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PROBLEMS OF SYNTHETIC OIL PRODUCTION

Discussion in Ruhrchemie, 1939

Gas Circulation Process

Dr. Michael has supplied the following data:

The optimum 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 monoxide at 20 atm total pressure is for instance only 2-3 atm. Operations are conducted to produce stationary conditions with a 75-80% conversion.

The proportion of CO:H₂ in the make-up gas is 4:5. 93% conversion can be obtained in 3 stages with this gas; a 96% conversion is possible with a CO:H₂ ratio 4.2:4.8. The proportion of the gas consumed in the synthesis is CO:H₂ = 4.2:4.8. With such a starting gas the proportion of CO:H₂ in the gas circuit remains approximately constant.

The following data are given on the gas conversion

	Gas after the first stage with a 72% conversion	Gas after the 2nd stage with 13.5% conversion, with CO ₂ scrubbing between the stages
CO ₂	25-30	20-25
CH ₄ + C ₂ H ₆	7-9	15
C ₂ H ₄ + C ₂ H ₆	2-3	5-6
N ₂		Up to 60%

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

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

Liquid constituents:

62% oil

8% alcohols in the water of the reaction

30% (C₄ with 86% olefines, 2/3 iso-C₄

(C₂ with 81% olefines

(C₂H₄

There is in addition 16-19% gasification

The oil consists of:

1/4 diesel oil with 2% by weight of oxygen

3/4 gasoline with 4% by weight of oxygen, with

75% of olefins in both fractions.

The 62% of oil produced consist of 47% gasoline, 14% diesel oil and 1% paraffin.

The alcohols are composed of

55% ethyl alcohol

25% propyl alcohol

5% acetaldehyde

10% acetene

2-5% higher alcohols

The oxygen is removed catalytically from the gasoline + diesel oil mixture (specific gravity 0.75-0.76) with 1¢ loss in the weight of the gasoline.

The octane number of the refined gasoline is 64-88, with 70-80% of unsaturated, and 50-60% fraction boiling below 100° C. The specific gravity of the unrefined gasoline is 0.720, after removing the oxygenated cmpds. 0.700-0.710 with the end point of distillation at 195°C; approximately 1% of the alcohol production (sic).

The diesel oil boils at 200-350° C, with a cetane number of 53 (without elimination of oxygen) and a pour point of -25° to -28°C. Catalytic polymerization of the unsaturated C₂, C₄, and C₅ fraction results in the production of the polymerization gasoline with an octane number of 97 by the research method and with 20% boiling below 100° C. The blended octane number is 120. The polymerization of ethylene gives a gasoline with an octane number of 93 and with 43% boiling below 100° C.

Catalytic cracking of the diesel oil produces a gasoline with an octane number 86-87 research , 75-76 motor method. The melting point of paraffin is 60°C, with some high melting paraffin present and small amounts of waxy substances.

The space/time yield of the gas circulation process is 0.95 kg of valuable products per liter catalyst and per day. The space/time yield is 0.8 with a gas containing a higher proportion of inerts.

The pressure loss in the catalyst layer at 20% total pressure amounts to only 1 m water column. 250-300 kwh of power per ton of product is consumed with a recirculation of the gas, with the thickness of the catalyst bed of 1 m.

The reactor in the experimented installation in Ludwigshafen contains 400 li of iron catalyst and produces 300 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 ncbm pure gas at 0° and 760 mm when operating in two stages (first stage 78%, second stage 13.5%) with

	CH ₄ + C ₂ H ₆	35 gm
Utilizable products, including oxygen		<u>160 gm</u>
		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 ₂ H ₅ OH	2 gm crude paraffin	10 gm C ₂ H ₄
3-4 gm propanol	21 gm crude diesel oil	17 gm C ₂
2 gm acetene	82 gm crude gasoline	14 gm C ₄
1 gm acetaldehyde		
0.5 gm higher alcohols		

Refining of 82 gm crude gave 77 gm refined gasoline
 Polymerization of the unsaturated compounds gave 30 gm polymerization gasoline

1 gm polymerization diesel oil

107 gm total gasoline

Dr Pier and Dr. Michael have given the following information on different problems of the Ruhrchemie 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 octane number of the product obtained with recirculation of the gas was about 10 unites higher than when operating with a straight path of the gas. The effect of the temperature manifests itself in that a larger proportion of paraffin is obtained at lower temperature. The catalyst however begins operating only at 260°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/cbm. Poisoned 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 at 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 kergasin.

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

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

Dr. Pier has presented a number of data on the properties of the products which were collected by Dr. Michael in December 1938.

Dr. Bütetisch pointed to the general connection between the demands made today on gasolines 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 Ruhrchemie and the I.G. is expected to produce valuable mutual incentives and complement each other.

The high percentage of iso-compounds in the C₄ fraction of the Michael process is at present particularly important, and it remains yet to be proved whether the proportion of iso-butylene could not be further increased to meet the demands of the iso-octane manufacture. Dr. Bütetisch considered it incorrect to increase the iso-octane production by way of alcohols.

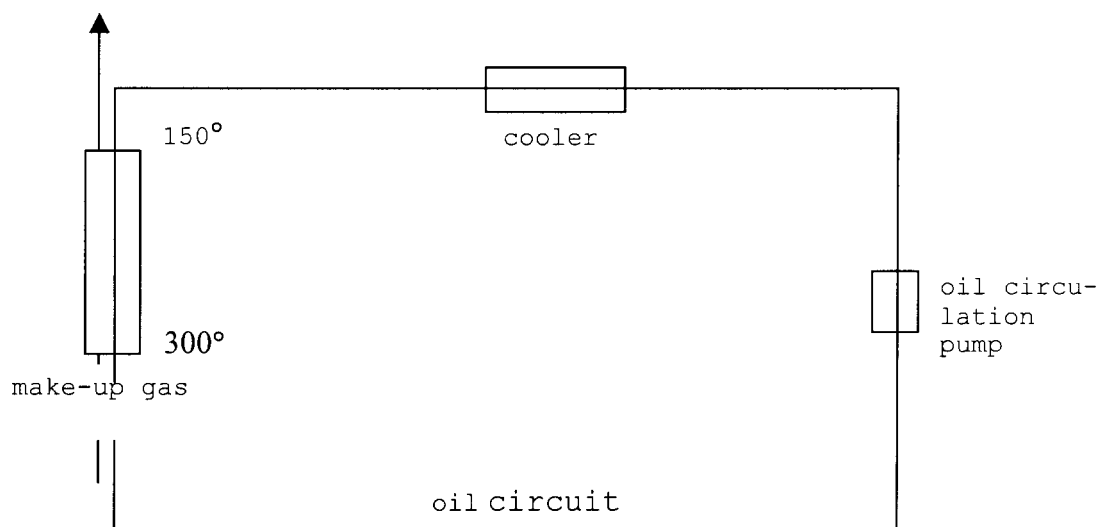
II. Manuscript by Dr. Duftschmid
The Oil Circulation Process

The carbon monoxide-hydrogen conversion is carried out in the liquid medium, making use of the oil circulation. A final 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 recirculated. The synthesis gas enters the reactor either con-currently 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 forms 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 measured catalyst temperature, but also regulates 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 reactors is very greatly simplified by the omission of indirect cooling, and it becomes no longer necessary to distribute the catalyst in thin layers.

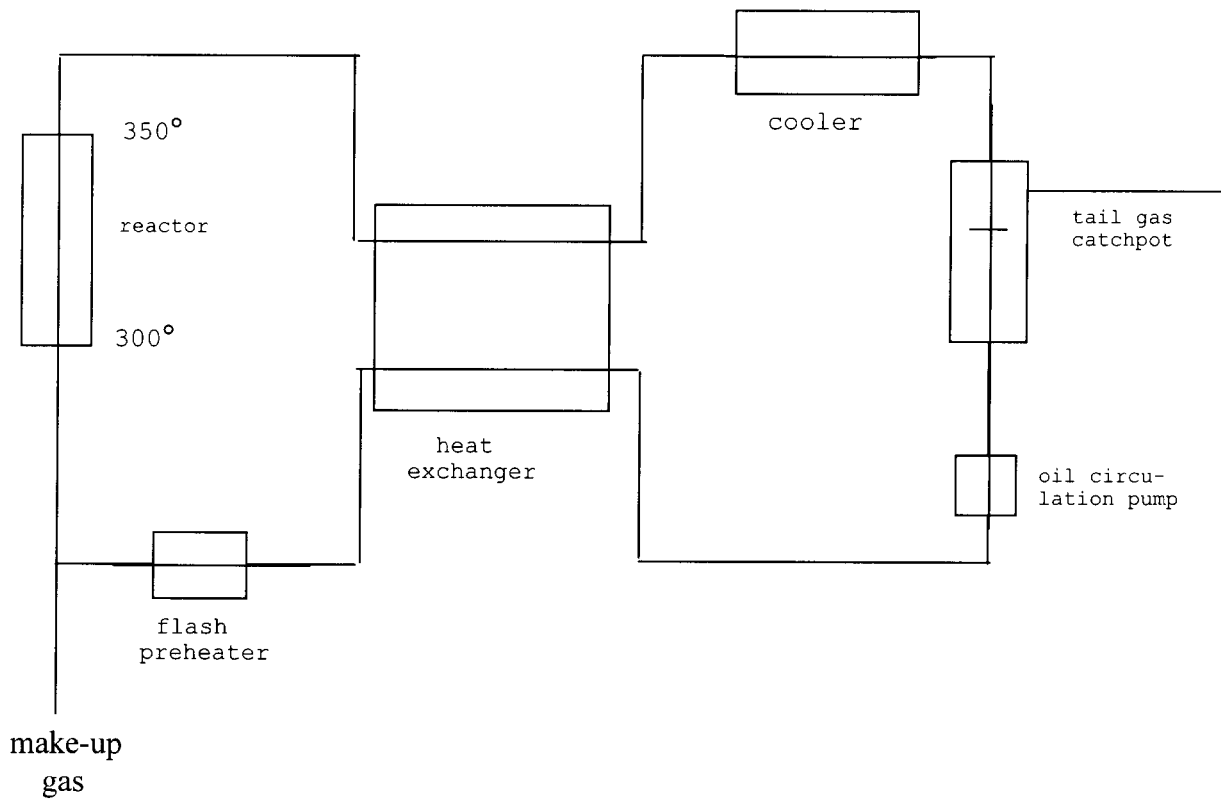
The process operates particularly well when working with the sensitive iron catalysts and especially at elevated temperatures and with greater loads.

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. 120° C). 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 motion. Bubbling vapor bubbles produce a good contact of the gases to be noted 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 reheated in a heat exchanger in the circuit. The rapid preheater is used in the starting and as separator of the end gas from 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 production. The circulation oil can be set for a selected boiling range by suitable measures, in particularly by the catchpot temperature.

The regulation of the circulation oil permits fixing 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 repumped 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° , where 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 difference 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 300-306°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 primarily of iron with small additions of various activators.

An insufficient reduction of the catalyst lumps must be avoided, because it results in the breaking up of the catalyst caused by deposition of carbon upon the oxalic 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 4 5:55 to 55:45 is used in the converter.

When operating with a make-up gas having a ratio of CO:H₂ = 55:45, the oil 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 recirculated after an intermediate scrubbing out of the CO₂. The synthesis gas after 50% conversion of 2 cbm make-up gas (CO + H₂) gave 1.26 cbm tail gas after the first stage, having the composition

16% CO₂
 3% CH₄
 81% CO + H₂

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

	gram per cbm (15°C, 755 mm)	gram per cbm (0°, 760 mm)	Per Cent
Water	68	74	--
CO ₂	375	409	--
C ₁ (C ₂)	25	28	--
<hr/>			
Gasol (C ₂ , C ₄ , C ₆)	23	25	17
Gasoline, -200°	54	31	41
Oil and solid hydro- carbons	48	52	36
Alcohols	8	9	6

Properties of the Products

	Per Cent Olefines	Per Cent O	
Gasol	55-70	--	
Gasoline	35-45	1.0-3.0	o.n. GS
Gas Oil	40-50	0.5-1.0	Cet. No. 78
Higher boiling and solid hydrocarbons	--	0.2-0.6	

The alcohols consist of 55-65% of ethanol, 25-30% of methanol, and balance of higher alcohols, acetone, and acetaldehyde. A space/time yield of 240 kg total products (gasol + gasoline + oil + paraffin + alcohols) were obtained in a 60 li high pressure reactor (i.d. 120, 6 m high) with an operating pressure of 100 atm. This figures to a space/time yield of 160 grm per li reactor space-catalyst space and per hour.

Signed-Dufts Schmid

In the subsequent discussion of the questions asked by the gentlemen of Ruhrchemie, Dr. Dufts Schmid gave the following additional information: The oil circulation amounted to 400 li per hour. For this reason the proper reduction of the catalyst and the absence of any oxide nuclei is important, because the latter would cause a carbon deposition. The size of the granular particles is therefore limited by the good reducibility of the catalyst.

Professor Martin attributed the differences in the products of the oil circulation and gas circulation to secondary reactions, and pointed that they may occur to a smaller extent in the oil circulation process, and possibly because of the better heat transfer in the oil circulation.

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. Duftschmid stated with respect to the life of the catalyst that the catalyst activity could be compensated in 2 1/2 months by a 10-15° rise in temperatures, 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 Ruhrchemie about which a report is to be made later.

The large space/time yield (gm of products per unit volume of cat/day) of the two I.G. 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 Ruhrchemie 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 (68-70) with a simultaneous somewhat higher space/time yield and a 95% utilization of the gas.

Of late the Ruhrchemie has used almost exclusively nickel-cobalt catalyst, but no iron catalysts. Even the oil circulation experiments mentioned by Dr. Alberts have not been carried out with iron catalyst.

Professor Martin stated that the production of diesel oil is not desired abroad, and asked whether it was possible to completely suppress the diesel oil production in the I.G. process, to which Dr. Ringer

replied that in 1943-1944 the diesel oil consumption in America may be sure to become as large as gasoline, and at equal prices. Dr. Michael states that the diesel oil production can be repressed by selection of a catalyst to the extent that only 5% of the liquid fraction would boil over 200°C, however with a higher methane formation.

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

Dr. Duftschmid mentions in addition that neither corrosion nor carbonyl formation have been observed in the oil circulation process, and that 1/2 the heat is removed as heat of vaporization of the boiling oil, and the other half by the gases or vapors.

III. Discussion of the Paraffin Synthesis

Professor Martin states 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. Roelen states that a total maximum paraffin production was 30% on the industrial scale and 40% in the laboratory.

Experimental Results of the Ammonia Laboratory

Dr. Wienzel says that when using Co catalyst, a maximum of 70% paraffin was obtained in the ammonia laboratory under approximately the same reaction conditions as used during the synthesis in the Ruhrchemie, with 125-140 gms yield in a single stage and with a production of 1-1.2% gasol.

Dr. Meisenheimer says that the test were run in a vertical 300 mm reactor, at 100°C, and that the Co catalyst contained twice as much Co per unit volume as the Ruhr 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 Oppau catalyst must be taken into consideration.

Experimental Results in Leuna

Dr. Wenzel tells that using the Co catalyst in horizontal reactors, with a 70-80 grm yield liquid products per ncbm 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 Winkler gas producers in which synthesis gas with 1-1.5% nitrogen and 0.4% methane can be obtained because of the high temperature (1050°C) in the upper part of the producers. 0.35m³ oxygen is consumed per ncbm carbon monoxide-hydrogen mixture; 0.6 kwh are required for the production of the 1 cmb of 98% oxygen, using the Linde-Frankl process.

Winkler states that according to the Linde calculation the cost of oxygen is 8 Pfg per cbm and drops to 1.3 Pfg per cbm only in very large installations. The cost of power in the Ruhr may be assumed to be 1.5-1.6 Pfg per kwh.

In the discussion of different gasification processes, Dr. Bütetisch was positive that the different processes are hardly comparable. The differences in the solid fuels, the temperatures in the producers, the permissible impurities in the gas, etc., must be taken

into consideration. Dr. Martin considers the gasification of the non-baking coal feed as being one of the most important problems in the whole field of bituminous coal, because coke should not be considered as the starting material, being usable for other purposes. Lean coals with for instance 1% tar and little volatile matter, or gas flame coals, which bake poorly and contain a large proportion of volatile constituents, must be considered. The gasification of the lean coals would be of particular interest for the Ruhr region. A coal from a new shaft in Concordia in Oberhausen is available, containing 2% ash. The production of synthesis gas from coke oven gas can at present not be considered, because all of the gas is sold as a power fuel.

Dr. Winkler mentions that the gasification problems for one baking coal has already been solved; such a plant is in operation in Japan. The gasification of lean coals is particularly difficult, because it will require a high oxygen consumption. Tests will be required for every new kind of baking coals.

Dr. Bütetisch points out the importance of grading of either the brown or the bituminous coal, and that additions may occasionally help during gasification, as for instance the addition of clay as practiced in Leuna and which is obtained on the ground.

Dr. Alberts mentions the possibility of adding gasifiable additions, such as grude (LTC coke).

Professor Martin believes that synthesis gas installations must as far as possible be operated with oxygen because of the possibilities of changes in the composition in the synthesis gases possible with it.

V. Gas Shift Reactions

Dr. Schiller, Oppau, reports on the different possibilities of producing synthesis gas from hydrocarbons. The paper is essentially a repetition of one already reported in the USAG report (v. Dr. Peters Report of November 11, 1938, p. 66).

VI. Sulfur Purification

Dr. Winkler reports on the inorganic and organic sulfur purification with activated charcoal and that one may count today on a life of 4-5 years for charcoal. The process can only be used for water gas. Cyclic sulfur compounds are not removed in the process.