of the opinion that a difference in the distribution of the active centers of the catalyst in the two processes may be of particularly great importance to the nature of the products.

Dr. Dutchedahl stated with respect to the life of the catalyst that the catalyst activity could be regenerated in 2 1/3 months by a 10-15° rise in temperature, but an upper limit existed for the process at 400° because of the incipient cracking reactions.

Professor Martin points to the possibility of the reactions between the olefines and water gas in the circuit and mentions experiments of the Rohmcochemie about which a report is to be made later.

The large space/time yield (ton of products per unit volume of cat./day) of the two I.C. processes may be of importance in America, because lower installation costs are more important there than higher conversion.

Professor Martin mentions the gas circulation experiments of the Rohmcochemie made with spherical catalysts, with which more light boiling products and less paraffin was produced with a gasoline of a higher olefine content and a higher octane number (65-70) with a simultaneous somewhat higher space/time yield and a 65% utilization of the gas.

Of late the Rohmcochemie has used almost exclusively nickel-sulfate catalysts but in some catalysts, when the gas circulation experiments are carried out, they have not been treated out with iron catalyst.

The catalyst used in the I.C. process is of a type which is not regenerated, but the catalyst used in the I.C. process is completely regenerated. The catalyst used in the I.C. process is of a type which is not regenerated, but the catalyst used in the I.C. process is completely regenerated.

Dr. Ringov replied that in 1912-1914 diesel oil production in America may be sure to become as large as gasoline, and at equal prices. Dr. Michael stated that the diesel oil production can be increased by reduction of catalyst to the extent that only 3% of the liquid fraction would boil over 300°C, however with a higher methane formation.

Dr. Ringov stated that it probably will be more profitable to crack catalytically the middle oil produced in the gas circuit.

Dr. Ringov stated in addition that neither corrosion nor catalytic poisoning have been observed in the oil circulation process, and that the heat is removed as heat of vaporization of the boiling oil, and the other half by the gases or vapors.

III. Characteristics of the Paraffin Synthesis

Professor Martin stated that the formation of paraffin during synthesis is favored by the high Co concentration in the catalyst, a low reaction temperature, a high residence time of the gas, and a high carbon monoxide concentration in the gas. The pressure in this case plays no very important role.

Dr. Ringov stated that a total paraffin production was 30% on the industrial scale and 40% in the laboratory.

IV. Characteristics of the Paraffin Synthesis

Dr. Ringov stated that a total paraffin production was 30% on the industrial scale and 40% in the laboratory, under approximately the same reaction conditions as used under the synthesis in the Fischer-Tropsch process, and that the yield in a single stage was a production of 1.2% paraffin.

Dr. Meisenheimer says the tests were run in a vertical 300 mm reactor, at 190°C, and that the Co catalyst contained twice as much Co per unit volume as the Nihr catalyst.

Professor Martin points to the fact that in later additions to the existing Fischer installations made for the purpose of increasing the paraffin production, the use of the Opan catalyst must be taken into consideration.

Experimental Results in Leuna

Dr. Kiesel tells that using the Co catalyst in horizontal reactors, with a 70-80 gm yield liquid products per norm of synthesis gas, 70-75% paraffin have been obtained in Leuna, and less in vertical reactors.

IV. Gasification of Solid Fuels

Dr. Winkler tells of the different possibilities of production of synthesis gas in various gas producers in which synthesis gas with 1.5% nitrogen and 0.4% methane can be obtained because of the high temperature (1050°C) in the upper part of the producers. 0.80 m³ oxygen is consumed per norm carbon monoxide-hydrogen mixture; 0.6 kWh are required for the production of 1 unit of 80% oxygen, using the Linde-Tweil process.

Winkler states that according to the Linde calculation the cost of oxygen is 5 RM per ton and large to 1.5 RM per ton only in very large installations. The cost of power in the Ruhr may be assumed to be 1.5 RM per kWh.

In the discussion of different gasification processes, Dr. Bütcher was pointing out that the different processes are highly comparable. The differences in the results are due to the conditions in the producers. The

points like irregularities in the gas, etc., must be taken into consideration.

Dr. Martin considers the possibility of non-baking coal-bed as being one of the most important problems in the whole field of bituminous coal,

because coal-bed is not to be considered as the starting material, being suitable for other purposes. Some coals with low moisture 1/2% and

little volatile matter, but gas little coal, which, this quality and contain a large proportion of volatile constituents, must be considered.

The gasification of the lean coals would be of particular interest for

the following reasons. The first one is that in Germany in Gelsenkirchen is

the largest, the second is that the production of synthetic gas from

lean coals is the most important, because all of the gas

is used for the production of synthetic gas.

The gasification of lean coals is particularly important, because it will

allow the production of synthetic gas from lean coals.

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changes in the composition of the synthetic gases possible with it.

V. Gas Shift Reactions

Dr. Schiller, Dept., reports on the different possibilities of producing synthetic gas from hydrocarbons. The paper is essentially a repetition of one already reported in the CAGS report (V. II. Federal Report of November 13, 1944, p. 68).

VI. Sulfur Dioxide

Dr. Schiller reports on the inorganic and organic sulfur processes with potential changes and that can give about today on a life of 4-6 years for design. The process can only be used for water gas. Sulfur dioxide synthesis gas not produced in the process.