Frames 43-44

Hydrocarbon synthesis in presence of iron catalysts, according to letter from Ruhrchemie, 6/13/41

The Ruhrchemie representatives reported in October 24 to November 30, 1938, that the activity of the iron catalyst was greatly improved, but the tests for industrial hydrocarbon synthesis were discontinued because cobalt catalysts are much more active, and iron catalysts consume much more carbon.

Frames 45-49

Patent application on production on liquid hydrocarbons from gaseous carbon compound, by Sacher, Lucerne, Switzerland

<u>Patent Claims</u>

1. Process for the production of liquid hydrocarbons from methane, ethane, propane, characterized by heating the mixtures of these gases mostly to 150-500° C. to cause them to interact, and keeping them at these temperatures less than 1800 seconds including the time for preheating, in the presence of 40 to 4,000 gm. of water/$m.^3$ of gas and in the presence of free oxygen, oxides of carbon, unsaturated hydrocarbons, metal oxides and their salts, as substances to combine with the water.

Frames 50-51

Organic substances in the water stream of the hydrocarbon synthesis by the foam process. February 22, 1943

The byproducts of hydrocarbon synthesis with iron catalysts consist principally of CO_2 and a small amount of H_2O. For instance, about 100 kg. of water are formed in the foam process at 250° C. to 600 kg. of products, without including organic compounds in the water. Should only water and no CO_2 be formed, 700-800 kg. would be expected.

Water soluble products, which include alcohols, aldehydes, ketones and acids, are distributed between the oil and the water streams, depending on their solubility in water and their amounts. The water stream may contain up to 30% by weight of these substances, which is particularly important because the lower acids, especially acetic acid, dissolve in water, and the solutions are corrosive, introducing iron from the catalyst or the reactor walls. Soda solutions are usually added to neutralize free acid wherever the gas and product streams may form liquid water.

Dr. Boente has investigated the water stream obtained in the recycling process at 325° synthesis temperature. He found in it the following substances:

Acetaldehyde	10% by wt.
Acetone	5
Ethanol	55
Propanol	20
Butanol and higher alcohols	10

The total concentration of these substances in the aqueous stream was 10% by weight on the average; there were in addition about 1% by weight of free acids.

The remarkable absence of methanol among the alcohols was confirmed in special tests, and leads to the conclusion that aldehydes and alcohols were formed in the oxo reaction.

The water-solubles formed in the foam process under different conditions (liquid phase, colloidal catalysts, 230° C.) and primarily at lower temperatures were also of interest. One might have expected to find the same substances as before.

The aqueous stream from a 1.5 m.^{3} foam reactor at 20 atm. and 250° from a gas mixture $CO:H_2$ equals 5:4 was tested. The aqueous solution was colored yellow-brown by the dissolved iron, because it had already come in contact with air.

Testing for Acids

The acids[1] are neutralized in the aqueous stream with soda, and the salts formed evaporated to dryness. Acids were then set free with phosphoric acid. The phosphoric acid contained 11% water which was taken into consideration in the subsequent distillation in a Widmer still for the separation of the individual acids.

The aqueous stream contained 3.5% acids of the following composition:

Formic acid	5% by wt.[2]
Acetic acid	65
Propionic acid	25
Higher acids	5

0.27% by weight of iron on the basis of water formed was in combination with the acids. This meant that 1/5 of the acids in the water were in combination with the iron.

Acetaldehyde was distilled from the aqueous stream and the water supersaturated with potassium carbonate, the alcohols separated were distilled and the potash solution redistilled to separate alcohols remaining in it. Potassium carbonate was again added to the distillate and the alcohols separated.

The salted out alcohols still contained some water, which was taken into consideration in their determinations. A 2 m. column with Raschig rings was used in the distillation.

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[1] The b.p. of acids were: Formic acid 101°, acetic acid 115°, propionic acid 141°, n-butyric acid 162°, i-butyric acid 154°.

[2] Formic acid was identified by reduction of silver nitrate.

Acetaldehyde	2-4% by wt.3/
Acetone	1-2
Ethanol	45
Propanol (sec.)	15
Propanol (prim.)	20
Higher alcohols	15

The total percentages of substances in the aqueous stream amounted to 24% by weight of the total products except gasification, the acids 0.8%, alcohols, acetaldehyde and acetone 55% by weight.

/s/ Schmidt and Michael

Frames 52-53

Hydrocarbon equilibria in gas synthesis May 5, 1943

Intersections of the equilibrium curve with the abscissa (lg. $K_p = 0$) or "zero free energy".

	lg. $K_p = 0$	Formation of hydrocarbon + CO_2
Methane: $CO + 3 H_2 = CH_4 + H_2O$	900° K	920
Ethane: $2 CO + 5 H_2 = C_2H_6 + 2 H_2O$	760	800 (in agreement with Butefisch's
Propane: $3 CO + 7 H_2 = C_3H_8 + 3 H_2O$	730	770 results)
Hexane: $6 CO + 13 H_2 = C_6H_{14} + 6 H_2O$	690	740

Butefisch's data for zero free energy

	lg. $K_p = 0$
Methanol: $CO + 2 H_2 = CH_3OH$	410° K
I-butanol: $4 CO + 8 H_2 = C_4H_9OH + 3 H_2O$	660° K

Frames 54-59

Report on operations of a 1.5 m.^{3} foam plate reactor for hydrocarbon synthesis. May 3, 1942

The reactor consisted of a tube for 20 atm. pressure, 8 m. high and 0.5 m. diameter. The tube was filled with a paraffin wax from the production, and iron catalysts 1-5 µ grain size. The foam plate was located in the bottom part of the tube, and the gas entered through it at the bottom in fine bubbles. Settling of catalysts is avoided and the cooling of the liquid is aided by recycling it about once every three minutes. The liquid passes an outlet separator, in which the gas is separated from the vapors of the liquid phase products, next a cooler, where the liquid gives up its excess of heat, and finally a centrifugal pump, which forces it again from below through the foam plate and into the reactor.

3/ The b.p. of these compounds were: Acetaldehyde 20°, acetone 55, ethanol 78, sec. propanol 82, prim. propanol 97, higher alcohols over 100°.

The liquid phase generally increases in amount during operation, and an overflow pipe is installed into the catchpot, which regulates the level of the liquid phase. The catalyst is retained in the reactor in a settling tank inside the catchpot, in which the catalyst can settle and become separated from the overflow of the liquid. The liquid, and the gases leaving the catchpot enter then a hot catchpot at 120°, which removes the paraffin wax and protects the colder equipment parts following it from being plugged up with wax. A water-cooled catchpot and finally an ammonia-cooled catchpot come next.

The reactor is surrounded with an oil jacket for starting. The oil is driven by pumps through an electric preheater into the oil jacket. A cooler can be substituted for the preheater, permitting occasionally also the cooling in the oil jacket.

<u>Operating Experience</u>

The reactor was first put on stream 1/4/42, at which time no cooler was yet provided in the outer liquid phase circuit. The cooling was to be done in the oil jacket. The porous plate consisted of quartz grains cemented together with glass, with 0.1 mm. pore size, which worked satisfactorily in smaller reactors.

The porous plate was, however, found to be destroyed several hours after starting. The plate cracked by thermal stresses, because gas entered the reactor cold. No suitable less porous firebrick was available, and a plate similar to the first one, but supported above and below by iron, was used, while the gas was preheated in a steam-heated preheater. The cracking of the stones was in that way overcome.

Difficulties with the liquid recycling pump were already experienced after two days of operation after a new start. The catalyst was forced into the pump stuffing boxes and eroded the shaft.

New pumps were installed in which an oil was slowly forced inside through the stuffing boxes, no longer permitting the liquid phase to enter the stuffing boxes. A middle oil fraction 250-350° obtained in the synthesis was used as the protecting oil. About 20 kg. were daily consumed. Experience showed, however, that pump difficulties were in that way suddenly and completely overcome.

Operations were resumed on 1/19. Many difficulties arose in the following cold winter weeks through freezing at the gas mixer in Oppau. The tubes had to be heated with steam and provided with traps.

Increasing difficulties were experienced after about 2 weeks with the cooling of the jacket oil, and it seemed as if the wall of the reactor became insulated on the inside through deposition of catalyst on the cylinder wall. Operations were stopped and the unit dismantled. The reactor, however, was found to be clean.

The reason for the trouble was not clear, a stronger oil pump was installed, and also an oil surge tank.

Operations were resumed on 2/14. Difficulties were, however, not overcome, and operations stopped at 2/19 to install a cooler into the liquid phase cycle, which was already made.

The quartz foaming plate was replaced at that time by a firebrick plate with twice the porosity, namely 0.2 mm. pores.

Operations were resumed at 2/28. The space-time yield, however, dropped greatly towards the end of March, and operations were stopped after 32 days. Investigations showed the catalyst to have become sulfurized. The sulfur content of the gas rose to 5 mg. S/m.^{3} for a while.

Organic sulfur was then eliminated by scrubbing the gas with 40% soda before absorption in the purification Lux mass. Ruhrchemie purifies its gas in that way at 250° and atmospheric pressure. Our gas reaches us, however, at 23 atm. pressure, and operations have to be continued at that pressure. At temperatures only slightly above 200° C. the Lux mass became strongly heated in isolated points and carbon monoxide became already reduced in the purifier. A few active points were evidently reduced by the gas, resulting in wild reactions with large heat evolution. Other parts in the neighborhood also became heated to high temperatures and reduced. The only thing to do was to replace the purification mass and use it at 150° C., i.e. at too low temperature for reduction. No sulfur was found in the gas recently, and the theory could not be confirmed.

The reactor was again put on stream on 5/7 with new catalyst and operated for 31 days without recycling difficulties. A cooling coil was installed at the overflow separator to retain the higher boiling fractions when the liquid phase begins to decrease in amount. The recycled liquid phase from the reactor was sprayed upon part of the coil kept at about 30° below the operating temperature, and stayed upon it. Dismantling showed that the catalyst deposit kept increasing upon that coil and finally formed a cover above the whole width of the catchpot. This formation could not be melted. Pieces were probably broken off now and then, fell down and plugged up the connecting lines to the cooler.

The cooler consists of rising and descending cooler coils, and was also completely plugged up, with some clearance only in the center.

No other difficulties were observed. The wear of the pump was investigated. No erosion was noticed after 100 days of operation.

The coolers were probably plugged up by the remarkable formation of the catalyst layer in the outlet head. The coil was eliminated to give no other opportunity for the formation of the sediment.

The porous plate with 0.2 mm. pores caused a reduction in the space time yield against the 0.1 mm. plate, and the latter was therefore reinstalled, and the reactor again put on stream with the old catalyst. Operations are being still continued.

In general, troubles resulting in stopping operations were not inherent to the process. They all could or can be overcome. The total run has extended over 105 days. The catalyst had to be replaced once because of poisoning with sulfur. The present catalyst has been used for a total of 1-1/2 months.

/S/ Michael.

Performance and yields of the foam process
from results of tests in 1.5 m^3 reactor.

Operations were varied during the run with the 1.5 m^3 reactor. The porous plate, throughput, operating temperature and to a certain extent also the gas composition were all varied. The operating balance was derived in a period during which all conditions were kept constant. Such was the case between 6/22 and 7/1. The operating conditions were as follows:

Temperature	252° C.
Pressure	20 atm.
Gas throughput	117 m^3/m^3 reactor space
CO : H_2	5:4

Single pass, with no recycling

Additions to replace catalyst loss and to further increase the catalyst concentration 807 kg. oil with 50% catalyst

Products	5,690 kg. oil phase
Alcohol and aqueous stream	243 kg.
	5,933 kg.

To be subtracted from the above:

807 kg. oil added,
also the protecting oil in the pump
190 kg.
997 kg.

New products formed: 4,936 kg.

Twelve percent gasol not included in the above figure and determined analytically must be added to the last figure, increasing the total to

5,536 kg.,

which represents the catalyst space time yield of 0.36 kg./l., day.

To calculate the total production, 5 percent gasification must be added, increasing the total to

5,830 kg.

During the 10 days, the amount of gas used was 175x24x10 = 42,000 m^3, containing 2 percent inerts, or

37,600 nm^3 pure gas

The products contained 2.5% O, and with complete conversion the amount of products would amount to 8,010 kg. which corresponds to 73 percent conversion.

175 m^3 gas entered the converter each hour,

97 m^3 left the converter

Gas analysis:

	Inlet	Outlet
CO_2	0.8	30.4
C_mH_{2m}	0.0	3.0
H_2	40.8	28.4
CO	53.6	27.8
Hydrocarb.	2.0	4.0
Increase	1.6	2.0
N_2	2.8	6.4

Only gases obtained in a laboratory test were additionally converted in a second pass. A reactor with 75% conversion was installed in front of a second reactor. Between the two reactors CO_2 was absorbed. The conversion in the second reactor reached 63 percent, which represents a total conversion of over 90 percent. No doubt can exist, that similar results could be obtained with recycling products from large reactors.

Ludwigshafen, 6/3/42 /s/ **Michael**

Frames 60-62

Leuna discussions of alcohol synthesis. July 11, 1941.

Differences in results obtained in Leuna and Oppau are discussed, and the Leuna directions given for the alcohol determination in synol products.

Frames 63-64

Conversion of gas synthesis products into alcohols, fatty acids and sulfonates, by Michael. June 19, 1942.

65% C_6 - C_{11} alcohols can be obtained by oxonation and hydrogenation of foam process products. In addition also about 20% of higher alcohols C_{20} for which uses remain to be found.

40% middle oils 200-350° C. can be converted to sulfonates with an increase in weight amounting to about 50% due to the addition of H_2SO_4. The residue can be converted to phenylmepasin sulfate. About 40% fatty acids can instead be obtained by the Reppe process.