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Hydrocarbon Synthesis from Carbon Monoxide and  
Hydrogen With Iron Catalysts

(Gas Circulation Process and Foam Process)

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Introduction

The following material deals with researches conducted by the author from 1935 to 1944. These notes were put down largely from memory because very little data is still available. Valuable documents such as laboratory books and diaries of the pilot plant were completely lost. They were shipped for the most part to Hassmersheim near Heilbronn to safeguard them from bomb damage and there they completely disappeared in the war disorders. A small but very important part was lost in February 1945 when the house of the author was completely destroyed by bombs and fire. Also missing, unfortunately, are many of the abridged reports, and often the most important, which were preserved at other places. Much of the material was recreated by questioning former collaborators who have been partly scattered throughout the country.

For these reasons we are compelled to omit the once abundant statistical material. Nevertheless, the following description of the process should be sufficient. What could no longer be verified was omitted.

The first of the following synthesis processes that are described, the gas circulation, was reported in detail to the Standard Oil Co. of New Jersey, to Mr. Keith of the Kellogg Co., New York, and to the Shell Co. together with the pilot plant data.

### I. The Gas Circulation Process

The synthesis of hydrocarbons from carbon monoxide-hydrogen mixtures with cobalt catalysts after Fischer is characterized by gasolines with poor motor behavior and Diesel oils with good motor behavior. Since the predominance of gasoline motors resulted in a demand for good gasolines, the production of synthesis products was based with this goal in mind. From 1935 onwards the experiments conducted by the author also pursued this end. Orientation experiments demonstrated that fundamentally better gasolines could be obtained by the use of iron catalysts, but their use presents us with disproportionately great difficulties. The solution of these difficulties was still to be discovered. These difficulties stem from the quite considerable heat of reaction of the hydrocarbon synthesis which necessitates an extensive division of the reaction chamber for heat removal. This is effected in the case of the cobalt catalyst, which works below 200 degrees, by a narrow bundle of tubes combined with a parallel set of plates. The iron catalyst, however, offers us greater difficulties. Temperatures of 300 degrees and higher and medium pressures must be used if it is desired to produce a good grade of gasoline with the iron catalyst. However, this is not possible with the Fischer apparatus because difficulties will arise after a little while which will make continued operation of the reaction impossible.

These difficulties consist of two deleterious reactions which in principal may also occur with the cobalt catalyst if sufficient care is not employed. However, these difficulties occur more readily and more intensely in the case of the iron catalyst. These are:

Methane formation and decomposition of carbon monoxide to soot.

The more rigorous working conditions necessary for gasoline production by means of iron catalysts promote the appearance of these detrimental reactions.

These difficulties, to which the iron catalyst is liable, furnish the reason why this metal which is so important as a catalyst in many reactions has heretofore not been employed in this synthesis.

#### The Reactions

The basic reactions of hydrocarbon formation are as follows:

1.  $\text{CO} + 2 \text{H} = \overset{|}{\text{C}}\text{H}_2 + \text{H}_2\text{O} + 41.0 \text{ calories}$  (1)
2.  $2 \text{CO} + \text{H}_2 = \overset{|}{\text{C}}\text{H}_2 + \text{CO}_2 + 50.4 \text{ calories}$

Reaction 1 occurs almost exclusively when cobalt catalyst is employed; reaction 2 predominates when iron catalyst is used.

The heat of reaction of 2 exceeds that of 1 by about 9 calories, that is, by about 20 per cent. The heat of reaction when iron is used, therefore, is appreciably greater than in the case of cobalt. Equation 2 may be considered to occur by equation 1 and the following water gas reaction:

3.  $\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2 + 9.4 \text{ calories}$

At temperatures of 300 degrees and below the last equilibrium tends almost entirely in the direction of carbon dioxide.

The detrimental reactions are as follows:

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(1) The symbol  $\overset{|}{\text{C}}\text{H}_2$  indicates that the  $\text{CH}_2$  group is meant as a part of a hydrocarbon molecule in an inserted state. By energy of formation of the group is understood the increase that the heat of formation of a straight chain paraffin of  $n$  C-atoms undergoes if it is enlarged by  $n - 1$  C atoms.

4.  $\text{CO} + 3 \text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} + 48.7 \text{ calories}$
5. or  $2 \text{CO} + 2 \text{H}_2 = \text{CH}_4 + \text{CO}_2 + 58.1 \text{ calories}$
6. and  $2 \text{CO} = \text{CO}_2 + \text{C} + 40.1 \text{ calories.}$

With rising temperature the hydrogenation velocity increases more markedly than the aggregation velocity with which the  $\text{CH}_2$  radicals are strung together in chains. Consequently,  $\text{CH}_4$  formation begins more and more to predominate with rising temperatures.

Reaction 6 which results in the formation of soot starts at temperatures upwards of 350 degrees as a result of the decomposition of primarily-formed iron carbide.

Methane formation, like soot formation, is markedly promoted by pressure. They appear whenever heat accumulation and, as a result, overheating occurs due to deficient heat removal. In this connection it must be noted that a certain amount of methane formation occurs at all temperatures where carbon monoxide reduction takes place and that its percentage proportion in the total production of the hydrocarbons drops in accordance with the drop in synthesis temperature. Hydrogenation always occurs to a limited extent whenever iron catalysts are used. Also a small amount of saturated hydrocarbons, possessing more than one C atom, are obtained with progressive increase of the degree of saturation toward the larger molecules.

When iron catalysts are used the products contain a little oxygen. The occurrence of this oxygen is attributable to the Oxo reaction which also occurs with the same catalysts at 120 degrees under pressure with olefins, CO and  $\text{H}_2$ , aldehyde groups  $-\text{CHO}$  being added to the double bond. Since the double bond, as is shown by the cases investigated, is terminal, either straight-chain aldehydes or

aldehydes with a  $\text{CH}_3$  group in alpha position will be formed, depending on whether the aldehyde group is terminal or at the next to the last C atom. Since the reaction conditions under which the synthesis takes place are not optimal for the Oxo reaction, only a partial formation of Oxo products occurs, the aldehydes being hydrogenated to alcohols for the most part. In addition, the Oxo reaction is paralleled by the acid formation by addition of CO and  $\text{H}_2\text{O}$  to olefins discovered by Reppe. Occurrence of Canizzaro acid formation from the aldehydes formed by the Oxo reaction by disproportionation into alcohols and acids is also conceivable. The ketones that occur are probably formed from the acids, the esters from the acids and alcohols or, according to Reppe, by addition of CO and alcohols. It must be noted in this connection that, under the prevailing conditions, the higher alcohols readily split off water and turn into olefins.

#### Catalyst Conditions

The Fischer Synthesis takes place at temperatures below 200 degrees and is largely conducted at ordinary pressure. At these temperatures the higher boiling products are separated out on the catalyst in a liquid state. They form a protective film on the catalyst which acts as a brake against the appearance of harmful reactions on the catalyst.

When pressure is employed the proportion of higher-boiling products in the total product grows. The film of liquid on the catalyst is thereby reinforced and a counterinfluence is created to the appearance of detrimental reactions promoted by pressure.

Higher temperatures and pressure must be used if iron catalysts are employed for gasoline. We begin to approach more closely conditions

at which soot formation can occur. The iron is obtained in a pyrophoric, i.e., highly dispersed state, in the reduction. The synthesis reaction proceeds with a tendency toward the formation of  $\text{CO}_2$ , the heat of reaction rising as much as 20 per cent as compared with the CO catalyst. The content of higher-boiling products decreases the higher the synthesis temperature selected. Consequently, the conditions for the presence of a satisfactory film of liquid on the iron catalyst are not favorable. Moreover, the reaction density, i.e., the amount of product and the production of heat in the time unit pro volume unit, is appreciably greater than in the Fischer Synthesis. Hazards are thereby considerably increased.

If the circumstance does occur in which these violent reactions take place, they will happen in the following manner: Somewhere in the catalyst there is a narrow, as it were, point-sized, highly active area where a markedly heightened reaction velocity prevails. In that spot the production of heat is extraordinary, but the heat removal, for some reason or other, is not satisfactory. The temperature rises, the reaction thereby proceeding even more violently and, consequently, the temperature becomes even higher with a progressive increase in the formation of methane and soot until these are produced exclusively. The soot acts as a heat insulator. The overheating reaches over to the neighboring catalyst sections and leads to the identical result. In spots temperatures may occur which are several hundred degrees higher than the requisite temperature. In short, the reactor must be shut down and the catalyst removed.

#### Experiences in Small-Scale Experiments

These were the conditions at the time the first fundamental

experiments were conducted on a small scale in tube reactors with a diameter of 15 mm. which were placed in an electrically heated aluminum core with automatic temperature control.

Since the reactor output was too little without pressure, a pressure of 10 atmospheres was applied. In time this was raised to 20 atmospheres and this pressure was maintained.

A  $\text{CO} : \text{H}_2 = 4 : 5$  mixture, as it occurs in water gas, was used as gas. This gas composition roughly corresponds to the ratio at which  $\text{CO}$  and  $\text{H}_2$  are consumed in the catalysis with iron. Conversion of  $\text{CO}$  with  $\text{H}_2\text{O}$  therefore permits a saving of  $\text{H}_2$ . The nitrogen content was largely 1 - 2 per cent. There was no carbon dioxide of any importance. Sulfur was removed from the gas to about 1 mg. per cbm.

To retain any iron carbonyl which might be present since it decomposes to form a highly active catalyst in the reactor which forms soot, the gas was run into a vessel containing activated charcoal. After that it was passed through a dust filter.

Highly active precipitated catalysts containing reduction-resistant oxides as well as some alkali apart from iron were used as catalysts.

It was demonstrated that at temperatures of 300 degrees and higher - such temperatures were necessary to obtain good gasolines - catalyst decomposition and soot formation occurred after a time, e.g., one day.

An attempt was made to counteract this difficulty by adding all sorts of additions to the iron. However, success was only achieved with those additions which caused a decrease in output, i.e., the



"success" consisted only of the fact that the reaction was subdued and thus the tendency toward uncontrolled temperature increase was diminished.

As a result of the arbitrary arrangement of the catalyst particles the gas does not follow a straight course in the Fischer tube, but - as was shown by experiments with aerosols in glass tubes - travels from the center to the wall and then back, heat transport occurring therefore not so much by radiation and conduction as by convection. There is naturally no regularity. It can therefore come about that the gas in the tube axis may remain for a long period of time in the middle of the tube before again traveling to the wall to give up heat. In such instances the temperature difference between center and wall is higher than usual and may become dangerously high for the iron.

The circulation conditions naturally are improved if higher flow velocities are used, gas turbulence being promoted in this manner. At the same time, however, there is increasing danger that any hot points present may be fanned and thus be heated to a dangerously high point, just as a glowing spark may be fanned to bright heat by blowing.

#### The Iron - Sinter - Catalyst

At this point an attempt was made to eliminate the difficulties by physical means, namely, in the following way. The catalyst was to be assured of good heat-conducting properties in all its parts until no more isolated highly-active catalyst particles with too little heat capacity existed. In this way any point-sized overheating which might occur would be rendered impossible by the removal of the heat.

This effect was achieved by the reduction with hydrogen at high temperatures of a catalyst prepared by precipitation. A temperature of 800 - 850 degrees was found suitable at which reduction was conducted for about 4 hours (File numbers 9131, 9261, German patent 729290; file numbers 9919, 9960, 10189, 10190, German patent 763688). The catalyst was sintered thereby and showed rounded corners and edges and the entire texture became denser. The fine structure was coarsened.

This catalyst justified expectations. It achieved the same output as the unsintered catalyst and reaction conditions became so stable that for months on end there were no difficulties in the way of operation.

Catalyst preparation was simplified by using iron powder as starting material which was obtained by the decomposition of iron carbonyl in heat. It consists of iron globules of about 2 - 5  $\mu$  diameter and under the microscope revealed a polished surface like that of drops of mercury.

This powdered iron was pasted with water containing about one per cent dissolved borax, formed into flat cakes, and then cut into cubes with a lateral length of 1 cm. It was then sintered in a cylindrical electric oven with many trays for several hours at 850 degrees in a hydrogen atmosphere.

Catalysts which were prepared in the described manner met all requirements in regard to output and stability. Addition of third substances, such as alumina, etc. did not result in any improvement but, if used to any great extent, caused a regression, and was therefore omitted thenceforth.

Also, the iron fused catalyst, as it is obtained for the ammonia synthesis by burning iron to  $\text{Fe}_2\text{O}_3$ , introduction of alumina and alkali into the melt and reduction with hydrogen, is suitable. It is recommended, however, that it be sintered before use in order to attain greater stability.

#### The Gas Circulation Process

In the case of the sintered catalyst an investigation was conducted to see if it might not be possible to use wider tubes in order to cheapen the design of the tube reactors. None of these experiments, despite partial successes, led to any satisfactory result so that a new method of heat removal was undertaken.

It consists of the following: The interval of time between heating and removal of heat, which in the tube reactor is left to change, is now controlled. The gas is conducted from the catalyst to the condenser in short regulated intervals, overheating thus being avoided with certainty.

This is accomplished by a rapid circulation between catalyst space and condenser. The sojourn in the reaction chamber is regulated to so short a space of time that possible heating of the gas cannot exceed a narrow temperature range, for example, 10 degrees. The gas then passes to the condenser and is there cooled down to a point where it is the same as at the entrance to the catalyst space (file number 10824). (Drawing on page 166)

The sketch shows the system. If heating of 10 degrees is permitted the gas must be recirculated for about 100 times until it has finished reacting or, what amounts to the same thing, 1 per cent

of the circulating gas is constantly diverted and 1 per cent of make up gas supplied in its stead. Consequently, nowhere in the system is virgin gas found, and this fact alone renders it impossible for the reactor to get out of control. Nevertheless, the capacity of the reactor is not inferior to that of a tube reactor with an equal catalyst volume.

Contact time of the gas in the reaction chamber is only about  $1/2$  of 1 second. Appreciable gas velocities are necessary therefore, and it is advantageous not to make the catalyst bed too high. In general, measures should be taken to keep the flow resistance of the gas in the catalyst arrangement as low as possible.

The catalyst space can be enlarged as much as desired at right angles to the gas flow. Its shape is extremely simple, consisting of an empty cylinder with one or more nets for the reception of the catalyst.

For reasons of economy the by-pass tube through which the gas is recycled should be constructed more narrowly than the reaction chamber.  $1/10$  of the reactor cross section was selected. In this way the gas velocity is stepped up tenfold. In its passage into the further catalyst space with its much slower flow the shape of the space must be so chosen that no hazardous eddies are created which might impair the required laminar flow through the catalyst bed. However, laminar flow is necessary, for only that guarantees that the gas will flow through the catalyst bed with uniform speed throughout the entire cross section and will not stay too long in one spot causing it to become too hot. Above all, as experience has demonstrated, change in direction of the route of the gas and widening of the cross section must not coincide or violent eddies will arise, rendering impossible a uniform flow through the whole cross section. This will lead to local gas stagnation and

heat accumulation in case the catalyst bed is situated directly under an eddying area of this kind. Such a case will be discussed later in describing the experimental reactors. To keep the gas path as simple as possible an axial blower in preference to a centrifugal should be selected in order to maintain a laminar flow in the whole circulation system if possible. In carrying out this reactor system on a large scale it is advantageous, for the sake of better control and attendance, to place the motor on the outside of the pressure chamber and to pack the shaft leading into the gas chamber by means of labyrinths. The motors in the pilot plants were placed in the pressure chamber to ensure simplicity.

Apart from the above-described "hot" circulation a "cold circulation" was also maintained on a smaller scale. In this a small portion of the recycle gas was cooled down to water temperature in order to separate the water and the higher-boiling products from the recycle gas. It was carried out in such a manner that, outside of the one per cent of the circulating gas which was supposed to leave the reactor constantly, three more per cent was conducted into the product separator and there, after cooling to the temperature of cold water, returned to the hot circulation in a heat exchange with the outgoing gas.

The conversion in the reactor can be intensified if the carbon dioxide is removed from the returning gas after cooling. If the fresh gas contains little inert gas, such as  $N_2$ ,  $CH_4$ , the gas in one stage can be converted to considerably more than 90 per cent with eventual intensification of the recycling. It would be more advantageous to add another synthesis stage only if there were an increase in the content of inert gas.

### Expenditure of Power for the Circulation

To obtain a picture of the amount of power requisite for the recirculation it is expedient to compare it with the compression power.

If a mol of a gas is compressed to 20 atmospheres in two stages, theoretical compression energy will amount to 2.8 watt hours. If the gas which is under a pressure of 20 atmospheres is subjected to a more severe compression of 0.1 atmospheres by the blower after completion of the first stage in order to compensate for the loss of pressure, energy of the order of 0.7 watt hours will be consumed. This will be increased to 1.4 watt hours if a second stage is added.

The ratio:  $\frac{\text{circulation power}}{\text{compression power}}$  amounts to about 30 per cent and dwindles to about half if the gas resistance is diminished, that is, to 15 per cent. This is the case with the multi-stage reactor which will be described later. Additional savings of power are effected by special catalyst arrangement as well as by increase of temperature span in the reaction chamber.

### The Steam Boiler

In the Fischer apparatus there is a temperature difference of a few degrees between the extensively subdivided catalyst space and the surrounding steam boiler water. In the gas circulation process the temperature difference can be considerably increased, for example by 50 degrees. In this way it is possible to keep the heat exchange surface with the circulating water relatively small and to cheapen the steam boiler considerably.

without the stability of the temperature suffering. In this way the steam temperature is lower but its temperature, as a result of the appreciably higher reaction temperature in gasoline operation, is nevertheless much higher than in the Fischer Process. This is of use when it is employed for power.

#### Operation of a Gas Circulation Reactor on a Laboratory Scale

Circulating reactors of five liters capacity were constructed with an "internal circulation" for laboratory purposes.

The gas circulation, as is shown by the attached diagram, (p 167) : accomplished by a centrifugal blower above the catalyst chamber. The blower forces the gas through an annular catalyst chamber and sucks it back through an axial hollow chamber. Regulation of the circulation speed is accomplished by a throttle valve situated in the hollow space. The motor is installed in a special chamber connected with the reaction chamber. The driving shaft passes through the narrow connecting space with so little play that the fresh gas flowing from the motor chamber into the reaction chamber suffices to prevent the circulating gases from penetrating into the motor chamber. Water cooling was installed at the constriction to protect the motor chamber from the heat of the reaction chamber. The reaction chamber is surrounded by an annular electric heater. Heat removal at this reactor size is accomplished by radiation.

The reactor was equipped with automatic temperature regulation so that it was possible to maintain the reaction temperature at the

same point for months at a time. The motors were of the alternating current type with short circuit rotors. In one case one of these motors ran for 10 months without interruption.

The reactor gases were withdrawn at the base of the reactor. This was followed by a steam-heated separator for the reception of the high-boiling products and the middle oil which would solidify at ordinary temperature. After that for the recovery of the gasoline there came a water-cooled separator after which pressure was let down. The let down gas was then dried in a chloride of lime tower and then passed through a glass separator to remove the light gasoline and the liquid gases. The glass separator was cooled with a carbon dioxide-alcohol mixture. Beyond this was situated the gas meter which measured the amount of the outgoing gas. The quantity of the feed gas could be calculated from this. Later the quantity of feed gas was directly recorded by dry gas meters constructed for pressure. The gases were frequently subjected to an additional cooling with liquid air in order to recover completely the hydrocarbons - even to the methane which was incompletely retained. The abundantly present carbon dioxide was removed beforehand in order to avoid any difficulties with it.

As for the purification of the fresh gas, it can be stated that it was received practically completely purified of sulfur (down to  $1 \text{ mg/cm}^3$ ). It was repeatedly sent through activated charcoal, caustic potash and finally through cellulose wadding. The composition, which corresponded largely to that of water gas, namely,  $\text{CO} : \text{H}_2 = 4 : 5$ , was produced by mixing the pure gases or by admixture of CO to the fresh gas of the isobutyl oil plant which was prepared in a  $\text{CO} : \text{H}_2 = 1 : 2$  ratio. The nitrogen content amounted to about 1 - 2 per cent.



Operation of the Reactors on a Commercial Scale

In large scale operation we departed from the "internal circulation" because in an exterior circulation the individual parts of the apparatus could be controlled more closely and are more readily accessible. The system, it is true, will then require more space and the steel requirements in general will be greater. On the other hand, the construction of the individual apparatus parts becomes very simple. A cylindrical vessel which is resistant to pressure with one or more built-in grates on which the catalyst can be charged suffices as a reactor. We can manage with a relatively small tube condenser for cooling purposes. This condenser must be designed for greater steam pressures as a result of the higher working temperature. An axial flow fan is recommended for maintenance of the gas circulation at a pressure difference of about 1 m. water column for technical flow reasons.

The first pilot construction was a reactor for 400 liters of catalyst. The arrangement of reactor, condenser and blower was the same as in the schematic drawing of the gas circulation process. Just as in the laboratory, the blower motor was placed in the pressure chamber for the sake of simplicity. The fresh gas was conducted into the motor housing in order to render it impossible for the circulating gas to flow into it. The catalyst had a bulk height of 80 cm. The gas flowed through the catalyst bed from top to bottom. Where the gas from the circulation returns to the reactor violent eddies might be caused. For this reason various devices have been installed in order to cause the gas to flow through the catalyst bed in a uniformly laminar manner. (See the attached drawing.p. 168)

The fresh gas was added to the circulating gas in an amount of roughly 1 per cent. The gas entered the catalyst chamber at 320 degrees and left at 330 degrees. In the subsequent condenser it was cooled

down to 323 degrees, and by admixture with the cold fresh gas it lost another 3 degrees, returning to the reaction chamber at 320 degrees. 1 per cent of the circulating gas is constantly removed after the condenser and conducted to the separators <sup>(1)</sup>. The first separator was maintained at 100 degrees with steam, the second at the temperature of cold water, and the third was cooled with ammonia to -40 to -45 degrees. However, the steam was removed from the exit gas with calcium chloride beforehand in order to avoid clogging of the low temperature condenser by formation of ice. At this point the gas was naturally not depressured before low temperature cooling as was the case in the laboratory apparatus. For the exit gas was to be conducted to a second synthesis stage or be recycled to the first reactor for the purpose of complete utilization after removal of the carbon dioxide with a high pressure water wash.

In starting, the reactor was brought to the temperature in the following manner: steam at a pressure of 20 atmospheres was conducted through the condenser - steam of higher pressure was not available - and the circulation was set in operation. The missing temperature span, up to the point where the reaction set in, was bridged by an electric heating element placed in the gas circulation. Once the reaction was in operation and the cooling regulated, the temperature remained steady and the entire system had so much inertia that it took a few hours before a slight regulation was needed. Gas conversion ran to 78 - 82 per cent and the CO<sub>2</sub> content of the exit gas 30 - 45 per cent. The product obtained per liter of catalyst space daily amounted to 0.8 kg with an hourly synthesis gas feed of 270 liters per liter of catalyst space.

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(1) In this way 1/3 of the reaction heat is lost. To avoid this in large-scale operation the fresh gas is brought to reaction temperature in the heat exchanger beforehand with the gas leaving the reactor.

Occasionally a second synthesis stage was attached to see what degree of conversion could be attained. To this end a pressure water wash was attached in order to remove  $\text{CO}_2$  and a 5 liter circulating reactor was pressed into service for want of a suitable apparatus. A suitable gas stream was branched off from the total exit gas. The total conversion attained together with this second reactor amounted to 92 - 93 per cent. The output per liter catalyst space per day was only 0.6 kg product as a result of the higher content of inert gas. This is  $\frac{3}{4}$  of the output of the first stage. The exit gas consisted largely of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$ . The CO disappeared almost entirely. 157 grams of utilizable crude product was obtained per normal cubic meter of ideal gas ( $\text{CO}$  and  $\text{H}_2$  without inert gases) passed to the reactor.

Noticeable amounts of gaseous olefins are present in the circulating gas after intense cooling and these are lost in the water wash since the solubility of these olefins in water is not inconsiderable; indeed, the larger the molecule the greater the solubility. For this reason experiments with alkalid liquor were conducted, the alkalid liquor possessing a pronounced selective solubility for carbon dioxide. It can also be regenerated by heating. The quantity of water employed in this instance is so slight that no noticeable losses of gaseous hydrocarbons can occur. The experiment was conducted for about 8 weeks without noticing a drop in the action of the liquor.

Toward the end of a two-month operating period the catalyst generally showed a distinct decline in productivity. Its surface had become coated with material which could be extracted with hot benzol or xylol, whereby it recovered its original activity. In operation at  $300^\circ$  and lower temperatures this regeneration occurred in a shorter time. On this basis the previously described recycle was incorporated. Thereby we succeeded in keeping the catalyst surface clean for a much longer time.

4 Cbm Reactor

As a further step in approaching the conditions of large-scale production, a reactor for 4 cbm catalyst was constructed. Its design, which is shown by the attached diagram, was fixed by the viewpoint of the best possible space utilization with the least gas resistance. For this reason the reactor and the catalyst bed were so arranged that the catalyst bed made up the bulk of the available inner space. The height of the catalyst bed was 80 cm., and the entire catalyst bed contained 4 m<sup>3</sup> of catalyst. It was assumed that the pressure difference existing between the upper and the lower side of the catalyst bed would cause a uniform penetration of the catalyst bed in all its parts. Here too cooling was effected by water which was supplied in a high pressure coil situated in the gas circulation. Steam was produced at a pressure of 60 atmospheres. Heat control was effected by regulation of the steam pressure. (Diagram p. 169)

In this operation provision was also made for a so-called cold circulation which, as was already explained above, consists in a small portion of the gases from the hot circulation being cooled down to the temperature of cold water in order to separate out water and high-boiling products. During the contact time in the reactor system the gas was passed about three times through the cold circulation. In this manner the accumulation of high-boiling products on the catalyst was greatly protracted.

The reactor was started by conducting 20 atm. steam into the condenser and into an electric heater. The gas circulation was set going and in a few hours the apparatus reached a temperature at which

the reaction began to set in, whereupon the normal working temperature was attained. The reactor produced about 3 tons daily. After 7 - 8 weeks the  $\text{CH}_4$  content of the exit gas rose with simultaneous falling off of the yield. A thermoelement showed abnormally high temperature.

The reactor was thereupon shut down and opened. At the lower part of the catalyst bed, more toward the gas entry side, there was discovered a pocket of soot which was encroaching more and more on the surrounding territory. At the center of the heat development the catalyst particles were found thickly encased in soot, the particles being partially decomposed with formation of scale. It was evident that the gas velocity in flowing through the catalyst bed was not uniform and was so slight at the spot in question that the foreseen temperature rise of 10 degrees was far exceeded. As a result carbon monoxide decomposition and marked methane formation set in in time. The soot which was in process of formation rendered the gas stagnation worse and the deleterious reactions began to spread to the surrounding territory. The following factors are of importance in explaining this manifestation:

The passing of the circulation pipe line into the reactor caused a tenfold increase of the flow cross section. Moreover, the gas was forced to change its direction at the same spot. The sudden retardation of velocity evidently caused the formation of violent eddies which, promoted by the space arrangement, led to a marked disturbance of the flow in the catalyst bed. An above-normal gas velocity probably prevailed in one sector, whereas the gas almost stood still in another part and became too hot as a result.

To eliminate this difficulty baffle plates were installed to curb the violent gas movements. Moreover, the catalyst bed was divided

into 3 horizontal layers separated by thin empty spaces for pressure equalization. Conditions were bettered as a result but difficulties were not entirely eliminated. After about two months of operation the beginnings of local soot formation were again noticed at approximately the former spot.

It was therefore concluded that the form of the reactor in use was unsuitable in principal and that it must be replaced by another which would take into consideration the knowledge acquired. The following design was contemplated: An upright cylinder to contain alternating layers of catalyst and cooling elements, for example, 7 one upon another, or 7 systems superimposed one upon another in series, as is shown in the attached drawing. In this way it is possible to use high and wide cylinders and to maintain a laminar flow. An irregular gas flow can only occur at the top where the recirculated gases enter. This hazard can be eliminated by installing baffle plates. (Drawing p. 170)

Another way of carrying away the reaction heat would be to cool with admixed cooling gas, thereby surrendering the use of the heat of reaction. After a temperature rise of 10 degrees about 3 per cent cooling gas would have to be supplied and thoroughly mixed with the aid of baffles. Since a temperature rise of  $10^{\circ}$  is equivalent to a gas conversion of about 1 per cent, only one per cent of the 3 per cent cooling gas need be make-up gas. The 2 per cent, which is withdrawn from the gas in process of conversion, is cooled and again mixed into the hot gas.

Cooling by cooling gas can be combined with the gas circulation, it being thus possible to omit the installation of cooling elements between the catalyst beds in multi-stage reactors. The cooling elements

can be replaced by mixing baffles. In addition another solution was contemplated. The catalyst could be used for a very short time, with drawn and regenerated, or replaced by a cheap catalyst. For this purpose reactor designs should be used which would permit charging and removal of the catalyst without interrupting operation. Attempts were made to regenerate spent catalyst containing carbide and oxide by oxidation with air and subsequent reduction (File number 11217, German patent 756609). Good results were attained insofar as the oxidation, which was carried out at 500 - 600 degrees, penetrated to the inmost core of the entire catalyst particle. Otherwise the particle decomposed at once when it was used again with attendant scale formation. An alternative procedure consists in burning the spent catalyst with pure oxygen with attendant melting in order to produce a fused catalyst, such as is employed in the ammonia synthesis. In every one of these cases the question must be investigated whether, in view of the cheapness of iron and of the moderate requirements in regard to purity necessary if the contact time in the reactor is kept short, it pays in general to regenerate spent catalyst, especially if a cheap processing of compact iron represented by the fused catalyst is contemplated.

It was not possible to undertake experiments with new reactor designs as a result of wartime restrictions. Moreover, the requirements of war, as will be explained below, directed the synthesis researches into new paths.

Special steels are not necessary as construction material for the reactors. Ordinary steel can be used as long as it possesses the tensile strength necessary for the temperatures in question. Experiments which extended over a period of years showed that neither carbonization or decarbonization of the steel occurs under these conditions.

Composition of the Products of the Gasoline Synthesis

The products obtained in the synthesis showed certain variations in their composition. The following table gives an average of the reaction conditions:

Pressure:		20 atm.
Mean temperature:		325°
CO : H <sub>2</sub>	=	4 : 5
Output per day per liter catalyst space:		0.8 kg.
Catalyst:		Sintered catalyst fr carbonyl iron with 1% of sodium borate

Composition of the Useful Products (in percentages by weight)

Gases	{ Ethylene	8 %
	{ Propane	3 %
	{ Propylene	9 %
	{ Butane	2 %
	{ Butylene	8 % (of this 65 % isobutylene)
	Gasoline to 200°	48 % (70 % olefins)
	Middle oil 200 - 325°	14 % (50 % olefins)
	Alcohols (in the product water) <sup>(1)</sup>	7 %
	Product over 325°	1 - 2 %
		<hr/> 100 %

(1) About 10 % by weight of oxygen-containing products were found in the product water. In addition there was about 1 % by weight of free acids. The acid-free product had the following composition:

acetaldehyde	10 % by weight
acetone	5 % " "
ethanol	55 % " "
propanol	20 % " "
butanol and higher alcohols	10 % " "

The presence of methanol could not be determined. Its absence indicates that the oxygen-containing compounds are formed by the Oxo reaction.



In addition there is a gasification (methane and ethane) to the extent of 18 - 20 per cent (Total product counted as 100).

#### Description of the Products

The considerable yield of markedly unsaturated gases and the not inconsiderable amount of iso-butylene is noteworthy. Polymerized gasoline can be produced from the olefins, as well as isooctane from the iso-butylene. The butane can be used for alkylation.

45 per cent of the gasoline constituents boil up to 100 degrees. In the crude state it possesses an octane number of 70 - 75 and still contains 2 - 4 per cent of oxygen in the form of alcohols, acids, esters, aldehydes and ketones. It needs refining before it can be used in a motor. This is accomplished by passing the gasoline in the vapor phase over active alumina and, in addition, passed over alumina <sup>(1)</sup> mixed with  $\text{Cr}_2\text{O}_3$  and ZnO at 380 - 400 degrees <sup>(2)</sup> in order to improve the odor. The oxygen in the form of  $\text{H}_2\text{O}$ , CO and  $\text{CO}_2$  can be removed leaving an insignificant remainder of less than 1/2 per cent. The loss of weight of the gasoline amounts to 5 - 6 per cent.

By this treatment the octane number (Research) rose to 84 - 86 and the octane number (Motor) to 75 - 78. Subsequent refining with granosil at 200 degrees <sup>(3)</sup> and admixture with a stabilizer <sup>(4)</sup> produced a satisfactory storage-stability which was confirmed by a two-year period of storage during which time it stood up to all tests.

- (1) Active alumina was impregnated with 10 per cent  $\text{Cr}_2\text{O}_3$  and 3 per cent ZnO in the form of their nitrate solutions and the nitrates thermally decomposed.
- (2) File number 11075 (German patent 735276)  
1/4 kg product were passed through hourly per 1 catalyst space (both catalyst charges taken into account).
- (3) 1/8 kg of product were passed hourly per liter of granosil.
- (4) Naphtol.

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.

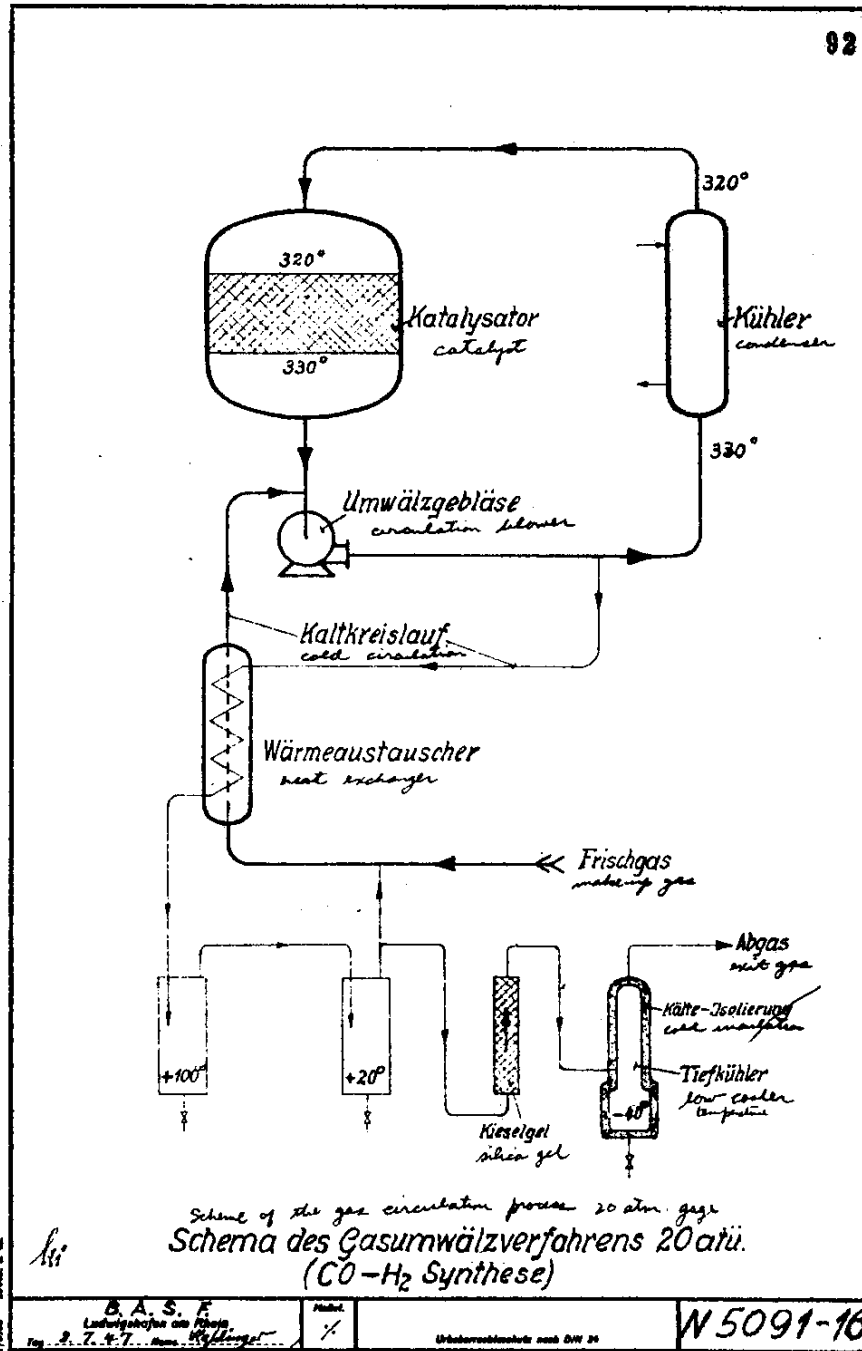
## II. The Foam Process

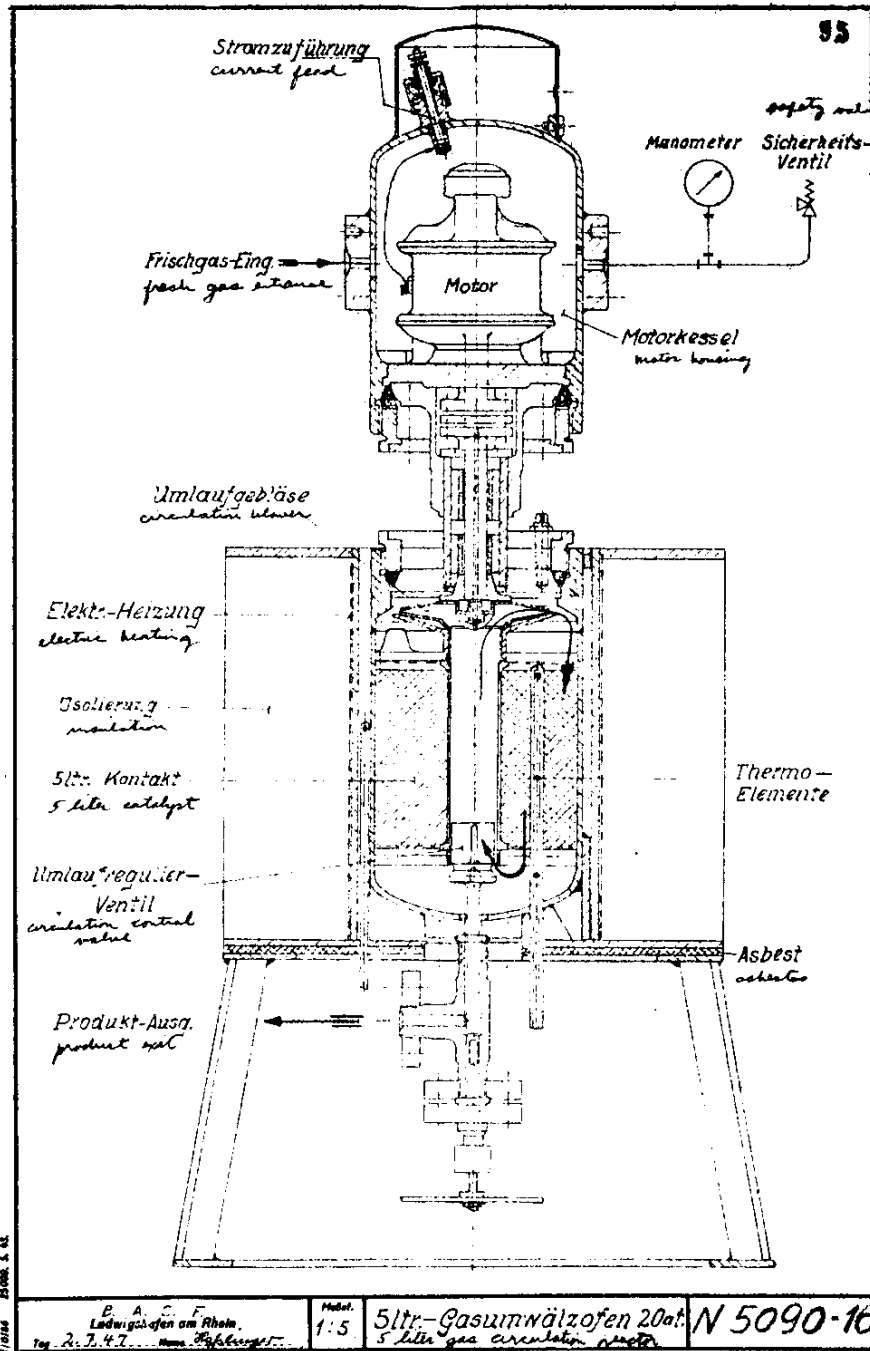
After the outbreak of the war a shortage of soaps and detergents was soon felt which was caused by the falling off of imports of fats and vegetable oils.

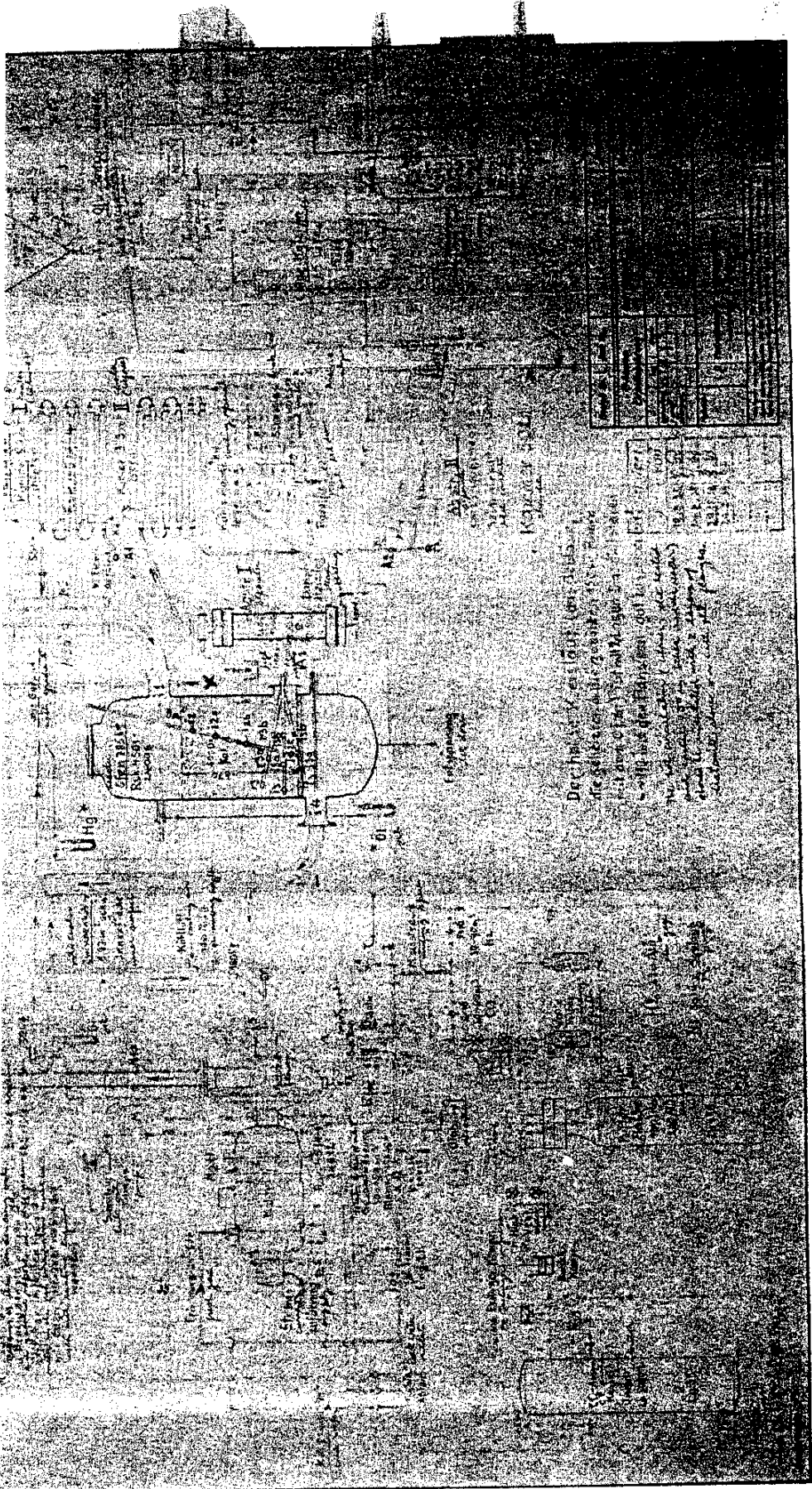
To make up this shortage alcohol sulfonates were produced in Leuna which possessed excellent detergent action and insensitivity toward lime. The raw material was middle oil of the Fischer Synthesis which was completely saturated by hydrogenation. It was subjected to sulfochlorination in the presence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







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4 Cbm REACTOR. Drawing referenced on page 106.

