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UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUELS
LOUISIANA, MISSOURI

T-464
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December 15, 1948

THE STATUS OF HYDROCARBON SYNTHESIS FROM CO-H_2 MIXTURES

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TOM Reel 164, Frames 143-153 July 24, 1941

Gas Circulation Process
(For Gasoline Production)

The gas circulation process was developed to overcome the peculiar difficulties of the CO-H_2 synthesis with iron catalysts which requires a very careful heat regulation. Temperatures of 300° and above, which must be used for the production of high anti-knock gasolines, can no longer be obtained in tubular or plate reactors.

In the gas circulation the heat of the reaction is not led away through the wall but by the reaction gas itself and led to a waste heat boiler outside the reactor where it is cooled to 50° below the reaction temperature; the waste heat boiler can be maintained relatively small in size because of the large difference in temperature. No complicated insets have to be built inside the reactor. The temperature interval inside the reaction space is limited to 10° by the absorption by the gases of the heat of the reaction, and the makeup gas must be circulated about 100 times between the reaction space and the waste heat boiler in order to leave the circuit with a 75-80% conversion. In addition to the above hot circuit, there is a cold circuit with a circulation inside the cold circuit of about three times. Its purpose is the removal of water by cooling to the temperature of the cooling water and the deposition of the high molecular weight reaction products which would otherwise clog the catalysts. The gas which finally leaves the system is cooled to about +40°C, and the light gasoline and the greater part of the gasol are also condensed.

The carbon dioxide is now removed and the gas led through a second stage which is about four times smaller, and the total conversion is increased to over 90%.

Catalysts

A catalyst of very high mechanical strength is required because of the great gas velocity (the time of residence of the gas in the catalyst bed is less than one second). Operations up to 300° with sintered carbonyl iron and a small amount of borax have been found satisfactory. This catalyst shows no tendency for "going through". Its heat conductivity is so good that no local temperature rises develop due to overheating. The life of this catalyst has been found to be around 4 1/2 months in small scale tests.

The pressing of the catalyst powders must be done with very vigorous shaking, since only in that way can a homogeneous catalyst grain be obtained, and the catalyst would otherwise show a tendency to scale during operation.

Operating Conditions

High-test gasoline is obtained by operating at a temperature of 300°C or over. The breaking down of CO to carbon is prevented by not permitting the temperature to exceed 330°C. A pressure of 20 atm has been selected. The efficiency at smaller pressures is lower, while at higher pressures the C content is higher. The space/time velocity in the first stage is 0.8 and 0.6 in the second stage. The gas mixture has the same proportion of $CO:H_2$ as in water gas, namely 4:5 and even closer to 1:1. A high content in inerts slows down the production. The gas production with oxygen is therefore recommended. The sulfur content must be below 2mg S per cubic meter.

				Finished Products
Gases (except methane and ethane)	30%	(ethylene 8%) (propylene 9%) (propane 3% (butylene 8% (butane 2%	15 polymere gasoline or 35 alk. benz. (5% iso butene)	7% ethylene lubricant 8% propylene lubricant 7% iso octane
Gasoline, -200°C	47%, refined 44%, o.n. 84			44% motor gasoline
Middle oil, 200-350°C	15%, cetane number about 50			15% Diesel oil

			Finished Products
Paraffin, +350°	1-2%		1% paraffin
Alcohols in water of reaction	7%	(55% ethanol (20% propanol (Balance: butanol, acetaldehyde, acetone and acids	7% alcohols
	100%		

18-20% gasification (methane + ethane) to 80-82 parts of the above products

Refining of Gasoline

The crude gasoline contains 3-4% O and must be refined. This is done by passing at atmospheric pressure over alumina at 380° and finally over bleaching earth at 200°C. The loss of material amounts to 5-6%. The octane number of the crude gasoline is thereby increased from 70-79 to 84 (research method), with 50-55% boiling below 100°C after refining. The refined gasoline is stabilized with alpha naphthol, and has shown a storage stability of 2 1/2 years in a special storage test.

The Unsaturated Gases

The olefines can be used in a variety of ways; the butylene fraction contains 62% iso-compounds and can be used for the production of technical grade iso-octane; propylene and ethylene can be used for the production of alkylbenzols as well as for the production of aviation lubricants.

Diesel Oils

The middle oil, 200-350°C, contains 1-1 1/2% oxygen and can be used as a Diesel oil without any pretreatment. The cetane number is 50, the pour point -28°C.

Lubricants from Middle Oil

The middle oil produces with SO_2 66% of refined products which will form 60% motor oil obtained by polymerization with $AlCl_3$.

Yields

Two stage operations with a total conversion of 91-92% of liquid products (after polymerization of the gasol) will produce 133 g without ethylene recovery, and 142 g with ethylene recovery, (which requires a Linde plant), per ncbm of pure gas. About 80% of the production is gasoline and 20% Diesel oil.

Large Scale Tests

A circulation reactor which was originally planned for 800-1000 te/ann of crude products and had a layer of catalysts 60 cm deep has been used at 325°C for a long time with an inert-rich off-gas of the butyl plant, with an adjusted CO content.

The reactor operated as expected. It indicated the desirability of improvements in one respect only. The cross section of the gas circuit changed up to 1:10, and the velocities of the gas stream could change correspondingly. They originated in the turns in the gas path. Gas eddies were locally produced which interfered with the passing through the catalyst bed. Dividing the catalyst bed into several intermediate spaces on different levels and with small intermediate spaces was an improvement. The new constructions are made with this in mind.

Foam Process

This is a process in the liquid phase with the finest dispersion of a floating catalyst, and the gas must in this process be distributed throughout the liquid in the form of the minutest bubbles. Such a fine subdivision is obtained by either intensive stirring or by using fine-pored foam plates. This method of operation offers the advantages of avoiding any local overheating of the catalyst which may lead to a high methane production and to a deposition of carbon, and the gasification is lowered to an insignificant amount. In addition, the catalyst is used in its simplest form and can be renewed without interruption of operations. High boiling products of the reaction are used as the suspension medium, and principally the paraffins.

The foam process was developed for the production of an olefinic middle oil. The amount of higher boiling constituents in the liquid phase is increased in this process, and when operating for the production of gasoline at 300°C and over, the high boiling products are distilled over and must be returned. The preferred pressure is 20 atm, like in the gas circulation process.

The foam is produced by means of stirring with a vertical shaft mixer a short distance above the bottom of the vessel. This arrangement has been found satisfactory in small scale runs, but still offers certain technical difficulties in large scale operations.

The use of a foam plate in place of a mixer is technically simpler and may be readily incorporated into large scale operations.

The catalyst sinks in the liquid phase in the course of time, and the total liquid must be slowly moved upwards. The gas and the liquid are separated above in a catchpot and the liquid again returned from below to the reactor. The cooling can be done during the return of the liquid to remove the heat of the reaction.

Catalyst and Reaction Conditions

A finely divided highly active iron catalyst is well adopted for the process, e.g. a finely ground reduced precipitation oxide catalyst. Oxygen is excluded by grinding the catalyst in oil.

The space/time efficiency increases with the pressure, better efficiency results in a saving of reaction space, and the equipment costs are kept low by operating at 20 atm pressure.

When operating for the production of middle oil and paraffin the synthesis is done in the temperature range of 200-250°C, while in the processes for gasoline the temperature range is around 300°C in order to obtain high octane numbers.

More CO than H_2 is consumed in the reaction gas. A proportion of $CO:H_2$ between 55:45 and 60:40 is recommended.

Middle Oil Process

The purpose of the middle oil process was the production of a maximum amount of olefines. Iron obtained from red iron oxide, finely ground with a small amount of potassium carbonate or potassium borate was used as a catalyst.

The operating temperature was 240-250°C. The space/time yield of the stirred reactors was 0.4, in the foam plate reactors 0.2, calculated to the volume of the liquid phase. A certain choice is left in the product distribution by the proper selection of catalysts. The preferred proportion of products was:

Gasoline, -200°C	31%
Middle oil, 200-350°C	30%
Paraffin, +350°C	39%
	100%

In addition:

Gasol		2-4%
C_3, C_4 alcohols in the water of reaction		4%
Gasification	less than	5%

When operations are run in more stages, e.g. in three stages, it is recommended to convert 50-60% of the CO-H_2 mixture present in every stage, with an intermediate removal of CO_2. When the contents of the inerts in the makeup gas are low, operations can also be conducted in one stage by returning the gas to the circuit after washing out the carbon dioxide.

Quality of the Products

The gasoline obtained in the process for middle oils has an octane number (R.M.) of 72 after refining.

The olefine content of the middle oil has been obtained by hydrogenation measurements to be:

Fraction	Olefine Content
200-250°C	70%
250-350°C	56%
300-350°C	44%

The olefine content of a 230-350°C fraction of one run was found to be 60% average in spite of the low olefine content of the higher fractions as found by the determination of the hydrogenation number.

The straight chain compounds of the individual fractions have been found to be:

200-250°C	69%
250-300°C	70%
300-350°C	74%

The amount of products is distributed approximately similarly to that in the individual middle oil fractions.

A careful cracking of the paraffin at 400-420°C gave

		Olefine Content
Gasoline, -200°C	15%	-
Middle oil, 200-250°C	15%	69%
Middle oil, 250-350°C	55%	51%
Residue, 350°C	8%	-
Coke	5%	-
Gas	1-2%	-

Only about one-third of the paraffin is of sufficiently low molecular weight to permit its direct use for paraffin oxidation.

Uses for Middle Oil

Detergents

A direct addition of H_2SO_4 to the olefines of the middle oil of the 230-350°C fraction produces sulfonates according to the work done at the main laboratory of Ludwigshafen, and they may be considered very high-grade detergents. The balance of the neutral oil, unless used as Diesel oil, can be converted into Mersol, an excellent detergent, by sulfochlorination, or into aryl sulfonates by condensation with benzol and sulfonation.

Turkey red oils, or leather oils, can be produced by sulfonation of the unsaturated constituents (230-350°C) with emulsification of the saturated constituents.

Leather oils can also be made by oxidation of the middle oil fraction 270-350°, and leather fats can be obtained by oxidation of paraffins (Dr. Pfirrmann).

Fatty acids and soaps can be produced by the addition of carbon monoxide and water to olefines (230-350°C, Reppe process).

Aldehydes and alcohols can be obtained by the addition of carbon monoxide and hydrogenation to the olefines (oxo process of the Rurhchemie).

Lubricants and Fuels

The more strongly branched middle oil of the gasoline process can produce lubricants with viscosity number of 105 which will meet all the specifications by polymerizing with aluminum chloride after purification with sulfurous acid. The middle oil from the middle oil process is still better suited for the production of lubricants because of the larger proportion of straight chain compounds. The heavy naphtha, +100°C, can be polymerized together with the middle oil. A lubricant with the viscosity number of 114, and a viscosity of 2.0°E at 100° can be obtained with a 47% yield. It meets all the requirements. The middle oil fraction 200-320°C has a cetane number of 60 when used as Diesel oil. Its pour point is -10° and is therefore not entirely satisfactory. It can, however, be made to meet the standards by lower cut and by a light cracking of the higher constituents.

Gasoline Process

Increasing the temperature to 310°C and returning the distillate to the liquid phase, produces the following products:

Gasoline, -200°C		60%
Middle oil, 200-350°C		30%
Paraffin		10%
		100%
Gasol		6%
Alcohols		6%
Gasification	about	5%

The enriched gasoline so obtained has an octane number (R.M.) of 78, after refining - 90.

The gasoline process has not yet been tested experimentally over a longer period of time.

The Yield in Liquid and Solid Products is Higher Because of the Lower Gasification

160-170 grams of liquid products can be readily obtained per normal cubic meter of the pure gas, to which gasol will have to be added. It is expected that yields of over 170 g will be obtained in the future.

Test for the Application of the Gas Circulation and the Foam Process for the Production of Synol Products

Tests with the synol catalysts of different size of particles have been run in the 4-liter gas circulation reactor.

Operations were conducted for five weeks at 195°C with a 3-5 mm particle size and the space/time yield of 0.4-0.5. After five weeks the space/time yield decreases suddenly. The catalyst was plugged up with the products, some of the catalysts became soft and could be ground up between the fingers. Recirculation of the products with a 30% conversion produced only one-half the alcohol yields against the Leuna synol process. Olefines replaced the mixed alcohols. Conversion was then further reduced in order to reduce to one-third the residence time with the catalyst. The products have not yet been studied any closer.

Coarser particle of catalyst (12-15 mm) had a longer life, but the space/time yield obtained with them was only 0.2.

Operations could not yet be conducted by the foam process at 195°C with the finest size of catalyst, because the space/time yield was too low. At 210° the space/time yield of 0.12-0.15 has been reached. Investigations showed the products to contain 75-80% of the alcohol contents of the Leuna products. The experiments are being continued.

/s/ Michael