The middle oil as Diesel oil had a cetane No. of 48 - 50. Viscosity, Engler degrees at 20 degrees was 1.16. The oxygen content approximated 2 per cent. The small quantity of high-boiling products had the character of a mixture of paraffin and a light machine oil.

II. The Foam Process

After the outbraak of the war a shortage of scaps and detergents was soon felt which was caused by the falling off of imports of fats and vegetable oils.

To make up this shortage alcohol sulfonates were produced in Leuna which possessed excellent detergent action and insensitivity toward lime. The raw material was middle oil of the Fischer Synthesis which was completely saturated by hydrogenation. It was subjected to sulfochlorination in the presence of ultraviolet light. In this manner alcohol sulfonates were obtained.

Since the middle oil obtained with the iron catalyst is largely unsaturated with the double bond terminal, as was shown by investigation, an attempt was made at direct sulfonation with sulfuric acid. The results were successful. Sulfuric acid esters were obtained which were the equal of alcohol sulfonates in regard to detergent action and, on the whole, cheaper in price.

The gasoline process was not at all suited to the production of middle oil for this purpose. The yield is relatively low and experiments demonstrate that the middle oil produced at lower temperatures is more straight-chained and therefore qualitatively

uperior for this purpose. Since appreciably more middle oil is imultaneously formed at a lower temperature, we were naturally faced ith the problem of reducing the synthesis temperature as much as possible.

An economical gas conversion with the sintered catalyst used n the gas circulation can no longer be achieved below 260 degrees.

It was therefore decided to carry out the reaction in the iquid phase which would permit the use of the iron catalyst without azard in a highly activated form in a finely-divided, to a certain xtent, colloidal dispersion which would guarantee absolute temperature ontrol. In addition, the catalyst is continuously extracted of its wn accord. Particular attention, however, must be directed to an ffective contact between liquid and gas since the solubility of the as in oil under the conditions of the synthesis is very slight. In onsequence the gas must be mechanically dispersed in the liquid in he form of very fine gas bubbles.

Experiments with Nozzles

Gas dispersion was first attempted by means of fine nozzles. ariously arranged nozzles were placed into the reactor at different pots. However, satisfactory fineness of the gas bubbles was not attained.

The Stirring Reactor

At this point an attempt was made to apply the principle of he stirring reactor which had been proved to be reliable in other rocesses. An upright cylindrical reactor was used with a shaft projecting settling of the catalyst which would otherwise occur.

The best foam (dispersion) plates were those sintered together from quartz sand with glass as the cementing agent. They were mostly employed in a round conical shape, 4 - 5 cm thick. Asbestos foil served as packing material. At first the varying heat expansion of iron and foam plate caused some difficulties. It was possible to place several such plates on the bases of reactors with large cross sections. Moreover, a strong iron grating was ground onto each plate in order to enable it to withstand the existing pressure differences without breaking. A pore size of 0.1 and 0.15 mm. is suitable. The pore diameter of 0.2 mm, shows a noticeable drop in output.

Attempts were also made to employ filter candles in place of filter plates. However, it was established that an upright pore wall, and, to an even greater extent, a downwardly inclined pore wall produces larger bubbles. But since a filter candle contains such surfaces whether it is in a vertical or horizontal position, its use for this purpose was abandoned.

The Reactors on a Laboratory Scale

The reactors for the foam process on a laboratory scale possessed the essential features of the process: Gas dispersion by means of dispersion plates, slurry circulation and degassing of the slurry. The slurry circulation takes place by means of a central tube introduced into the axis of the tube. The fine gas bubbles produced by the dispersion plate ascend in the annular part of the reactor cylinder. Because of this the slurry in this part of the reactor became lighter than in the central tube. A circulation pattern following the principle of

the "mammoth" pump occurred, the slurry ascending in the annular part, being degassed at the top, and again returned to the bottom through the central tube. The temperature was determined by means of thermocouples which were placed at varying levels in the reactor and from these it was possible to establish whether the slurry circulation was functioning or not.

Apart from these 3 m high reactors with a capacity of 3 liters, 10 and 25 liter reactors constructed on the same principle were employed.

Reactors on a Semi-Works Scale

300 Liter Reactors

On completion of a 300 liter reactor constructed according to the same design as the laboratory reactors it was found that automatic slurry circulation could no longer be attained with certainty and that if the circulation was broken for one reason or another, it could no longer be set in motion because of the sinking of the catalyst in the meantime.

The following occurred then: As a result of the gradual settling of the catalyst the catalyst concentration in the reactor, especially in the lower part, was higher and the slurry was therefore heavier than in the circulation in which the slurry is supposed to flow downwards.

As a result the buoyancy of the gas bubbles no longer sufficed to set the circulation in motion.

A circulation pump was therefore placed in the slurry circulation which was shifted to the outside of the reactor for readier accessibility.

1.5 cbm Reactor

The 1.5 cbm reactor was constructed according to the dispersion principles already described.

The reactor was a cylinder 8 m in height with a capacity of 1.5 cbm; the gas separator had a capacity of 600 liters. The slurry circulation line had a cross section 1/10 of the reactor.

Two circulation pumps coupled in parallel, one serving as a reserve, were used to pump the slurry around. Each pump could be interchangeably disconnected. At first some trouble was had by the stuffing boxes because hot reactor liquid and catalyst penetrated the stuffing boxes and acted as an abrasive on the shaft. Moreover, there was also the danger that the slurry which passed to the outside would ignite as a result of the pyrophoric iron contained in it if it ran into absorptive lining, e.g., the insulation of the reactor. The catalyst would dry up as a result of the absorption of the liquid and ignite. This difficulty was solved by perforating the packing and slowly forcing into it middle oil which stemmed from its own production and was not a foreign substance. A portion of the forced—in oil went inside and thus actively prevented penetration by the reactor slurry into the packing box. From time to time it was necessary to withdraw the stuffing box and replace the packing at intervals.

14 cbm Reactor

Finally, a lh cbm reactor was constructed for large-scale operation. It can be visualized by the attached drawing. The reactor was not put into operation because a sufficient supply of synthesis gas requisite for the operation of the reactor could not be released on account of the war.

(Drawing p. 173)

The Catalyst

The catalyst in the liquid phase can be used in the most highly ted and the most finely divided form without fear of danger, as is se in the gas phase. This intense activity can be attained in several The catalyst, for example, can be produced by the conventional method cipitation. Finely divided colcothar, as obtained by combustion of arbonyl vapor, can be used . Iron carbonyl vapor can also be (2) osed directly in the reactor slurry . The latter is the simplest a cheapest process and gives the best catalyst.

The catalyst was produced from colcothar in the following way:
har was pasted in water containing 1 - 2 per cent sodium- or potassium
, kneaded, formed into cakes, dried, cut into smaller pieces and
d at the lowest possible temperature with considerable hydrogen
p the water vapor pressure low. The pyrophoric catalyst, after cooling
thdrawn from the reactor protected by carbon dioxide, introduced
iddle oil of its own production and ground to a highly divided
e fineness of 2/u. Greater fineness could not be attained by grinding.
ttling velocity in middle oil was tested in standing cylinders. In
ay a gage for the fineness of the grinding is obtained.

The requisite amount of catalyst suspension was charged into
(3)
actor into which a previous charge of liquid had been introduced.

ile number 13042.

ile number 13668.

^{50 - 300} kg per cbm slurry of the catalyst just described or a smaller fraction thereof if the catalyst is produced by the decomposition of iron carbonyl.

when the reactor was first put into operation it was charged with purchased paraffin. As production progressed it was more and more displaced by the new formation of slurry. Then iron carbonyl was used it was decomposed in the slurry itself. The requisite alkali was run into the slurry in the form of alcoholic potassium hydroxide or sodium hydroxide solution.

Additions of other substances to the catalyst were tested in various instances. However, their addition did not result in any noticeable change in the results.

Slurry Circulation with Fixed-Bed Granular Catalyst

Attempts were also made to use the catalyst in a fixed granular form, to fix it in the reactor, and to effect the liquid circulation by a central tube. If this is done a suspended catalyst is not used, the liquid is much lighter and has less friction, and the liquid circulation therefore proceeds automatically without any trouble according to the principle of the mammoth pump since the liquid charged with gas bubbles which flows upward through the catalyst bed is specifically lighter than the degassed liquid that flows downward through the central tube. An important simplification of the apparatus was achieved by omission of the pump.

The experiments on a laboratory scale produced good results, not at all inferior to those attained with a suspended catalyst. The liquid circulation was conducted with absolute safety.

A 300 liter reactor was constructed in order to test the process on a larger scale according to the same principle. The liquid was recycled axially. The catalyst was placed on a number of perforated plates placed one on top of the other. The reactor was never put in operation on account of the war.

Foam Process Experiences

The temperature inertia of the apparatus in the foam process is dinarily great and upsets are not likely even if attendance is ed.

The gas mixture was established with an excess of CO in order in a higher percentage of olefins in the middle oil. A CO: H₂ = as composition was usually used. At 250 degrees 0.35 - 0.45 kg product ained per liter catalyst space per day. At 240 degrees about 0.35 kg are obtained.

However, a difficulty occurred after two months operation. The began to dwindle and irregularities appeared in the temperature nation. The reactor was shut off and opened. The following picture d: A ring-shaped coating of catalyst several cm. in thickness had remed at the reactor wall. The thickness of the coating lessened below appeared in the vicinity of the dispersion plate.

Deposits had also been formed in the gas separator. Catalyst I to parts of the separator free of liquid. This catalyst deposit ned an opportunity of further reaction to the already reacted gas. Indicate the deposit of the lack of heat removal. A portion is the cooler which contained a cooling coil. No deposit appeared in many circulation where the slurry, as a result of the narrower cross a, had a higher velocity.

The deposit was examined and was found to consist chiefly of i FeCO₃, that is, iron compounds, which are stable in the reaction

gas prevailing in the upper section of the reactor and which contains (1) an abundance of CO₂ and H₂O vapor.

The deposit was readily crushed and did not give the impression that it was held together by crystalline forces. We were tempted to assume the formation of an adhesive, high-molecular, organic substance, probably containing oxygen, which was sparingly soluble in the reactor slurry and which was stable in the atmosphere of the upper part of the reactor. The attempt to find such a substance, however, was not successful.

An attempt was made at this point to overcome this difficulty by installing stirrers which were constantly to slowly scape the reactor wall. In this way the formation of deposit was to be prevented. However, after about three more months it turned out that the reactor jacket itself remained clear but that thick deposits were formed on the stirrer rods and that these deposits in part dropped onto the dispersion plate and were detrimental to the gas dispersion. There was naturally much less opportunity for the formation of deposit than before but another device would have been needed to keep the stirrer clear. More and more methods were supposed to be tried to obviate this difficulty but they could no longer be put into effect as a result of the accumulating war exigencies.

⁽¹⁾ Alteration of the reactor gas at a gas conversion of 73 per cent showed the following analysis of the incoming and outgoing gas:

Constituents of the	Incoming Gas	Outgoing Gas
co	0.8	30.4
C _n fi _{2n}	0.0	3.0
H ₂ CO	40.8	28.4
	53.6.	27.8
saturated hydrocarbons	2.0 ^x)	4.0 ^{xx})
N_2	2.8	6.4

x) Average C content 1.8 (x) Average C content 1.5

The reactor was to be made shorter in order not to force excess gas conversion in one pass and to avoid a high percentage of ${\rm H}_2{\rm O}$ and ${\rm CO}_2$.

It was assumed that then the conditions for deposition of the catalyst would no longer be favorable.

Furthermore, an H2-rich mixture with a possible excess of hydrogen, or even a CO : $H_2 = 1$: 2 ratio was to be tried since we knew by experience that hydrogen-rich mixtures are detrimental to the formation of resinous substances.

Or a small portion of the slurry was to be constantly run over an absorbent in order to remove high-molecular, resinous substances or, in case the suspended catalyst caused difficulties, a hydrogenation with hydrogen was to be effected with such care that the resin-formers would be hydrogenated and not the olefins.

Moreover, the catalyst was to be witndrawn from the reactor continuously or in regular intervals of time, purified and again returned to the reactor, or replaced by a new batch. This could be readily done in the liquid phase without interrupting operation.

An attempt was made to reemploy a sample of the reactor deposit as a catalyst. It was again ground with middle oil. The sample was run in an experimental reactor and it turned out that after two days it approximated the output of a moderately good new catalyst. The table follows:

Composition of Catalyst and Reactor Deposit

	Catalyst from reactor liq- uid, 2 months	extracted, lying dir- ectly on the reactor	Deposit extracted, lying more toward the interior	Deposit as in column 2, run for 2 days in lab. reactor
Total content of Fe		wall		
	77 %	65.4 %	63.3 %	80.0 %
Metallic Fe	26 %	10.6 %		•
Degree of reduction	22 a	·	3.6 %	48.0 %
	33 %	16.0 %	5.7 %	60.0 g
CO ₂ liberated	2.4 %	11.0 %	13.0 %	
eco ₃	6.3 g	·		2.0 %
as carbide	·	29.0 %	34.2 %	5.3 %
ar out of de	0.1 %	1.1 %	0.25 %	2.8 %

The higher degree of reduction in the laboratory reacton must be attributed to the fact that a more rapid liquid circulation was maintained here than in the large-scal experiment for external reasons, with a consequent decreased gas conversion. Catalyst deposition was never observed in the small-scale reactor.

The Products of the Foam Process

The foam process at 240 - 250 degrees is differentiated for the most part from the gas circulation (process) in regard to products by the following features:

The higher fractions are present in about equal proportions with the gasoline fractions. The products have a more straight-chained construction. The oxygen content is somewhat higher. Gas production decreases more markedly. The gasoline does not attain the resistance to knocking of the gasolines produced at a higher synthesis temperature; conversely, the Diesel oil is superior for the same reasons. Gas formation constantly dwindles.

This tendency persists to the lowest attainable synthesis temperatures.

The product yield can be varied within certain limits so that in one instance the higher-boiling products can be promoted, and in the other instance the lower-boiling ones. The following is an average

composition of the product (1)

	% by weight	Olefin content (2)	Oxygen content
Liquid gas (C ₃ , C ₁) Gasoline to 200 degrees Middle oil 200-325 degrees Paraffin above of 325 degrees Alcohols in the product water (mainly ethanol)	10 30 - 40 25 - 35 20 - 30 5	75 - 80 % 70 % 50 - 60 % - -	6 - 8 % 3) 3 - 5 % 4) 2 - 4 %

Gasification in the form of methane and ethane runs to 5 - 8 per cent.

The proportion of paraffin can be increased at the expense of the lower-boiling constituents by the use of markedly alkalized catalyst.

(1) It depends on the following reaction conditions:

Pressure: 20 atmospheres
Temperature: 250° (240°)
CO: H₂ = 5: 4
Quantity of fresh gas 120 cbm per catalyst space per hour
Gas conversion: app. 70 %
The yield of utilizable crude product in 2 stages at 90 % conversion
amounted to 175 grams per normal cubic meter of ideal gas.

- (2) Olefin determination was not conducted by the iodine method because a part of the oxygen compounds also react to iodine. The hydrogenation number method was therefore employed.
 - 3) The alcohol content of the gasoline fraction up to 100 degrees amounted to about 5 per cent because the alcohols boiling in this range were dissolved in the product water for the most part.
 - 4) The alcohol content of the middle oil fraction amounted to 8 12 per cent. Apart from this, esters, acids, aldehydes and ketones together approximately equalled the quantity of alcohol.

Use of the Products

The gasoline obtained at a synthesis temperature of 240 - 250 degrees does not have a high octane number even in a refined state. The octane number (research) is 60 in an unrefined state, and 70 - 75 in a refined state. For this reason, if gasoline is to be the main product, a higher synthesis temperature should be selected.

On the other hand, since it contains 70 - 75 her cent terminal olefins, it is suitable for the production of aldehydes and alcohols by means of addition under pressure of CO and H₂ by the Oxo reaction and subsequent hydrogenation at 180 degrees, or for the production of fatty acids by addition of CO and H₂O according to Reppe.

To this end it is advantageous to use narrow fractions. The addition products thus fall out of the boiling range and are readily isolated by distillation. C₆ and C₇ alcohols are thus obtained from the 50 - 100° fraction with a 65 per cent yield; C₈ - C₁₁ alcohols are obtained from the 100 - 150 degrees fraction with a similar yield. Moreover, 20 per cent higher alcohols of about C₂₀ are obtained. The residual gasoline together with the unused gasoline fraction gives a gasoline with an octane number (research) of 60. Since the CO addition takes place partly at the terminal atom and partly at the next C atom, alcohols are partially obtained with a methyl group in the alpha position.

The alcohols obtained in this way can be advantageously used in the production of lacquer.

Middle Oil

The middle oil obtained at a low synthesis temperature is more suitable as a Diesel oil than that obtained at a higher temperature.

Whilst the latter possesses a cetane number of only 40 - 50, the former possesses a cetane number of 75 - 80. The Engler viscosity at 20 degrees is 1.16.

The suitability of the middle oil obtained at a low temperature for the production of sulfuric acid esters and alcohol sulfonates was the real cause for the development of the synthesis in the liquid phase. The chains of 13 - 18 carbon atoms give valuable fine detergents.

The olefins have the advantage that they can be converted directle into sulfuric acid esters with sulfuric acid. 40 per cent of the middle of can be directly transformed. The best product is obtained from the 230 - 3 degrees fraction. The separation of the sulfonates from the unconverted of is accomplished by ethanol, etc. If necessary the residual oil, after hydres genation, can be converted into alcohol sulfonates by sulfochlorination, or converted in the same way to Igepal NA with benzene.

The olefin contents and the straightchainedness (1) oil fraction were determined as follows:

Fraction 200 - 250° 250 - 300° 300 - 350°	Olefin contents 70 % 56 %	Straightchainedness 69 % 70 %
300 - 3500	. 44 %	70 % 74 %

Another use of middle oil is for the production of lubricating oil. 35 - 40 per cent of a lubricating oil with a Viscosity Index of 85 is obtained by condensation with AlCl₃. Heating oil amounts to 10 - 15 per cent and a Diesel oil with a cetane number of 60 - 70 amounts to 50 per cent

⁽¹⁾ The straightchainedness was determined by the Schaarschmidt method as improved by Dr. Leithe in oil completely converted into saturated paraffins by hydrogenation.

Paraffin

The obtained paraffin has an oxygen content of 2 - 4 per cent. It can be readily freed of oxygen and simultaneously saturated by hydrogenation. Its appearance will then be pure white; it is hard, no longer sticky and useful for the most varied purposes. For example, it is suitable for polishing wax and shoe polish. Where lower quality is satisfactory it can be used without hydrogenation.

Two-thirds of the paraffin boils above 450 degrees and forms high-melting paraffin. The first third can be used for paraffin oxidation directly after hydrogenation whereas the high-melting paraffin must first be subjected to careful thermal cracking to obtain a chain length suitable for paraffin oxidation.

Furthermore, cracking turns 70 per cent of the total paraffin into middle oil containing 70 per cent olefins. This is also a means of obtaining olefin-rich middle oils. The following was obtained by careful cracking of the paraffin at 400-420 degrees:

Gasoline to 200°		15 %	olefin content	
Middle oil	200 - 250°	15 %	69	
P	250 - 350 ⁰	55 %	51	
Residue ahove	350°	8 %		
Coke		5 %		
Gas		1 - 2 %		

It is used in the same way as the original middle oil.

Sintered Catalysts

for Low Synthesis Temperatures

The sintered catalysts that have been further described in the preceding pages are sintered in a reduced, i.e., metallic condition.

Their activity is thus neutralized to a certain extent.

Another category of sintered catalysts is obtained if the sintering is conducted before the reduction and the reduction carried out at the lowest possible temperature with a great deal of hydrogen. Special effects will be obtained if substances such as tungsten oxide, barium oxide, etc. are introduced (1). Catalysts of this kind possess a remarkable thermal stability and a high activity which permits of a lowering of the synthesis temperature to 230 degrees and beyond, and thus makes possible the production of almost exclusively straight-chained paraffins. They can be used in the conventional Fischer reactor.

A special characteristic of these catalysts is their preference for the formation of paraffin. The following was produced in one instance:

Liquefied gas (C3, Ch)	4 %
Gasoline up to 2000	17 %
Middle oil to 3500	19 %
Paraffin	60 %

The catalyst was prepared in the following manner:

Iron powder, obtained by thermal decomposition of iron carbonyl, wax mixed with several per cent of WO₃, pasted with a little water containing 1 per cent of potassium borate (basis iron) and kneaded. This was pressed into pellets and ignited at 850 degrees with air for 4 hours. They were then reduced at 450 degrees with a great excess of hydrogen.

It is often more advantageous to use precipitated iron as the starting material or to undertake the precipitation with the other substance. Among others, the following substances are suitable as the other substance: barium, magnesium, chromium and molybdenum.

(1) File number 14131.

Dependence of the Composition and Quality of the Products on the Reaction Conditions

In general the following regularities depending on the external conditions can be set up:

Higher pressure steps up the oxygen contents of the products. If the pressure is raised from 20 to 100 atmospheres, for example, it will increase almost threefold.

Higher synthesis temperature gives better gasolines, inferior Diesel oils, branching of the products is greater, and the gaseous products and the gasoline become more important at the expense of the higher boiling products.

Lower synthesis temperature gives less valuable gasolines, but better Diesel oils. The straightchainedness is higher. Approximately the same quantities of gasoline, middle oil and paraffin are obtained. If special catalysts are introduced paraffin will become the main product. The formation of gaseous products progressively dwindles. The oxygen content increases. The products are more suitable for further chemical working up.

Gas mixtures richer in carbon monoxide yield a somewhat higher degree of unsaturation in the products. The use of hydrogen-rich gases has a favorable effect on the catalyst life. A higher alkali content promotes the formation of higher-boiling products.

Michael

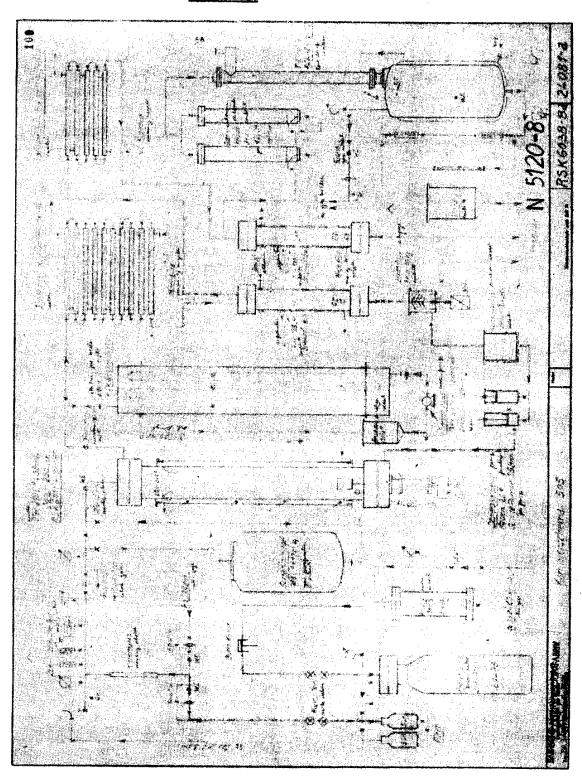
Listing of Several Reports and Memoranda

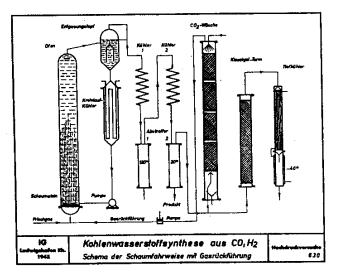
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06747	Haussmann Foam Process = Olefins March 21, 1942
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