

The Oil Circulation Process1. General Comments on the Oil Circulation Process

In the synthesis of hydrocarbons from carbon monoxide and hydrogen, large quantities of heat are evolved which must be conducted away from reaction chamber in a suitable manner.

This problem had heretofore been technically solved in the Fischer-Tropsch process by dividing the catalyst into relatively thin beds and by charging it into narrow tubes and pockets. The reaction heat is thereby indirectly conducted away by water under pressure.

The use of iron instead of cobalt catalysts poses greater problems of heat removal because iron catalysts only react at temperatures higher than those of cobalt catalysts, the danger of spontaneous carbon monoxide decomposition consequently becoming appreciably greater. In addition, the known iron catalysts react principally at elevated pressures thus further promoting formation of methane and carbon monoxide decomposition.

These considerations led to the development of the oil circulation process. This process (discovered by F. Duftschmidt, E. Linckh and F. Winkler) and developed by the Fritz Winkler experimental team since 1935 at the I. G. Farbenindustrie at Oppau is differentiated from the Fischer-Tropsch process principally by the fact that the quantities of heat evolved in this markedly exothermic reaction are directly taken up and removed by a liquid medium located in the reaction chamber.

It should be mentioned at this point that a second process was later developed by the I. G. Farbenindustrie at Ludwigshafen by Dr. Michael in which work was also done in the liquid phase with circulation of oil. This is the so-called foam process, which is most clearly

differentiated from the oil circulation process dealt with here, by the fact that finely divided catalyst suspended in a circulating oil is employed in the foam process. This process was developed in Ludwigshafen since about 1940. These two processes embody differing viewpoints in still another respect. The Oppau oil circulation process employs oil evaporation for the removal of the reaction heat and is therefore characterized as a synthesis in a boiling liquid. The Ludwigshafen foam process, however, substantially features a non-evaporating liquid medium, thereby representing a further development of the principle already proposed in 1928 by the I. G. Farbenindustrie A. G. (M. Pier) of conducting the synthesis in a high-boiling, non-evaporating liquid medium.

The I. G. Farbenindustrie interests, and in particular the BASF works, immediately obtained the basic rights and also acquired technical leadership in this field by the development of the two processes.

The present report deals only with the oil circulation process since the foam process has received separate treatment.

The oil circulation process operates with a fixed granular catalyst. As a result of the immediate removal of the heat it is possible to do without division of the catalyst into thin beds. The synthesis reactor consequently acquired a much simpler shape without the necessity of any built-in installations. In the indirect heat removal process the quantities of heat conducted through the wall of the catalyst chamber per unit of time are quite limited. However, this limitation is largely done away with in the direct heat removal method of the oil circulation process. As a result a greater capacity can be achieved in the oil circulation process with regard to time and reactor space. Also, power consumption

in operating the oil circulation is slight and possesses hardly any importance in determining production costs.

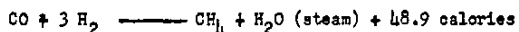
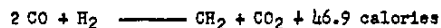
In 1936 and 1937 the process was developed to a semi-commercial stage (200 liter reactor), and run under high pressure (100 atm. gage). In 1938 it was developed into a medium pressure process (15-20 atm. gage) and worked out as a two-stage process similar to the Fischer synthesis. The first stage of the medium pressure process was tested in a 1.5 m³ reactor for 5 months with an output of 9 ton/month. The second stage was successfully tried for a period of one month in a makeshift 0.2 m³ reactor (unfortunately a complete two-stage pilot plant was unavailable).

The process was thus proved to be practical and safe. The robustness of the catalysts is characteristically indicated by an experiment with the afore-mentioned 1.5 m³ reactor in which the catalysts were used without harm after the reactor had been in disuse for two years, the spent catalyst lying in the oil residue of the reactor during this time.

Past experimental results, however, justified plans of a reactor height of about 18 meters for large-scale units. It was also planned to conduct the synthesis in one stage.

2. The Principle of Heat Removal by Means of Oil

The quantity of heat evolved during the conversion is computed according to equations



to roughly 4000 calories per kilogram of liquid hydrocarbon produced if it is assumed that the conversion proceeds to 80 per cent according to the first equation with 20 per cent methane formation, i.e., if about 165-170

grams of liquid hydrocarbons are formed, including liquifiable gas, for every 1 m³ of converted CO - H₂, which is the case in the procedure dealt with here.

The principle of working in the liquid phase consists in collecting this evolved heat by the oil itself and removing it. This can be accomplished in various ways; by simply conducting away the heat in the heated oil in the form of sensible heat, or by removing it from the reaction chamber by evaporation of the oil in the form of latent heat of evaporation.

In the first case the liquid medium consists of oil which is not vaporizable under the reaction conditions; in the second case it consists of oil containing vaporizable constituents under the conditions of the reaction, or containing an oil fraction which is vaporizable under these conditions.

If the heat is removed only in the form of sensible heat, a rise in temperature within the reaction chamber will be the precondition for removal of the reaction heat.

The quantity of oil to be put into circulation per kilogram of made products is calculated simply from the equation:

$$\Delta t (G_g h + G_o \vartheta + G_w \cdot W) = 4000$$

if Δt signifies the temperature rise in the reaction chamber

G ... the final gas quantity necessary for each 1 kg. product

G_g ... the specific heat of the final gas

G_o ... the specific heat of the oil

W ... the oil to be recirculated for each 1 kg. product

W ... the quantity of heat formed for each 1 kg. product

G_w ... the specific heat of the steam.

If the quantity of final gas $G = 2.7 \text{ m}^3$ and the quantity of the made water $W = 0.23 \text{ kgs.}$ for 1 kg. of product at 90 per cent conversion are included in the above equations, the amounts of oil to be circulated are calculated as follows:

t	Q = kg Oil/kg product
= 5°	1600
= 10°	800
= 25°	320
= 50°	156

The quantities of circulating oil are appreciably higher in this case as compared to the second case since a part of the circulating oil is evaporated.

If the quantity of circulating oil is divided into an evaporating portion Q_1 and a non-evaporating portion Q_2 , we get the following equation:

$$\Delta t (C_g \cdot G + C_w \cdot W + C_p \cdot Q) + \lambda \cdot Q_1 = 4000$$

The quantities of circulating oil can be calculated on the basis of this equation, as was done, for example, in the table for various Δt and various portions of vaporizable oil.

Vaporizable portion of the circulation oil in %	Oil circulation quantity in kg/kg product at a temperature difference Δt					
	5°	10°	25°	50°	60°	80°
10	532	400	230	132	112	87
25	266	280	160	105	92	76
50	145	135	122	79	72	62
75	100	93	80	63	58	51

The oil circulation process is carried out by the following procedures:

(Diagrams I and II on page 133 c)

In the procedure according to Diagram I the circulating oil is cooled within temperature range $t_2 - t_1$ before being returned to the reactor.

This procedure approaches that of the above-mentioned procedure in that the oil medium contains relatively few vaporizable constituents. The extent to which this precondition is carried out depends on the temperature range t and the quantity of the final gas. It is evident that the boiling curve of the circulating oil cannot be freely chosen for even if relatively high-boiling circulating oils are employed, the oil will acquire a specific composition by condensation in apparatus K, depending on the working procedure.

The procedure according to Diagram II, on the other hand, permits cooling in the cooling device K to the extent that hydrocarbons are condensed in a wider boiling range, depending on the selection of temperature t_0 . A lower limit for t_0 is substantially conditioned by the fact that high-boiling paraffins are formed during the synthesis which naturally enrich the circulating oil. It is expedient, in general, not to exceed a temperature of 80 - 100 degrees in order to avoid obstructions in the tube of the cooling device of the steam producer caused by solidifying of these paraffins. It is also advantageous to cool below the strictly necessary temperature for low-boiling hydrocarbons would otherwise condense which evaporate on being reheated to t_1 before entering the reaction chamber. The heat exchanger, which is a section of the cooling device and is used to reheat the circulating oil, would then be unnecessarily large. The Oppau experiments which were conducted in order to develop the oil circulation process were always carried out according to the procedure shown by Diagram II. However, it was planned to revert to Procedure I for new plant units. In this connection, provision was to be made for the injection of lighter-boiling fractions, which are removed from the final gas in the form of condensates, into a supplementary circulation in the reaction chamber, as is shown by Diagram III:

(Diagram III on page 134)

3. Catalysts

After the granular fixed-bed catalyst was proved to be practicable, the oil circulation process was developed on this basis since this procedure shows considerable simplicity and distinction as compared with the catalyst suspended in oil.

Certain minimum requirements had to be met by the catalyst with regard to firmness and durability when the oil circulation procedure was adopted.

These requirements were fulfilled by the iron catalysts developed by Dr. E. Linckh, which were produced by melting iron with promoters in a current of oxygen into ammonia synthesis catalysts in the form of oxides (Fe_3O_4).

The fused cakes thus obtained are broken up into 6-12 mm. pieces and the catalyst is reduced with hydrogen at 450-500 degrees for the medium pressure synthesis, and up to 650 degrees for the high pressure synthesis. Deficient reduction of the pieces is to be avoided because a bursting of the nucleus, caused by a splitting off of carbon might occur. The catalysts are substantially composed of iron, with slight additions of silicon, alkali, manganese, and titanium oxide. The exact composition of catalyst No. 997, which is most often used as a standard in experimental work, is given in Part I, page 2 of this report.

The catalyst reduced in a reduction furnace installation apart from the synthesis reactor is charged into the reactor after cooling in the presence of carbon dioxide, or, particularly if the catalyst is reduced at temperatures below 600 degrees and is very pyrophoric, it is discharged from the reduction vessel into oil in the absence of air and is charged into the reactor.

The following figures are assumed in the plans for a catalyst reduction installation:

Reduction temperature	470 - 500° C.
Hydrogen current	200 - 300 liter per hour kilogram catalyst
Bulk density of the oxidic catalyst	2.5 kg./liter
Reduction time	6 - 8 days

The hydrogen is recirculated in the reduction installation. The hot hydrogen issuing from the reduction vessels is first conducted into a heat exchanger in a countercurrent to the cold hydrogen which is recycled to the reduction vessels. After passing out of the heat exchanger the hydrogen is cooled as far as possible and then, after separation from the condensed liquid, passed through a silica gel dryer for complete drying before being returned to the reduction vessels.

Moreover, the given conditions are dependent on the type of catalyst and its ease of reduction. The reduction temperature can be raised to 650 degrees for conducting the synthesis under high pressure. A substantial shortening of the reduction time is thereby attained.

4. Procedure and Equipment

After granular, fixed-bed catalysts in the reactor proved to be feasible, the oil circulation process was developed on this basis. It offers a substantial simplification in contradistinction to the catalyst suspended in oil.

An upright high pressure tube of 200 or 500 mm. internal diameter and a height of 6 meters served as the synthesis reactor. Apart from a central tube for the thermo elements, the reactor had no built-in stirrer. The empty reactor chamber was charged with catalyst. The

synthesis gas runs through the reactor (S) from bottom to top along with the circulating oil in a direct current. The hot oil and gas leaving the reactor surrenders its heat to the cold circulating oil in a heat exchanger (R). After passing out of the heat exchanger the oil is again cooled in a condenser or a steam generator (K1) to about 120 degrees. At this temperature the final gas is separated from the oil in a separator (A1). The made oil excess and if necessary the reaction water is drawn off from the separator (R). The oil is again conducted to the reactor (S) via the heat exchanger (R) and a supplementary pre-heater (VW) by a circulation pump, the oil in the separator in the meantime being maintained at a specific level. The supplementary pre-heater is merely used for starting. The final gas is cooled to approximate external temperature in another cooler (K2), gasoline as well as alcohol-containing water being separated in another separator. If the operation is carried out in two stages, then the final gas is conducted to the second stage which is coordinated with the first stage. In the second stage the final gas is either depressured and conducted to the activated charcoal plant (AK) or washed with oil without being depressured so that the light gasoline and $C_3 - C_4$ hydrocarbons still retained in it may be recovered.

(Diagrams on pages 135 and 136)

The fresh gas is also pre-heated in a suitable manner and admitted to the reactor from below.

5. The Oil Circulation

The oil produced in the synthesis itself is employed as circulating oil. In this procedure, as distinct from similar procedures, the use of high-boiling fractions, which remain almost completely liquid under the

reaction conditions, is deliberately given up. It is desirable for higher performance that vaporizable constituents be present in the circulating oil under the reaction conditions if possible. The boiling of the liquid in the synthesis reactor creates the conditions, on the one hand, for good contact of the synthesis gas with the catalyst, thus achieving a higher capacity, and, on the other hand, for favorable heat removal and temperature regulation.

The boiling range of the circulating oil may be regulated as desired by the condensation temperature of the separator (A) placed in the oil circulation. Two examples are cited as typical for the boiling range of the circulating oil:

Boiling under normal pressure at	Experiment at 100 atm. gage	Experiment at 25 atm. gage
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(Table on page 137)

The reaction can safely be kept at the desired degree of conversion and at the desired temperature by regulation of the quantity of recirculated oil.

The quantity of circulating oil is increased with the charge rate to the reactor. In the case of the plant units hitherto operated the quantity of circulating oil was adjusted for 70 - 80 liters per hour per kilogram of made product in the same period. In the case of larger units, where heat losses are of less importance, the quantity of circulating oil could probably be adjusted to a higher level. Future plans call for a quantity of circulating oil of 120 - 150 kg./hour per kg. of product.

6. Evaluation of the Experimental Results of the Plans for a Large Scale Reactor

(Graph on page 138)

It is evident from the two curves representing the temperature course and the distribution of the conversion in the experimental reactor that the procedure is especially more favorable for larger reactor units. It is clear that the temperature t_1 in the lower part of the 6 meter long experimental reactor was not very much in excess of the temperature at the start of the reaction, and that conversion in the lower part of the reactor therefore sets in very slowly, increasing by degrees with the gradual rise in temperature as a result of the slight conversion. Thus, the lower sector of the reactor was poorly utilized. Just as soon as temperature t_2 (sic) is reached, conversion also attains a corresponding increase. After temperature t_y near the upper end of the catalyst bed is passed, the conversion undergoes a similar rise with rapidly increasing temperature. This means that the proportion of vaporizable fractions present in the range of temperature is too small to conduct away satisfactorily the heat by evaporation. Since the boiling point distribution of the circulating oil is not subject to any arbitrary influencing, the process has therefore been expanded to this end (x) so that vaporizable "cool oil" is fed to t_y in order to check this undesirable temperature rise.

An experiment with a cold feed of this kind conducted in a 200 mm. reactor achieved the desired success. Since another oil pump was unavailable, this operation could only be carried out by a makeshift branching off from the main oil circulation with valve regulation. It was possible by

(x) English patent 515352, French patent 855515.

careful attention to arrest the undesired temperature rise in the upper end of the reactor to the desired extent. However, only an approximate 55 per cent conversion of the gas was attained because of the low (6 meter) height of the experimental reactor.

In planning a large-scale reactor unit the improvement of the process outlined in Diagram III, page 5 is offered, the temperature curve being shown in the following chart:

(Chart on page 139)

The temperature range Δt , which was previously maintained at 50 degrees, and often at 100 degrees, in order to attain a 50 per cent conversion in the 6 meter reactor, can be reduced to 25 degrees to insure the same degree of conversion with a reactor height of 9 meters. With reactor height of 18 meters it will be possible to carry out the entire 50 per cent conversion in one stage. It cannot be decided here whether the one-stage or the two-stage process is economically more advantageous for large scale production. The procedure which was conducted in the pilot plant up to 75 per cent conversion only produced a specific yield of 140-150 grams in the second stage as compared with a yield of 165-170 grams in the first stage. This difference in yield should have decreased as a result of the equalization of the reactor temperature and the lower peak temperature at the reactor exit which could be accomplished because of the better control of the process possible in a large-scale reactor. An increase in yield can therefore be counted on in large-scale reactor. However, in the following sections only those yield figures are given which were actually obtained in past experiments.

7. Synthesis Gas

In general a CO:H₂ ratio of 55:45 or 1:0.8 is necessary for the synthesis. Gases rich in hydrogen can also be used; however, they cause a shift in the composition of the product with proportionate increase of the hydrocarbons boiling in the gasoline boiling range and the C₃ and C₄ hydrocarbons.

The following table assembles the results of comparative experiments in which the CO:H₂ ratio was modified, conditions in other respects being the same. These comparative experiments were carried out in pressures of 15 to 20 atm. gage.

Expt. No.	CO:H ₂ ratio in fresh gas	CO:H ₂ ratio in conver- sion	CO:H ₂ ratio in end gas	C ₃ and C ₄ hydrocar- bons of total product	Oils over 180° of total product
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(Table on page 140)

The table shows the decrease in C₃ and C₄ formation with rising CO content of the synthesis gas and the simultaneous increase in the formation of high-boiling products.

The gas rich in CO which is necessary for the synthesis can be directly produced by oxygen gasification in Winkler generators. The desired CO:H₂ ratio can also be attained in the customary cyclic water gas production from coke, if a part of the steam is replaced by CO₂. A gasification medium consisting of 27 per cent by volume of carbon dioxide and 73 per cent by volume of steam is needed to attain a CO:H₂ ratio of 55:45 or of 1:0.82 according to experiments with Pintsch-Drehrost (rotary grate) generators. The water gas will then be composed of 12.7 per cent CO₂,

47.7 per cent CO, 39.0 per cent H₂ and 0.2 per cent CH₄. The synthesis itself produces the CO₂ necessary for gasification if the residual gas put through a CO₂ scrubber. This quantity of CO₂ is sufficient to produce the necessary quantity of synthesis gas rich in CO.

A final gas good for heating purposes is simultaneously obtained with the CO₂ scrubbing of the residual gas of the synthesis.

A gas rich in CO can also be produced from natural gas by using the carbon dioxide resulting from the synthesis process. It should be mentioned at this point that most of our experiments were conducted with synthesis gas poor in inert gases (2% N₂). However, we conducted a number of experiments with gases containing a higher proportion of inert gas (13%).

In the following example the composition of the final gases of the two-stage procedure are given with a synthesis gas free of inert gas.

	Fresh gas	Final gas - First stage	Final gas - second
Quantity m ³			

(Table on page I/41)

The composition of gases when gases containing inert gases are used can easily be calculated from these figures if it is assumed that inert constituents take no part in the conversion.

The synthesis gas must be purified from inorganic and organic sulfur. According to our experience the catalysts are not as sensitive as in the Fischer process. Fine purification to a sulfur content of 4-5 mg/m² should suffice.

8. Pressure

The medium pressure synthesis is conducted under 15-25 atm. gage. The results obtained at this high pressure have been cited in the individual sections of this report in comparison with the results of the medium pressure synthesis. Apart from the high capacity attainable, however, these results have little commercial significance since the compression costs cannot be compensated for by increased yields or by improvement of the properties of the product.

Pressures up to 200 atm. gage are briefly referred to at the conclusion of the report. These were used, however, in the formation of oxygen-containing products.

9. Performance

The medium pressure synthesis is capable of a continuous hourly output of 20-25 grams total product per liter catalyst.

The hourly output of the high pressure process was stepped up to 160 grams total product per liter.

10. Temperature

The temperature in the reactor rises from the bottom to the top. It is conditioned by the oil circulation. A temperature rise of 50 degrees C. was established in general in the experiments conducted here so that the following temperatures were recorded with maximum reactor charge rate:

	Reactor entrance	Reactor exit
First stage		

(Table on page 142)

However, as was mentioned before, an extensive temperature equalization is possible by using a more advantageous procedure, a temperature difference of 15 to 20 degrees C. being possible with a reactor unit temperature of 250-255 degrees C. in larger reactor units.

11. Yield and Conversion

145 - 150 grams of total product per Nm³ CO - H₂ were obtained on medium pressure reactors with a 90 per cent conversion in two stages.

This total product consisted of

- 13 - 15% liquifiable gaseous hydrocarbons
- 32 - 35% gasoline fraction, boiling range to 175° C.
- 18 - 20% middle oil fraction, boiling range to 175 - 320° C.
- 10 - 12% soft paraffin fraction, boiling range 320 - 400° C.
- 16 - 18% hard paraffin
- 5 - 6% water-soluble alcohols

The following page shows a chart giving conversions for two-stage conversion. The results are converted to an oxygen-free synthesis gas (ideal gas).

(Chart on page 143)

12. Properties of the Product

The products have a marked olefinic character. The olefin content drops with increasing molecular size, as is shown by the table:

(Table at top of page 144)

The oils also contain oxygen-containing constituents (alcohols and esters). The oxygen content of the low-boiling gasoline fractions up to 100 degrees runs to about 1.5 - 2.0 per cent. However, it can exceed this amount if the water-soluble alcohols produced are separated out in a

concentrated form with the gasoline fraction, for the gasoline partially dissolves these water-soluble alcohols (C_2H_5-OH). However, these water-soluble alcohols can be removed from the gasoline by treatment with water. The oxygen content declines with rising boiling point to 0.5 per cent in the fractions ranging from 200 - 400 degrees C.

The primary gasoline has an octane number of 68 (research) which is increased to 85 by addition of 0.1 per cent lead. After hydrogenation the octane number suffers a considerable drop.

The middle oil fraction yields Diesel oil directly. The cetane number is 75 - 78. A middle oil test gave the following values:

Specific weight at 15° C.	0.809
Flash point	66° C.
Pour point	-9° C.
Viscosity at 20° C.	1.70 E°
Cetane number	755 (sic)
Conradson test	0.3 %

The hard paraffin has a melting point in excess of 90° C. and can be used for all practical purposes (emulsifying wax and the like). The hydrocarbon products are branched to a certain extent.

(Tables on pages 145 and 146)

13. Results of Experiments with Synthesis Gases Having an Appreciable Excess of Hydrogen

The influence of an appreciable excess of hydrogen on the carbon monoxide has already been mentioned in the previous section on "Synthesis gas". The results of the experiments will be dealt with here in greater detail. Circulating depressured gases of the methanol or isobutyl alcohol

synthesis were used as the synthesis gas.

(Table follows on page 147)

The carbon monoxide is extensively converted when these hydrogen-rich gases are used; however, the greater part of the hydrogen remains in the final gas.

The working up of such hydrogen-rich gases frequently obtained as residual gases of other syntheses under pressure might very well have considerable commercial interest although the yields with respect to fresh gas would be relatively low. However, since only the CO portion of the H_2 is withdrawn from the synthesis gas, the CH_4 content of the final gas being increased, commercial application of the synthesis can be assured in many instances if the residual gas is worked up in a decomposition plant and again made available for other syntheses (e.g., ammonia synthesis). The yields in the above table are given as specific yields per m^3 of converted $CO-H_2$, in order to facilitate comparative evaluation.

It can be seen that water-soluble alcohols, consisting of 10 to 20 per cent ethyl alcohol, are principally formed under high pressures. In addition, the formation of C_3 and C_4 hydrocarbons is very great.

The formation of ethylene is not included in the yields given above although ethylene formation in individual experiments has reached a point where it can no longer be neglected.

In the following the example of Experiment 35a is subject to more intense consideration:

Procedure according to Experiment 35a

In the large-scale experiment conducted under a working pressure

of 15 atm. gage (one-stage conversion), 1000 cbm. of isobutyl recycle gas, containing 200 m³ of CO and 640 m³ of H₂, resulted in conversion of 130 m³ of CO and 165 m³ of H₂, with 770 m³ of residual gas containing 70 m³ of CO and 475 m³ of H₂.

The composition was

12.5 % CO₂

1.9 % C_nH_{2n}

9.1 % CO

61.4 % H₂

9.0 % C_nH_{2n+2}

6.1 % N₂

From this 56.1 kgs. of product were obtained, composed of

7.8 % ethylene

12.9 % propylene

6.8 % butylene

19.5 % propane and butane

15.0 % light gasoline

30.0 % gasoline and oil

5.6 % ethanol

2.4 % methanol

The synthesis was carried out in one stage under medium pressure of 15 atm. gage in such a manner that for 5000 m³/hour of isobutyl recycle gas a reactor unit with 12 m³ of catalyst space was used.

Catalyst life was estimated at one year. Not the slightest evidence of catalyst fatigue was observed in an experimental period lasting one and one-half months, using hydrogen-rich synthesis gas under a pressure of 20 atm. gage.

If $5000 \text{ m}^3/\text{hour} = 43.2 \text{ million m}^3/\text{year}$ of isobutyl recycle gas is passed through a synthesis installation of this kind, then $3840 \text{ m}^3/\text{h} = 33.15 \text{ million m}^3/\text{year}$ of residual gas will again be available after the synthesis and removal of the products in an activated charcoal plant. This can again be worked up for the NH_3 synthesis according to the decomposition process of Dr. Sachse.

From the conversion of the $1475 \text{ m}^3/\text{hour CO-H}_2$ withdrawn from the isobutyl recycle gas, 2400 tons/year of the above-mentioned composition are obtained.

Procedure according to Experiment 25c

Experiment 25c can be treated similarly to the example of Experiment 25a. A working pressure of 150 atm. gage was used, the other working conditions remaining the same. If 1000 m^3 gas containing $922 \text{ m}^3 \text{CO-H}_2$ are converted according to the oil circulation process, 777 m^3 of residual gas are obtained.

The analysis follows:

12.9 % CO_2

0.9 % C_nH_{2n}

6.2 % CO

72.3 % H_2

4.7 % $\text{C}_n\text{H}_{2n+2}$

3.0 % N_2

A product of 43.7 kg. was obtained, consisting of

17.70 kg. water-soluble alcohols (of which 12 kg. are ethyl alcohol)

11.05 kg. C_3 and C_4 hydrocarbons (about 40 per cent olefinic)

14.95 kg. oxygen-containing oils

Moreover 0.6 per cent by volume, i.e., 5.8 kg. of ethylene are

contained in the residual gas which is not counted in the yield.

383 tons of product per year would be obtained if 1000 m³ of synthesis recycle gas were worked up hourly. 777 m³ of residual gas of the above-mentioned composition would be delivered hourly to the synthesis decomposition plant for working up.

14. Experiments in the Production of Oxygen-Containing Products

The experiments described in the above section lead to the formation of oxygen-containing products.

When the researches of Ruhrchemie on the Oxo reaction became known at the start of the war, the question was universally raised whether such products could not also be obtained in the CO - H₂ synthesis in one operation.

In 1940 we received the assignment from Dr. Müller-Conradi of investigating the preparation of higher-molecular weight alcohols by the oil circulation process.

At the same time investigations were initiated in the Leuna Works which lead to the discovery of the Synol synthesis. The actual circumstance that led to the Synol synthesis was the fact that a method of treatment of fused iron catalysts was discovered which permitted lowering of the synthesis temperature to 195-215 degrees. In this connection it was shown that the low synthesis temperature was the decisive factor in obtaining higher-molecular weight alcohols.

The experiments which we were conducting at Oppau at that time assumed that elevated pressure and an excess of hydrogen in the synthesis gas was the most important factor in guiding the synthesis toward the formation of oxygen-containing products.

The experiments dealt with in the preceding section confirm the conception to the extent that increasing yields of water-soluble alcohol are obtained with hydrogen-rich synthesis gas and rising pressure. Both factors, however, forced the synthesis into the formation of low-molecular products.

We have already reported in the previous section that we obtained products relatively poor in oxygen when synthesis gas rich in carbon monoxide was used. These were the conditions under which we initially developed the hydrocarbon synthesis according to the oil circulation process at 1 atm. gage in 1935. We had already turned to experimentation with the oil circulation process at 200 atm. gage in a pilot plant at Leuna. The result of this pressure rise to 200 atm. gage was only a further shifting of the products toward the short chain lengths and an increase in methane formation. Besides, a very rapid catalyst fatigue was observed at high pressure. In 1936 (illegible) we made the observation that we actually arrived at reduced oxygen-containing compounds with gas rich in carbon monoxide under high pressure if we reduced the fused iron catalysts at 450 - 500 degrees C. instead of the previous 650 degrees for the high pressure procedure, as was already done in the medium pressure synthesis.

The following considerations were adopted in our experiments in the production of higher-molecular alcohols:

1. The reduction of the fused iron catalysts was to occur at the lowest possible temperature.
2. Conversion in the synthesis should be divided into more than two stages.
3. The catalyst space velocity should be kept as low as possible.
4. Overheating in the oil circulation must be avoided to protect any higher-molecular weight alcohols from decomposition.

All of these four considerations attempt to lower the synthesis temperature as much as possible in order to counteract the tendency toward formation of lower-molecular weight compounds as the result of high pressure.

The application of these conditions had the desired effect, to some extent, as is shown by the appended experimental data. It is beyond doubt, however, that our results have been surpassed by the Leuna Synol process and our experiments outstripped. The progress of the Leuna process is based on the fact that, with catalysts which can be used at 200 degrees C. and middle pressure, the molecule-reducing use of high pressure can be avoided, since the formation of oxygen-containing compounds can also be attained at these low synthesis temperatures without excessive increase in pressure.

The application of this Leuna know-how to the oil circulation process was obvious. An experiment was also conducted in which our fused iron catalysts were reduced with a great excess of hydrogen according to the experience of the Synol synthesis. However, it was found out that an excess of hydrogen is not effective in catalyst reduction if the particle size exceeds 2-3 mm. In any case an experiment conducted with a particle size of 8 mm. did not have the desired effect of lowering the synthesis temperature to about 200 degrees. It was not possible to conduct further experiments because of the progress of the war.

In this connection we present the results of one of the many experiments in the preparation of higher-molecular weight alcohols according to the oil circulation process. In this experiment the same catalyst was used that was employed in most of the earlier experiments in the production of hydrocarbons.

A report on experiments with other fused iron catalysts which according to the results of the investigators, is especially favorable for the formation of oxygen-containing products, is unnecessary since the results of the experiment are basically the same.

Procedure according to Experiment 25

A specific yield of 195 grams of product per 1 Nm³ of conversion product was obtained, using synthesis gas (CO:H₂ = 1.16), an hourly output of 40 grams of product/1 catalyst and a degree of conversion of 2 per cent of CO - H₂ in the first stage. Temperature 236 - 260 degree pressure 180 atm. gage. The product consisted of

- 24.0 % C₃ and C₄ hydrocarbons
- 21.6 % oil boiling to 150 degrees
- 12.7 % oil boiling at 150-250 degrees
- 9.0 % oil boiling above 250 degrees
- 32.7 % water-soluble oxygen compounds (C₂H₅OH).

A detailed investigation conducted by Dr. Leithe led to the following approximate composition of the total product:

- 8.5 % methanol
- 21.0 % ethanol
- 10.0 % propanol
- 6.5 % alcohols C₁ - C₁₂
- 2.5 % alcohols C₁₂ - C₂₀
- 11.5 % water-soluble fatty acids
- 5.0 % fatty acids C₅ - C₁₁
- 1.5 % fatty acids C₁₂ - C₂₀
- 26.5 % hydrocarbons to 200 degrees

3.5 % hydrocarbons 200 - 300 degrees)
 3.5 % hydrocarbons over 300 degrees) about half olefinic

List of Patents for the Oil Circulation Process

Fused iron catalysts: German patent 708512, November 14, 1935)
 French patent 812290) E. Linckh
 English patent 465668) F. Winkler

Oil circulation process: German patent applied Nov. 18, 1935)
 French patent 812598) E. Duftschmid
 English patent 468434) E. Linckh
 American patent 2159077) F. Winkler
 French patent 854617) " "
 English patent 516403)
 French patent 855515) " "
 English patent 516352)

DIAGRAMS I and II (referenced from page 15)

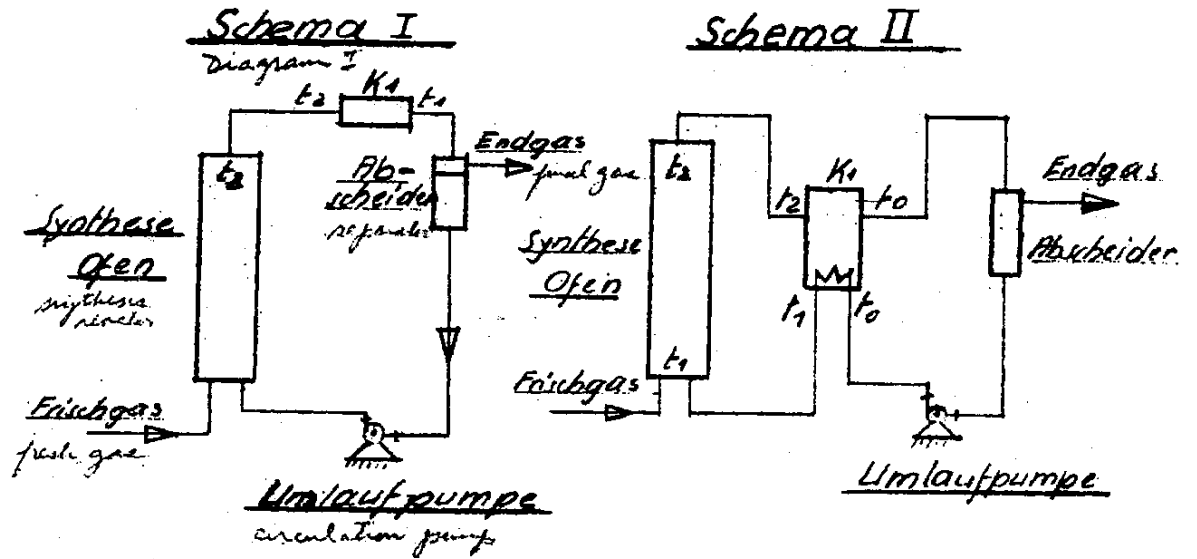


DIAGRAM III (referenced from page 17)

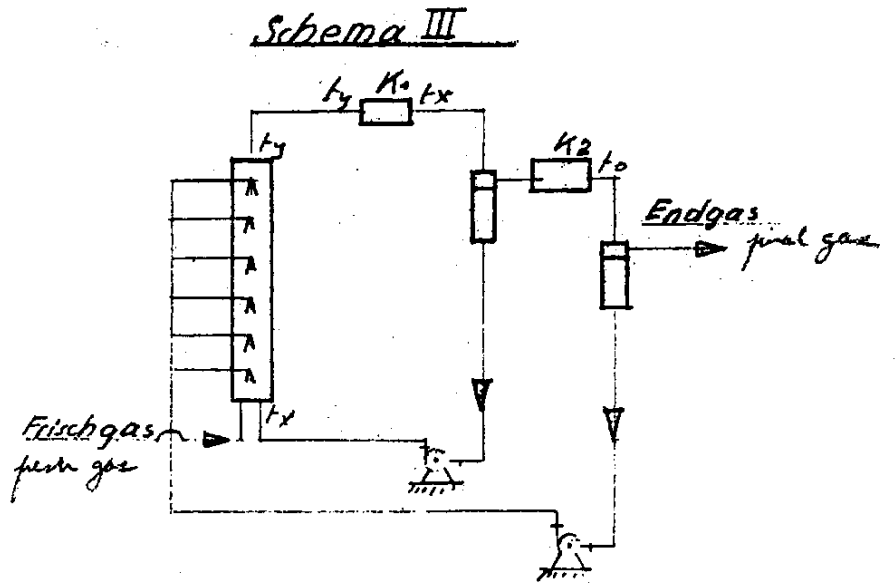
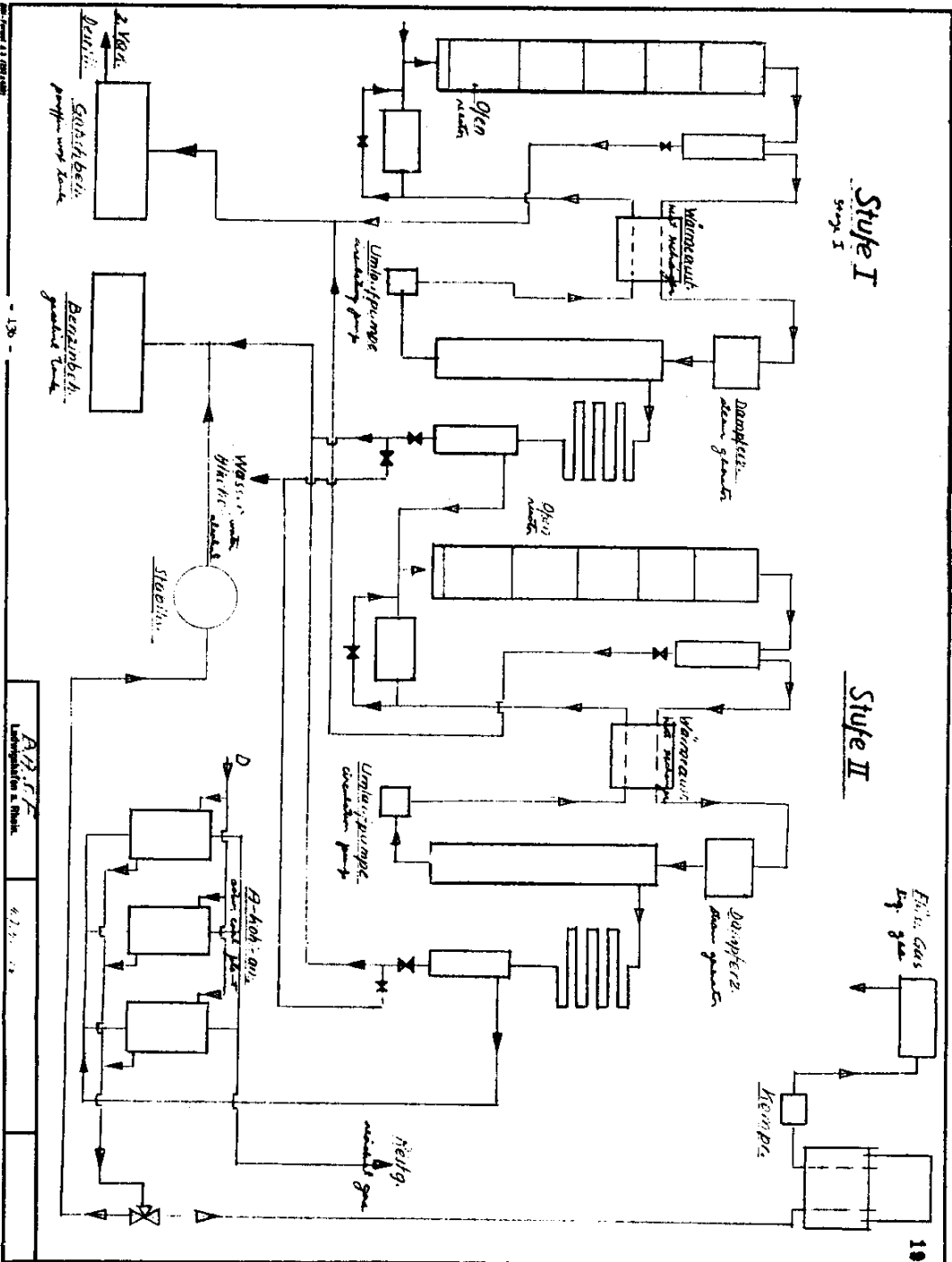
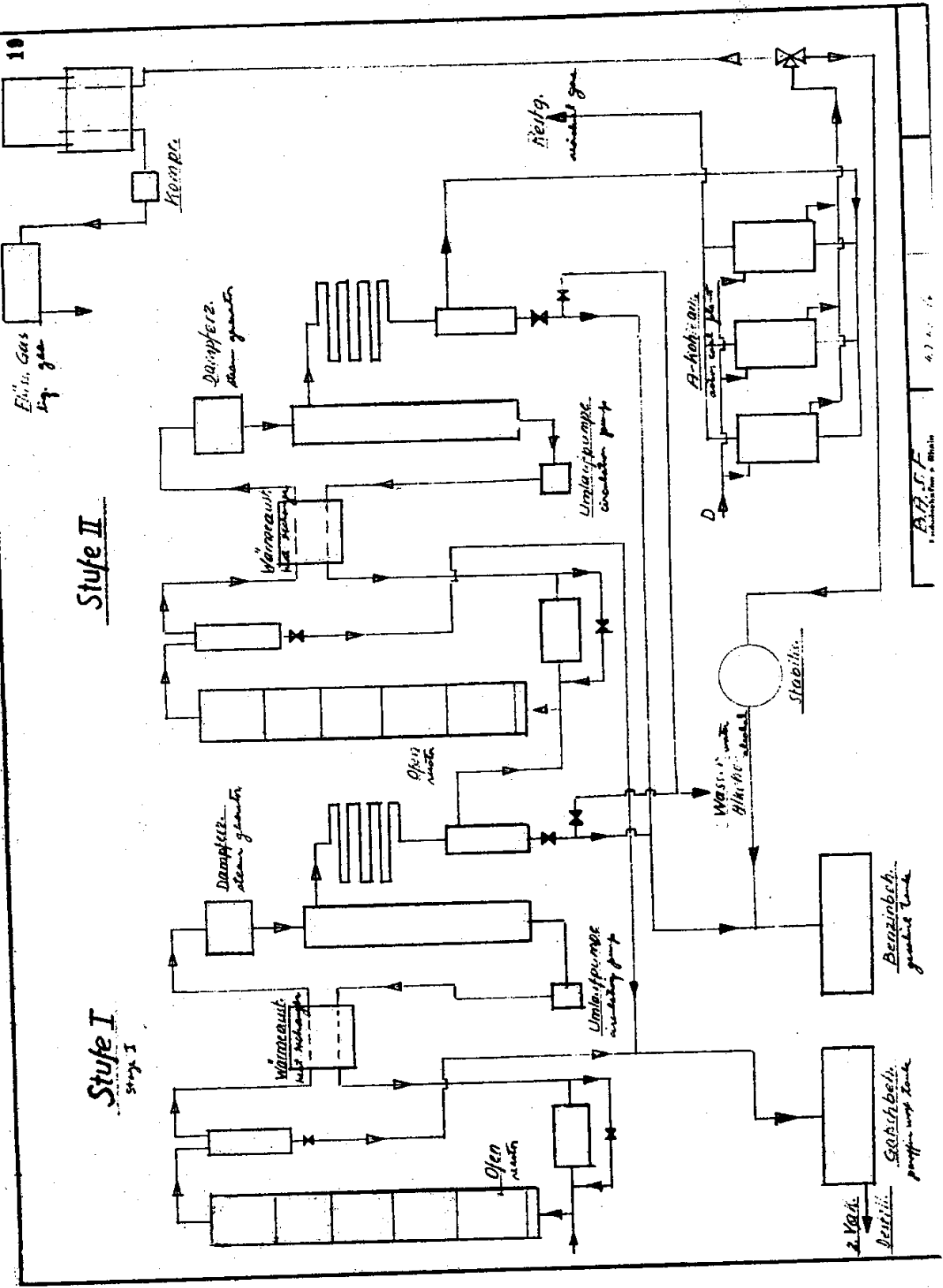
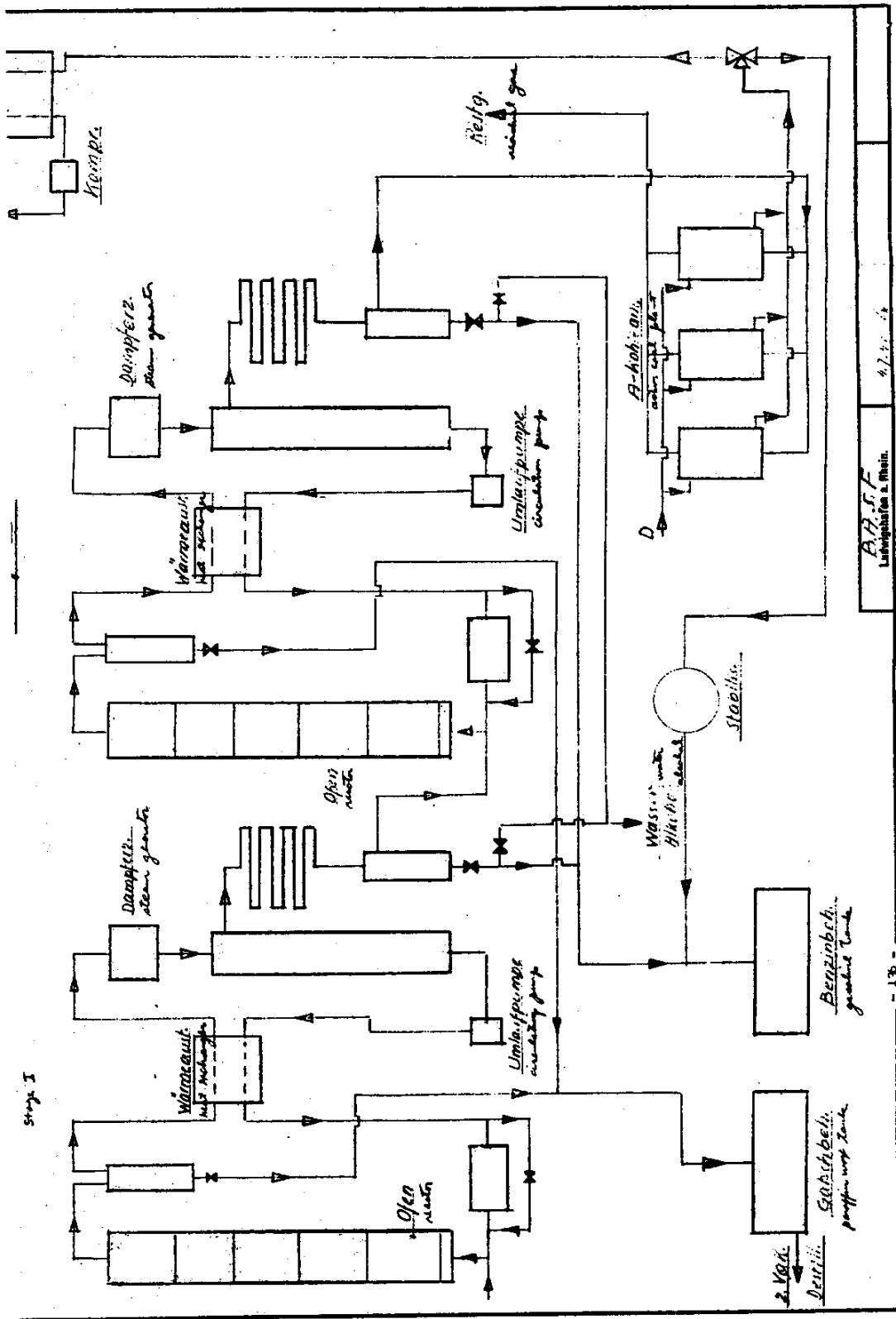


DIAGRAM (referenced on page 19)



2. system
Nef on 9.1.19





A.P.S.F.
Luftschiffbau & Rhein.

TABLE (referenced from page 20)

Es sieden unter Normaldruck bei	Versuch bei 100 atü	Versuch bei 25 atü
^{mit} Bis 100°	5 Vol.%	0 Vol.%
^{mit} von 100 bis 150°	15 "	0 "
^{von} " 150 ^{to} 200°	18 "	3 "
" 200 " 250°	14 "	12 "
" 250 " 300°	13 "	17 "
^{über} 300° ^{abw.}	55 "	58 "

GRAPH (referenced on page 21)

6. Auswertung der Versuchsergebnisse für die Planung einer großtechnischen Ofeneinheit.

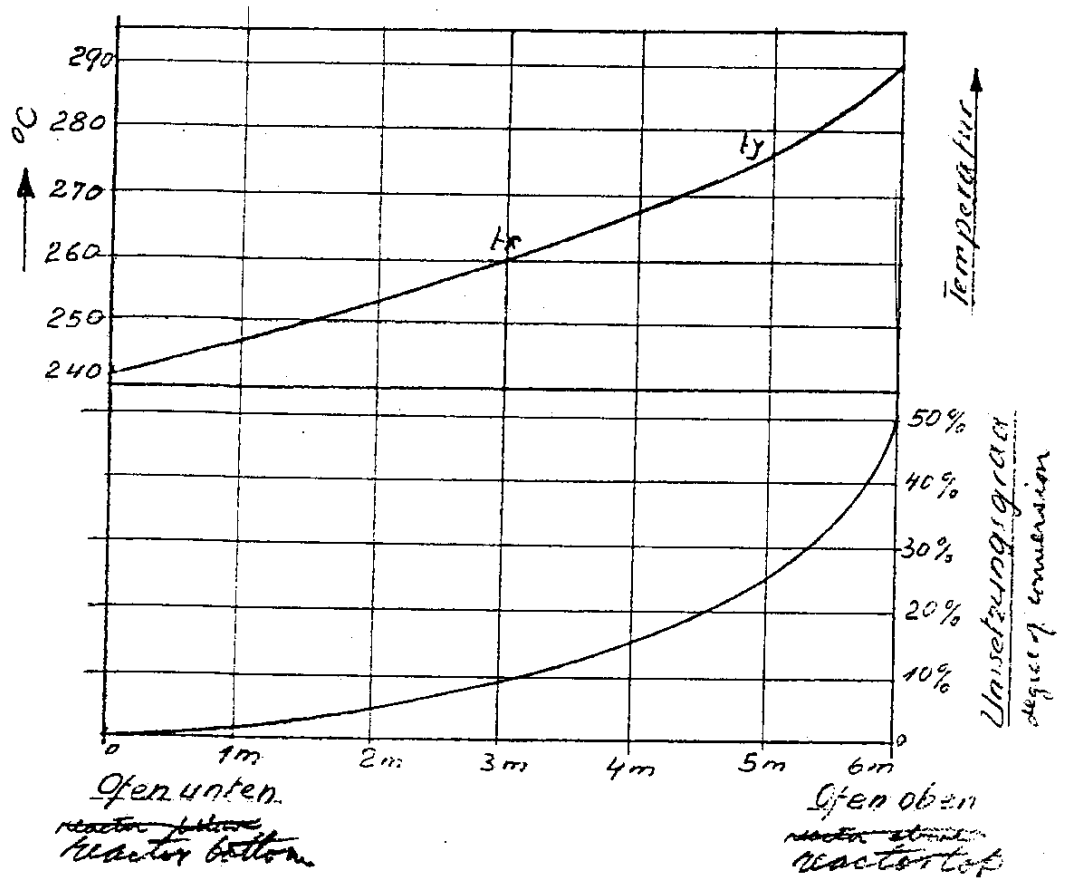


CHART (referenced on page 22)

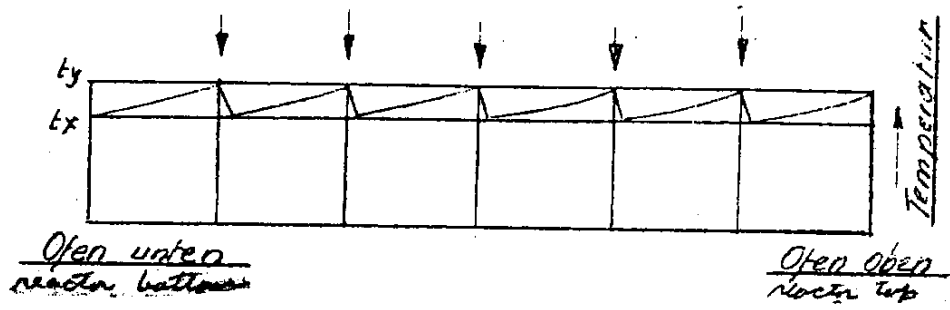


TABLE (referenced on page 23)

Vers. Nr.	CO: H ₂ -Verhältnisse in Frischgas	CO: H ₂ -Verhältnisse im Umsetz	CO: H ₂ -Verhältnisse im Endgas	Tem. Gesamtprodukt auf 300°C	Tem. Gesamtprodukt auf 100°C
35	1 : 5,17	1 : 1,28	1 : 6,74	45	9
35a	1 : 1,90	1 : 0,90	1 : 3,25	41	12
35b	1 : 1,68	1 : 0,92	1 : 2,62	35	12
37	1 : 1,15	1 : 0,72	1 : 1,55	32	22
31	1 : 0,71	1 : 0,72	1 : 0,68	19	48

TABLE (referenced on page 23)

Vers. Nr.	CO:Et-Verhältnis im Frischgas	CO:H ₂ -Verhältnis am Umsatz	CO:H ₂ -Verhältnis im Endgas	vom Gesamtprodukt entfielen	
				auf CO + C ₂ H ₄ + C ₂ H ₆ -Stoffe	auf C ₁ über 180°C
35	1 : 3,17	1 : 1,28	1 : 6,74	43	9
35a	1 : 1,90	1 : 0,90	1 : 3,29	41	12
35b	1 : 1,68	1 : 0,92	1 : 2,62	35	12
37	1 : 1,15	1 : 0,72	1 : 1,53	32	22
31	1 : 0,71	1 : 0,72	1 : 0,68	19	48

TABLE (referenced on page 24)

	Frishgas	Endgas 1. Stufe	Endgas 2. Stufe
Menge m ³	1	0.670	0.413
% CO ₂	-	20.5	55.3
% CnH _{2n}	-	2.0	0.86
% CO	56	36.4	29.8
% H ₂	44	38.1	25.0
% O ₂ + N ₂	-	3.0	6.0

TABLE (referenced on page 25)

	<i>Ofen-Eingang</i>	<i>Ofen-Ausgang</i>
<i>1. Stufe</i>	240 °C	290 °C
<i>2. "</i>	270 °C	320 °C

CHART (referenced on page 26)

Fließschema
Flow diagram
for 1 m³ Idealgas
56 % CO, 44 % H₂
Betriebsdruck 20 atü.
working pressure atm. gage

Verfahrensstufe stage		1	2
Endgasmenge quantity of final gas		0.67 m ³	0.42 m ³
Endgasanalyse: analysis of final gas	% CO ₂	20.5	55.3
	% CnHm	2.0	0.9
	% CO	36.4	14.8
	% H ₂	38.1	23.0
	% CnHm+2	3.0	6.0
CO + H ₂ in Endgas in final	%	79.5	37.8
Umsetzungsgrad des CO + H ₂ degree of conversion of CO + H ₂	%	50	35
<u>Produktion:</u>			
Benzin-Kohlenwasserstoffe bis 180° gasoline - hydrocarbons to		39.6 g	29.6 g
Mittelöl middle oil 180-300°		14.2 g	10.2 g
Wachparaffin wax paraffin 300-420°		8.8 g	4.9 g
Hartparaffin hard paraffin > 420°		16.7 g	9.3 g
Alkohole alcohols		5.7 g	3.4 g
Gesamtprodukt flüssig und fest total product liquid and solid		79.0 g	52.0 g
Flüssiggase C ₂ +C ₄ liquid gases			
Gesamtprodukt einschließlich C ₃ u. C ₄ total products including C ₃ and C ₄		90.2 g	62.2 g
Wasserbildung formation of water		22.7 g	13.3 g
Umlauf oil circulation		8.8 ltr.	6.5 ltr.
In beiden Stufen: Flüssiggas C ₃ + C ₄ in both stages		21.4 g = 14 %	
Benzin gasoline		57.8 g = 36 %	
Mittelöl middle oil		24.4 g = 16 %	
Wachparaffin wax paraffin		13.7 g = 9 %	
Hartparaffin hard paraffin		26.0 g = 17 %	
Alkohole alcohols		9.1 g = 6 %	
Gesamtprodukt flüssig u. fest including C ₃ + C ₄ total product liquid and solid		151.0 g	
Wasserbildung formation of water		152.4 g	
CO ₂ -Bildung formation of CO ₂		46.0 g	
CH ₄ (C ₂ H ₆) Bildung formation		451.5 g	
		12.8 g	

TABLE (referenced on page 26)

12. Produkteigenschaften.

Die Produkte haben einen stark olefinischen Charakter. Der Olefingehalt nimmt mit steigender Molekülgröße der Kohlenwasserstoffe ab, wie die Tabelle zeigt:

Olefingehalte beim Mitteldruckverfahren
olefin contents in medium pressure process

	<i>Gew. %</i> <i>% by wt</i>	<i>Olefingehalt</i> <i>olefin content</i>
<i>vom Gesamtprodukt</i> <i>of total product</i>		<i>%</i>
<i>Gasol (C₅H₁₂)</i>	<i>14</i>	<i>80</i>
<i>Ölfraction bis 100°</i>	<i>19</i>	<i>50-65</i>
<i>100-150°</i>	<i>11</i>	<i>40-55</i>
<i>150-175°</i>	<i>4</i>	<i>35-45</i>
<i>175-320°</i>	<i>19</i>	<i>20-35</i>
<i>320-480°</i>	<i>11</i>	<i>20</i>

F
F
F

TABLE (referenced on page 27)

	Paraffine <i>paraffine</i>		Olefine <i>olefine</i>	
	% geradkettig	% verzweigt	% geradkettig	% verzweigt
Fraktion 100-150°	a	20	12	25
	b	10	22	30
Fraktion 150-200°	a)	35	31	← 34 →
	b)	36	16	29
Fraktion 200-250	a)	53	37	30
	b)	38	32	12

efin-
ie

TABLE (referenced on page 27)

Vergleich der Ergebnisse des Mitteldruck- und Hochdruckverfahrens.
 Comparison of the results of the medium pressure and high pressure processes

	25 at	100 at
Temperatur der Katalysatorreduktion <i>Temperature of catalyst reduction</i>	480° - 500°	650
Temperatur im Synthesofen <i>Temperature in synthesis reactor</i>	245° - 290°	260° - 320°
Gasol-Kohlenwasserstoffe % <i>gasol hydrocarbon</i>	15	17
Benzin- <i>gasoline</i> %	40	40
Mittelöl- <i>middle oil</i> %	20	30
Paraffin- <i>paraffin</i> %	20	7
wasserlösliche Alkohole % <i>water-soluble alcohols</i>	5	6
Olefingehalt: <i>olefin content</i>		
a) Gasol-(C ₉ -C ₄) %	80	70
b) Benzinsiedebereich % <i>gasoline boiling range</i>	55	40
c) Mittelöl %	35	45
Sauerstoffgehalt: <i>oxygen content</i>		
Benzinsiedebereich %	15-20	1.5 - 3.5
Mittelöl % <i>gasoline boiling range</i>	1.0	0.5 - 1.5
Paraffin % <i>paraffin</i>	0.5	0.2 - 0.6

Table
 No. 1
 15
 35
 25
 25
 25
 25

TABLE (referenced on page 28)

Vorb. Nr. Exp. No.	Contact reaction temperature	Druck pressure atm	Synthesegas synthesis gas						Wasser- to gas	% by weight of total product				
			% CO ₂	% C _n H _m	% CO	% H ₂	% CH ₄	% H ₂		Von Gesamtprodukt enthalten Gewichtsprozente auf				
			C ₁ -C ₄ Alkohole	C ₅ -C ₆ Kohlenwasserstoffe	Benzin gewöhnliche Kohlenwasserstoffe	Mittelöl	Paraffin							
13 b	650°	100	5.8	0.4	21.0	61.0	5.5	5.5	167	15.7	47.2	30.5	3.1	3.5
35 a	480°	15	4.6	0.8	20.2	64.1	5.2	5.2	171	8.6	43.1	37.3	11.0	
25 a	480°	100	5.6	0.6	21.3	63.2	4.3	4.8	157	18.4	38.4	38.5	4.2	0.9
25 b	"	20	2.3	0.3	21.6	70.5	2.7	2.6	150	24.7	35.2	28.1	4.2	6.8
25 a	"	150	2.4	0.3	22.4	69.2	2.7	2.4	150	40.5	25.3	25.6	4.0	4.6
25 d	"	180	6.0	0.6	20.2	63.0	4.4	3.2	146	36.1	35.0	23.1	3.0	2.8