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THE FISCHER-TROPSCH SYNTHESIS IN THE LIQUID PHASE

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1. Introduction

The hydrogenation of carbon monoxide by the Fischer-Tropsch process[1] forms saturated and unsaturated compounds of the homologous hydrocarbon series. It permits the synthesis of hydrocarbons ranging from methane to high-melting paraffins with molecular weights above 20,000, depending on the catalyst, temperature and type of process employed. By-products such as alcohols, aldehydes, ketones, acids and esters are formed on a smaller scale. Small amounts of aromatic compounds are formed at high temperatures by secondary dehydrocyclization reactions from the primary hydrocarbons formed.

The F-T synthesis can be reduced to two fundamental reactions: one is the hydrogenation of carbon monoxide according to Eq. (1), which takes place preferentially on cobalt and nickel catalysts. The other reaction is the conversion of water (Eq. 2), which takes place most easily on iron catalysts as a consecutive reaction. The overall reaction (3) below expresses the hydrocarbon synthesis on iron catalysts:

$$CO + 2H_2 \rightarrow (-CH_2-) + H_2O \qquad R^{H^{227C}} = -165 \text{ kJ} \qquad (1)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad R^{H^{227C}} = -39.8 \text{ kJ} \qquad (2)$$

$$2CO + H_2 \rightarrow (-CH_2-) + CO_2 \qquad R^{H^{227C}} = -205.8 \text{ kJ} \qquad (3)$$

The consecutive reaction of Eq. (2) can be depressed by using lower temperatures and a shorter residence time and by circulating the synthesis gas, from which the water of the reaction was removed at an intermediate stage, so that the F-T synthesis can also take place on iron catalysts partly by way of water formation and partly by way of carbon dioxide formation. The olefin content of the synthesis product lies between 0 and 90%, varying considerably with the chain length and type of process. The content of n-α-olefins relative to the sum of n-olefins may be as high as 85%.

The primary products of F-T synthesis, because of their predominantly straight-chain structure and because of the position of the double bond at the end of the chain, are ideal starting materials for further chemical processing. In addition, they are remarkable for their great purity. In particular, the sulfur compounds present as impurities do not interfere with the subsequent processing of the F-T products.

A basic requirement for an economical production of chemical raw materials by means of the F-T synthesis is a high yield based on the synthesis gas used, because its cost amounts to about 80% of the production costs of the products. Optimum yields can be achieved only when the reactants CO and H_2 are present in the same ratio as they are used in the synthesis, i.e., the ratio of supply should equal the ratio of consumption. In a total stoichiometric conversion, the reactions of Equations (1) and (2) result in a maximum yield of 208.5 g per Nm^3 (CO + H_2).

One modification of the F-T synthesis is represented by the Kölbel-Engelhardt synthesis, which forms hydrocarbons from carbon monoxide and water.[1-3] The reaction converts water according to Eq. (2) and forms hydrogen "in situ," which then reacts with carbon monoxide according to Eq. (3). Thus, the K-E synthesis takes place according to the overall equation:

$$3CO + H_2O \rightarrow (-CH_2-) + 2CO_2 \qquad R^{H^{227C}} = -244.5\ \mathrm{kJ} \qquad (4)$$

The formation of hydrocarbons from carbon monoxide and hydrogen follows from Eqs. (1) and (2)

$$CO_2 + 3H_2 \rightarrow (-CH_2-) + 2H_2O \qquad R^{H^{227C}} = -125.2 \text{ kJ} \qquad (5)$$

The stoichiometric yield of the reaction according to Eq.(4) is 208.5 g, and according to Eq. (5), 156.2 g per Nm^3 ($CO + H_2$).

Undesirable side reactions to consider include hydrogenation of carbon monoxide to methane, decomposition of CO to carbon and CO_2, and oxidation of the catalyst.

Even though it was discovered in 1926,[1] the reaction mechanism of the Fischer-Tropsch synthesis has not yet been explained. The mechanism presented by Anderson and co-workers in 1951[4] considers the formation of enolic primary complexes from carbon monoxide and hydrogen on the surface of the catalyst, which grow into hydrocarbon chains by the stepwide splitting off of water and hydrogenation. The mechanism according to Pichler[5] postulates that the building of the hydrocarbon chain involves insertion of a CO molecule, adsorbed as a polycarbonyl on the catalyst, between the metal-alkyl bond while water is split off and hydrogenation takes place.

New proposals concerning the mechanism of the Fischer-Tropsch reaction, based on results of modern methods in surface physics, regard the dissociation of carbon monoxide on the catalyst as the first step in the reaction. Thus, they return to the older ideas about the role of the "active carbon" on the surface of the catalyst.[6]

The hydrogenation of carbon monoxide according to the F-T process represents a system of complex parallel and consecutive reactions which at the same time are balanced thermodynamically with respect to each other. Because of the great number of reaction equations involved, the calculation of such simultaneous equilibria has been made only under certain simplifying assumptions.[7,8] A treatment of the thermodynamics of the F-T reaction including all the reactions involved in the synthesis but assumed to take place independently of each other was published by Anderson.[9]

The micro-kinetics of the F-T reaction are not known in their individual steps. Several semiempirical equations[4,10-13] have been proposed for cobalt and iron base catalysts used industrially in solid bed reactors, but these equations partly contradict one another.

The main technical problems of the F-T synthesis include a rapid removal of the heat of reaction, amounting to about 25% of the heat of combustion of the synthesis gas; avoiding local overheating of the catalyst, which favors methane formation; and finally, a uniform distribution of the synthesis gas over the catalyst.

To solve these problems, various types of synthesis reactors have been developed.[1] These reactors may be divided into those with stationary catalysts (lamellar reactor, double tube reactor, ARGE reactor) and mobile catalysts (fluidized bed reactor, flying-dust reactor, three-phase slurry reactor).

This report is concerned with the liquid phase process in three-phase bubble column reactors, developed by H. Kölbel and P. Ackermann (Meerbeck Fuel Works, Rheinpreussen Corporation, Homburg-Niederrhein) during the period 1938-1953, when the disadvantages of the fixed bed process became obvious after the replacement of cobalt catalysts by iron catalysts in the fixed bed reactor (lamellar and double pipe reactor).[1] The liquid phase process was used in 1952-1953 at the Meerbeck pilot plant with a large-scale reactor unit (daily production 11.5 t synthesis products) operated by the Arbeitsgemeinschaft Rheinpreussen AG fuer Bergbau und Chemie, Homburg-Niederrhein and Heinrich Koppers GmbH, Essen-Koppers Co., Pittsburgh, USA.[14-16]

2. Principles of Liquid-Phase Fischer-Tropsch Synthesis

The liquid-phase F-T synthesis takes place in a bubble column reactor (Fig. 1) where the synthesis gas is converted on catalysts suspended in a liquid as fine particles. The synthesis gas flows as small bubbles through the catalyst suspension. The synthesis products, which are volatile under the operating conditions employed, are removed with the residual gas, and the liquid products are separated from the suspension. The heat of reaction is removed by water evaporated in cooling pipes immersed in the suspension.

The use of the bubble column reactor for F-T synthesis has the following advantages, which will be discussed in detail below:

(a) uniform temperature in the reactor

(b) high contact and reactor efficiency

(c) a catalyst efficiency of about 1

(d) good heat exchange

(e) favorable conditions for catalyst regeneration

(f) simple construction and therefore low investment costs.

Control of the heat of reaction, which reaches a considerable order of magnitude, does not present any problem. It is necessary to eliminate local overheating because it leads to methane formation and damage to the catalyst. The flexibility of the suspension reactor makes it possible to establish specific operating conditions permitting a selective control of the synthesis and therefore its economical operation. The bubble column reactor allows the introduction of synthesis gases rich in carbon monoxide without the risk of clogging or some other undesirable effect that might be caused by the liberation of carbon by the Boudouard reaction.

A certain disadvantage of the bubble column reactor is that the residence time behavior of the liquid phase and partly also that of the gas phase in a simple bubble column is for all practical purposes equivalent to the behavior in an ideal agitator vessel. This causes undesirable problems when higher selectivities are to be obtained, but such problems can be partially avoided by use of bubble column cascades in the stepwise process or by building elements into the reactor.[17] The special features of the three-phase bubble column reactor do exert an influence on the reaction process of the F-T synthesis. A discussion of the features of this reactor type will make subsequent remarks easier to understand.

Detailed information on the behavior of bubble column reactors can be found in the literature.[20] The problems of two-phase bubble column reactors with respect to reaction technology were summarized by Deckwer.[21,22] Mersmann and Gerstenberg[24] discussed the state of the art from the standpoint of process technology. Criteria for the selection and design of gas/liquid reactors were treated by Nagel, Hagner and Kürthen.[25] For information on the principles, design and application of three-phase bubble column reactors with suspended contact catalysis see the review by Hammer[26] and work of Kürthen and Zehner.[27]

Since the development work on liquid-phase F-T synthesis was halted at the end of the 1950's, there have been no major investigations of further development of three-phase bubble column reactors for this synthesis. Only since 1975 has there been new activity in this area.

2.1. Fluid-Dynamic Behavior of Bubble Column Reactors

The bubble column reactor[20,28] is a type of gas-liquid reactor with special features that can be reduced to a close linkage between microkinetics, hydrodynamics and mass-, energy-, and momentum transfer. The bubbles are produced by the gas distributor located in the lower portion of the reactor. In smaller experimental units, these gas distributors consist of porous plates, whereas in large bubble column reactors, jet distributors of various designs are used exclusively. At no-gas tube velocities $U_{Go} < 5$ cm/sec, a state of motion referred to as homogeneous bubble flow is established, the bubbles being of approximately equal size and rising in a uniform manner. The volume concentration of the bubbles increases as the gas load increases. Larger bubbles are formed by coalescence; they break up again after exceeding bubble size corresponding to the hydrodynamic equilibrium. This state of motion is referred to as turbulent (heterogeneous) bubble flow. Further increase of the gas flow leads to the formation of plugs.

In bubble column reactors of sufficient size, three reactor sections appear, each of which has a different hydrodynamic behavior. The inflow zone with a state of flow produced by the gas distributor is formed in the lower region. This state of flow changes in the middle region into a state of equilibrium between bubble coalescence and decay determined by the operating conditions and properties of the materials. Characteristic of this state is the fact that the relative gas content remains relatively constant in this section. A zone of higher gas content is formed in the upper section of the column because the gas bubbles at the surface need a finite time to burst.

The catalyst suspended in the liquid is in stationary equilibrium between sedimentation and the upward movement of the rising bubbles. According to Ref. 14, a uniform distribution of catalyst granules with an average size of 30 μm in the liquid-phase F-T reactor can be obtained if the gas load referred to the free reactor cross section exceeds about 3 cm^3/cm^2 s.

2.1.1. Relative gas constant and specific interfacial area

The complex hydrodynamic behavior of bubble column reactors makes it difficult to determine exactly the size of the bubble boundary, which determines the material exchange between the phases and, in the case of rapidly progressing reactions, the conversion, the reaction rate, and the reactor efficiency. As a first approximation, in calculating the boundary size, we can use the relative gas content ε_G, which is defined as the volume fraction of the gas in a unit volume of the gas-liquid dispersion. The relative gas content depends primarily on the material properties of the liquid phase. The composition and density of the gas exert little influence on the thermodynamic behavior of the bubble column reactor.

The material properties of the F-T paraffins used as dispersion fluid were determined by Calderbank[29] and Hammer.[30] Louisi[31] investigated the dependence of the relative gas content on gas throughput, temperature and catalyst concentration under the operating conditions of the liquid-phase F-T process. He observed that the relative gas content as well as the specific interfacial area in the region of homogeneous flow increases linearly with the gas throughput. Above 240°C, the relative gas content is no longer affected by the temperature of the suspension liquid. Increasing the concentration of solids by up to 10% by weight causes a decrease in relative gas content. The equation of Richardson and Zaki[32] as modified by Louisi can be used to calculate the relative gas content under the conditions of the liquid-phase F-T synthesis. In the region of homogeneous flow, the gas bubble diameter in molten hard paraffin without solids is almost independent of the linear gas velocity and amounts to 0.7 mm. With this value for the average bubble size, the specific interfacial area a for U_{Go} = 1.6 cm s^{-1} is about 600 m^2/m^3, and for U_{Go} = 3.6 cm s^{-1}, about 1,700 m^2/m^3.

These measurements agree with the older estimated values of Kölbel,[28] who gave a value of 1,500 m^2/m^3 for the specific interfacial area in slack wax in industrial bubble column reactors with suspended catalysts at the synthesis temperature.

2.1.2. Mass transfer

The specific interfacial area is directly related to mass transfer. Therefore, its determination as a function of the relative gas content, which can be obtained relatively easily with present measurement techniques, is one of the most important objectives of bubble column technology.

Investigations by Zaidi[33,34] have shown that the mass transfer coefficient in bubble columns for different material systems varies only slightly under distinctly different operating conditions. The approximate value for the gas-liquid mass transfer coefficient K_L is 0.1-0.2 cm s^{-1}.

The correlations of Hughmark[35] and Calderbank and Moo-Young[29] have proven valuable for the calculation of the gas-liquid mass transfer coefficient for carbon monoxide under the operating conditions of the liquid-phase F-T synthesis.

In a comparative study in which he has used his own results as well as those reported by a number of other authors, Deckwer et al.[36] summarized the fluid-phase parameters of the liquid-phase F-T reactor, as shown in Table 1.

2.1.3. Mixing in the liquid phase

Back mixing in the liquid phase is influenced by the pneumatic agitation of the rising gas bubbles. The latter transport the liquid upward in an axial direction in the vortex trail and in a radial direction through lateral displacement of the liquid toward the wall. By virtue of the principle of conservation of mass, this liquid rising with the bubbles must be transported convectively downward, so that a downward flow is set up in the stationary liquid phase. The axial dispersion coefficient of the liquid phase can be calculated to a first approximation as $E_L = 2.7\ U_{Go}^{0.3} d_R^{1.4}$, even though the physical characteristics of the liquid phase are not considered in this relation. But since finely ground catalysts are present in the liquid-phase synthesis, the particle dispersion coefficient E_S becomes almost identical with the value E_L.

Radial mixing becomes very substantial as a result of the above-described liquid displacement during the ascent of the bubbles, interfering with the formation of radial profiles. The mixing of the liquid phase causes a constant movement of the catalyst particles in an axial and radial direction. This results in a uniform contact loading and an increase in the life of the catalyst. The mass exchange in both directions of the phase transition permits the formation of concentration profiles for the reaction components in the liquid and in the gas phase.

2.1.4. Mixing in the gas phase

The diverse ascent velocities of the bubbles, due to a nonuniform size, to the coalescence of the bubbles and their decay, and to the formation of turbulence centers, leads to back mixing in the gas phase. The turbulence in the liquid phase grows with increasing gas velocity, and for highly viscous liquids leads to back mixing in the gas phase. For bubble column reactors 0.6 m - 2 m in diameter, the mixing in the gas phase is already of the same order of magnitude as the mixing in the liquid phase.

2.1.5. Heat transfer

The high values of the heat transfer coefficient can be explained by the thorough mixing in the liquid phase. The rising bubbles displace the liquid elements above the gas bubble in a radial direction toward the reactor wall. The liquid elements below the gas bubble are carried along in the vortex trail and are replaced by liquid elements with an opposite direction of flow. This gives rise in the liquid phase to a transverse motion which in turn results in convective heat transfer.

An increasing concentration of solid matter in the suspension causes a further increase in the heat transfer coefficient. This can be explained by the degradation of the laminar liquid boundary layer, which is constantly being torn in the presence of the solid material. Thus the increasing concentration of the solid material interferes more markedly with the formation of the liquid boundary film and increases the heat transfer.

In the region of homogeneous flow, under the operating conditions of liquid-phase F-T synthesis, the values of the heat transfer coefficient for $U_{Go} = 2.5$ cm s^{-1} range between 600 and 800 $kJ/m^2 s_K$. As the gas concentration increases, the heat transfer increases until it reaches a limiting value of about 1,100 $J/m^2 s_K$ in the region of heterogeneous flow ($U_{Go} > 5$ cm) at which point it becomes independent of the gas throughput. A correlation for calculating the heat transfer coefficient was published by Louisi[31] in the form

$$St = 0.118 \, (Re \, . \, Fr)^{-0.272} (Pr)^{-0.529}$$

A more general treatment of heat transfer in two- and three-phase bubble column reactors was published by Deckwer.[36] The working equation he proposed is listed in Table 1.

2.2. Course of the Reaction in the Three-Phase Bubble Column Reactor

The course of chemical reactions involving three phases is very complicated. The total conversion and the selectivity, which are among the most important parameters of a process, are determined by a large number of variables, including:

(a) hydrodynamic factors (gas distribution, interfacial areas, back mixing, sedimentation, convective heat transfer);

(b) physical factors (material properties, heat and mass transfer coefficients, absorption and adsorption coefficients of the reactants, porous diffusion coefficients, etc.);

(c) chemical factors (stoichiometry, thermodynamics, microkinetics);

(d) factors influencing the process (temperature, pressure, concentration, conversion).

Despite the large number of publications which have appeared in the field of gas-liquid systems and which were recently summarized by Deckwer,[37] only a few analyses of models are known which can account for systems operating under conditions prevailing in catalytic processes. The reactivity of a system is manifested in a change in the molecular flows of the fluid phases, caused by conversions which are usually high in industrial processes. Hence, the gas velocity and the fluid-dynamic characteristics are position-dependent. This means that only those models, developed for gas-liquid reactors, that in addition to dispersion phenomena in the liquid phases will also consider the appearance of a position-dependent gas velocity, can be of importance for the interpretation of catalytic three-phase bubble column reactors. In addition to these assumptions for applying these models to the three-phase bubble column reactor, we have to assume that the suspended solid with the liquid can be interpreted, not only from the fluid-dynamic but also from the reaction technology standpoint, as being a quasi-continuum.[30] A statement on this point is therefore possible only after determining the order of magnitude of the individual mass transfer resistances in the liquid phase and on the catalyst.

The total resistance of a chemical reaction in the bubble chamber is composed of the resistance to mass transfer and of the reaction resistance, so that we have to distinguish between two most important limiting cases.[38,39]

(a) The activity of the catalyst is low at lower reaction temperatures. Therefore, especially at low catalyst concentrations, the reaction becomes the rate-determining step. This region is characterized by the fact that the conversion increases sharply with temperature. The apparent activation energy approaches the value measured in the fixed bed.

(b) At higher reaction temperatures, the reaction takes place quickly, the mass transfer determines the rate, and the effective activation energy declines.

Between these two extreme cases lies a transition region where both the mass transfer and the reaction determine the macrokinetics.

The region where the influence of mass transfer becomes noticeable can, under certain circumstances, be controlled by the mass transfer of a single reactant.

In contrast to fixed bed reactors, the reactor efficiency does not approach a limiting value; rather, it shows a maximum for gas velocities at which the maximum boundary area is reached between the gas and liquid phase. A further increase in gas concentration leads to the formation of large bubbles and a decrease in interfacial area and, hence, in reactor efficiency. It is advantageous for technical purposes to bring the processes occurring in a three-phase reactor together with the individual and interacting quantities in a specific operating region and to present them as the throughput referred to the reactor cross section as a function of catalyst concentration (Fig. 2). In this process diagram, the sedimentation region is bounded by a curve. A throughput below the minimum causes catalyst settling, an uneven catalyst load, and incomplete unloading of the reactor. Another curve bounds from above the region of large bubble formation, where a reduced specific interfacial area leads to a decrease of mass transfer. The course of this curve is strongly dependent on the mass constants and the reactor geometry. The apparent density and viscosity of the suspension increase with the catalyst concentrations so that large bubbles are formed even at lower gas throughputs.

Thus far, no extensive experiments on liquid-phase F-T synthesis have been conducted with the aim of working out models for reactor dimensioning and optimization that could be used for technical purposes. This may be attributed, on the one hand, to a lack of industrial interest until 1973, and on the other hand, to the complexity of this reaction. The published studies report solely on the material and system constants. Kölbel and co-workers[13,14] indicated the solubility of a few reaction components in slack wax as a function of pressure and temperature.

The liquid-phase F-T synthesis cannot be inhibited by mass transfer of the reactants from the gas into the liquid phase by use of the catalysts known to date with a concentration of solidsof about 10-15% in the liquid phase. The k_La values for CO mass transfer, determined by Zaidi et al.,[33,34] make it possible to estimate the conversion in the case where all of the carbon monoxide which has passed from the gas into the liquid phase reacts on the suspended catalyst. A comparison of the calculated and experimental conversions for the F-T reaction as well as the CO methanization and CO conversion in the liquid phase is shown in Fig. 3. The conversion measurements for the F-T synthesis are indicated by the shaded area. It is apparent from Fig. 3 that only a fraction of the conversion rates for the methanization reaction are scattered along the diagonal. In this case, the reaction rate in the catalyst suspension was partially so high that the rate-determining step was the mass transfer. The data measured for both the F-T synthesis and the conversion reaction always lie below the conversions calculated for the mass transfer limitation. Thus, the mass transfer at the gas-liquid boundary is always greater than the reaction rate at the contact.

The possibility of interference with mass transfer at the particle can be excluded because the catalyst particles used in the liquid-phase F-T synthesis are small. It follows that it is the chemical reaction that constitutes the rate-determining step of the overall process. These findings indicate that greater conversion rates and higher space-time yields in the liquid-phase F-T synthesis can be obtained only through the development of improved, more active catalyst systems.

3. Liquid-Phase F-T Synthesis Procedure

The development of the liquid-phase process begun in 1938 by Kölbel and Ackermann was interrupted in 1944 by the events of World War II but was resumed in 1951. In 1953 it led to the startup of a pilot plant (Rheinpreussen - Koppers) with a production of 11.5 tons of hydrocarbons per day. The primary goal was the production of fuels as well as products for further chemical processing.[28]

Further investigations with the same objectives were conducted during the war (BASF,[40,41]) and after the war (U.S. Bureau of Mines; Fuel Research Station, London; Indian Institute of Technology; University of Tokyo), and variants of the liquid-phase process were developed. With the exception of the BASF process modified by the Bureau of Mines, the developmental work did not exceed the pilot-plant scale. In 1955, Koppers GmbH designed for the Indian government a liquid-phase plant capable of producing 250,000 tons/yr but it was never built because of the change in emphasis to petroleum.

Since 1974, new activities in the use of the liquid-phase process for the production of primary chemical products have become apparent. Interest is being shown mainly in the short-chain C_2-C_4 olefins,[42] medium-chain C_8-C_{12} olefin fraction and oxygen-containing products (aldehydes). However, few results of these pilot-plant investigations have been published.

The following paragraphs will describe the results achieved in a demonstration plant because they best reflect the industrial reality. Investigations performed on a pilot-plant scale by German as well as foreign companies will be considered. Finally, the possibility of selectively directing the liquid-phase F-T process toward the production of chemical raw materials will be discussed.

3.1. Description of the Rheinpreussen - Koppers Demonstration Plant

The process is briefly described by the flow chart of Fig. 4. The synthesis gas was produced in a Koppers water gas generator, CO_2 from the residual synthesis gas being added to the steam during the gas production period. It contained an average of 54-56% CO, 36-38% H_2, and also 3-5% CO_2, 0.1% O_2 and 2.6-4% N_2. The gas was subjected in the usual manner to a rough purification over iron oxide to remove H_2S, and over a hot purifying mass (Lauta mass and soda) to remove organic sulfur compounds to a residual sulfur content of 1-2 mg of S/m^3. The gas flows through two compressors a, the gas meter b, the measuring orifice plate c, through the heat exchanger g, where it is preheated by the residual gas stream coming from the reactor e, and enters at the bottom of the reactor e through a gas distributor with jets about 2-3 mm in diameter. The reactor is based on the design shown in Fig. 1. It consists of a pressure-resistant steel cylinder with a diameter of 1.55 m and a height of 8.6 m. At the top of the reactor is a steam collector f. From the latter, the feed-water supply goes to the inner down pipes of the cooling pipe register located in the reactor, and steam is removed through the annular space in the cooling pipes. The cooling pipe register ends about 1.3 m above the gas distributor. The reaction temperature is kept constant by controlling the saturated steam pressure in the steam collector.

The pipe register in the reactor was used during the formation of the catalyst to heat the suspension by the addition of steam, which was compressed by the condenser to a pressure corresponding to the formation temperature. The catalyst suspension was introduced or withdrawn by means of pumps k through nozzles at the bottom of the reactor and by way of agitator vessel o. The height of the suspension (≈8 m) was kept constant by a regulator either by filtering off the high-boiling fractions in the pressure filter n or by adding higher-boiling synthesis products from containers l. The reactor temperature was measured by twelve resistance thermometers attached at different heights, and recorded. Nine smaller nozzles mounted at different levels permitted the removal of suspension samples from the reactor.

The final gas leaves the reactor through a swan-neck and is precooled with fresh gas in heat exchanger g. Higher-boiling products partially condensed by the boiling range of the liquid medium are stored in containers h or i. Indirect cooling with water in l at about 30°C condenses products of the medium boiling range, and, out of the residual gas, the major portion of the water formed by the synthesis. The residual gas is determined quantitatively in the operating mode in a one-time passage through a calibrated orifice and gas meter b. After the carbon dioxide has been washed out in m, the residual gas is conveyed into the recovery plant for light-boiling and gaseous products (oil pressure washing and activated charcoal plant). The carbon dioxide is conveyed into the generator for the production of CO-enriched synthesis gases. After removal of most of the CO_2 and H_2O, the final gas together with the fresh gas is returned into the reactor by circulation cycling or in a multistage procedure.

The pump fills the reactor with fresh catalyst from agitator vessel o where the ground catalyst is mixed with the high-boiling synthesis products. When the reactor is emptied, a pump k conveys the suspension into centrifuge p which separates the catalyst from the liquid medium, which can then be used again. The spent catalyst can be regenerated.

If the synthesis is adjusted for the production of low-molecular compounds (Section 3.4.1.1), the removal of the liquid medium is often greater than the addition due to synthesis. In this case, the higher molecular weight product collecting in heat exchanger g is fed into the reactor by pump k, its flow being regulated by a liquid level regulator. If the process is geared toward products of higher molecular weights (Section 3.4.1.2), these products must be separated from the catalyst by continuous separation in filter n, and removed. The catalyst flows back into the reactor. After being removed under pressure in liquid form, the primary products are separated in separators i from the water of reaction. The separator yields oxygen-containing products, especially alcohols. The hydrocarbons from the containers are separated into fractions by distillation in the usual manner, depending on their intended use. Fig. 5 shows a photograph of the demonstration plant.

3.2. Catalysts

The development of the catalysts for the liquid-phase synthesis was based on extensive work done with iron catalysts[43] that were intended for use in the solid bed process. Compared to other types of processes, work in the liquid phase offers greater possibilities for the flexible use of catalysts, because it is not necessary to maintain certain temperature ranges and high gas velocities, or a high hydrogen content of the synthesis gases. Basically all the catalysts which are suitable for the F-T synthesis can also be used in the liquid phase. In contrast to other types of processes, mechanical strength of the catalyst is not required here. On the contrary, it is advantageous to have the catalyst granules break up when forming during the synthesis as a result of carbon formation, because this leads to a good dispersion in the liquid. Catalysts with a high content of supports are less suitable, since they lead to unusually high viscosities as compared to support-free catalysts, hindering the gas distribution and reducing the boundary area between gas and liquid, which area in turn determines the mass transfer.

It is for this reason that we considered primarily support-free iron precipitation catalysts during the developmental stage. They make it possible to use the highest concentration of iron in suspension, can be formed easily in a liquid medium, possess high activity, and produce stable suspensions. The optimum concentration of the catalyst in suspension proved to be about 10% in terms of the iron present in the catalyst. Lower concentrations reduce the reactor efficiency, and higher concentrations up to 20% can be used, but they increase the viscocity of the suspension and thus decrease the interfacial area, which affects the mass transfer and hence may cause a decrease in conversion. An optimum equilibrium is required between catalyst concentration, gas throughput and operating temperature.[44]

3.2.1. Starting materials for iron precipitation catalysts

The iron precipitation catalysts for the liquid-phase F-T synthesis were obtained from iron(III) nitrate solutions or mixtures of nitrate solutions containing 80% iron(III) and 20% iron(II).[43,45] Solutions of iron(II) cannot yield active catalysts because the iron in the oxide has to be present as iron(III), either as α or γ Fe_2O_3. After annealing, or at the latest during formation, the catalytically indispensable Fe_3O_4 is produced from these oxide forms. By adding about 20% Cu, one can also obtain an active catalyst from iron(II) solutions because during the drying of the hydroxide, the Fe(II) oxide is oxidized under the influence of atomspheric oxygen.

In the preparation of charges greater than those used in the operation of an industrial reactor, nitrate solutions were used that had been prepared by dissolving wrought iron scrap or steel turnings in nitric acid after it had been observed that the impurities contained in these materials like manganese, silica, carbon, and even catalyst poisons like sulfur and phosphorus did not reduce the activity. It further became apparent that the presence of small amounts of copper in the scrap (0.005 wt.%) was decisive for high catalytic activity.[46] Systematic investigations showed that gold, silver, and nickel present in minute concentrations have a similar effect. These metals act as reduction promoters which become effective during formation.

3.2.2. Production of the catalysts

Most suitable of all the precipitating agents in use are soda and ammonia solutions. Once the controlling influence of the exact dosage of alkali salt promoters was recognized,[47] where deviations of as little as 0.1 wt.% of K_2CO_3 (referred to Fe) may be significant, the precipitations were conducted with ammonia solutions so as to eliminate the promoter influence of sodium carbonate, which is strongly retained by the hydroxide after washing. The iron solutions, which generally contain 0.1 wt.% copper (referred to Fe), can be easily precipitated with ammonia despite the possible formation of readily soluble ammonia-copper complexes, because the highly surface-active ferric hydroxide always retains a sufficient amount of copper to activate the formation.[43] Precipitation with ammonia or ammonium carbonate has the additional advantage that the hydroxide can be filtered much more quickly and washed with 40% less water than for example in the case of catalysts precipitated with soda. Furthermore, the precipitant can easily be recovered with quicklime.

Precipitation is performed with hot solutions and with vigorous stirring in as short a time as possible, the precipitant being added to the solution. Brief boiling of the precipitate facilitates the filtration and titrimetric standardization of the precipitant against the iron solution. This standardization must be chosen so that once the precipitation is complete, the hydrogen ion concentration will be pH 7-7.3.[48-50]

Recent laboratory investigations have shown[51] that continuously conducted precipitations guarantee a better reproducibility of the catalyst properties, especially in the case of precipitations of multicomponent catalysts, for example as developed for the selective control of the synthesis in the direction of short-chain olefin production (see Sec. 3.7). In the precipitation of these two-component catalysts, a specified pH region must be rigorously maintained in order to inhibit the formation of amine complexes and to obtain the fullest possible precipitation. Other factors affecting the precipitation include the metal content of the metal solution, the metal concentration, the ammonia concentration, and the precipitation temperature. Of particular importance is the maintenance of a short residence time of the precipitate in the precipitation reactor. These factors led to the development of a modified zone precipitation reactor[52] with built-in stirring blades (Fig. 6). The preheated metal salt and precipitation solutions enter the base of the reactor tangentially. The catalyst suspension is picked up at the main overflow and conducted directly to filtration. The precipitation pH and temperature are likewise measured at the top. Such a zone reactor with 14 superposed stirring blades also shows, for a small liquid throughput, a residence time behavior similar to that of a cascade of 10 to 15 (depending on the throughput and stirring rate) ideal agitator vessel units.

Filtration and washing should be carried out as quickly as possible to prevent a change in the gel. Alkalinization is done either by adding potassium carbonate to the last wash water or by stirring the filter cake with dilute potassium carbonate solution.

The activity, selectivity, efficiency, lifetime and protection against carbon deposits are increased considerably if after drying, the ferric oxide catalyst is subjected to annealing at 250-350°C with air[53,54] or oxygen. The effect of annealing is causally related to the formation of short-period lattice defects, to the decrease in crystallite size[55] and to the shift of the pore-frequency maximum to larger pore diameters.[56]

3.2.3. Formation

The ferric iron must be converted to the metallic bonding state before the catalyst can be put to use. Iron-carbon inclusion structures such as carbides have bonding states similar to that of metallic iron. This bonding state is obtained by treatment with carbon monoxide or carbon monoxide-hydrogen mixture, or by consecutive treatment with carbon monoxide and hydrogen.

The suspension containing the catalyst, which was dried and ground wet in slack wax, is fed into the reactor filled with liquid medium and heated to a temperature 15-30°C above the final operating temperature. The reactor is then brought to the latter temperature as quickly as possible. The suspension is vigorously agitated with an inert gas (N_2, CO_2) at the final operating pressure (8-15 atm). As soon as the formation temperature is reached, the system is suddenly switched from inert gas to synthesis gas (CO/H_2 = 1.3-1.5; space velocity of about 2,000 h^{-1}). This causes a "formation wave" to set in during the first few minutes and results in a higher CO-conversion in the first stage of the reduction, as indicated by the high CO_2 concentration in the final gas, but this concentration decreases very quickly, then slowly rises again. As the CO_2 concentration asymptotically approaches a limiting value, the formation is completed several hours later. Depending on the desired throughput and conversion, the temperature is lowered by 15-30°C. The catalyst is now ready for use.[57,58] The formation temperature depends on the activity of the catalyst and on the product spectrum for which it was prepared. If the formation temperature is too high, the danger of "supercarbonization" exists; if it is too low, the formation does not get started. In both cases, there is a reduction in catalyst activity.

3.2.4. Regeneration

The activity of the iron catalyst becomes depressed because of poisoning, recrystallization, oxidation, and the formation of stable iron carbides and elemental carbon. Pilot-scale experiments have shown that the iron catalyst used in liquid-phase synthesis can be regenerated repeatedly and simply by oxidation so that it regains its full efficiency. Moreover, the formation of carbon is reduced to one-half of the amount measured in the presence of fresh catalysts, so that lifetime or contact efficiency can be increased considerably. At the same time, undesirable methane formation is also repressed. It is probable that "superactive" regions of the catalyst, which are especially active in catalyzing the formation of carbon and methane, are destroyed during annealing. In addition, as already st[illegible], structural changes must also be a contributing factor. Accordingly, the catalyst efficiency and lifetime increase. The selectivity in the direction of low-boiling olefins is also increased, so that 80% of the hydrocarbons formed, with an average olefin content of over 80%, will boil below 200°C.

3.3. Operation Results of the Demonstration Plant

At the time when the demonstration plant was in operation (1952-1953), the interest in the Fischer-Tropsch synthesis was essentially confined to the production of gasoline. Accordingly, the processes and the operating mode of the demonstration plant were totally geared toward this goal. Table 2 summarizes typical operational data and synthesis results obtained by the demonstration plant.

The chief technical problem of heat removal from the reactor was definitely solved. The temperature gradient in the reactor never amounted to more than ±1°C. Overheating regions could not be detected, even though the reactor gas load had been increased to 5 times the specified amount. Complete removal of the heat produced by the conversion of 1,000 m^3 of synthesis gas per hour required less than 50 m^2 of cooling pipe surface area. Grinding of the catalyst [illegible] μ fineness and a turbulent mixing of the suspension provided a uniform distribution of the catalyst in the suspension. The difference in concentration of the suspension between the bottom and top of the bubble column amounted to no more than 0.2-0.6 wt.% Fe. No deposits of the catalyst on the cooling pipes and reactor wall could be detected. The catalyst efficiency up to regeneration amounted to 400 kg of hydrocarbons per kg Fe. The gas load for complete synthesis gas conversion could be raised to only 3 m^3/kg Fe/h because of insufficient compressor output. Results of pilot-scale experiments have shown, however, that for industrially justifiable conversions the gas load can be increased to twice that amount.

The high selectivity with respect to methane formation could also be achieved in a large industrial reactor. Despite the high temperature required for the manufacture of gasoline as the main product, only about 4% of the total hydrocarbons produced were in the form of methane and ethane. A comparison of the results for a laboratory reactor of 6 ℓ capacity and a large industrial reactor of 10,000 ℓ capacity, both operated under the same conditions, with the same gas and the same catalyst, demonstrated (Columns a and b of Table 2) that the reactor was capable of being enlarged on a scale of 1:1666. All the results were in mutual agreement except for the reactor efficiency because, owing to the narrow reactor cross section, the gas load and hence the space-time yield of the laboratory reactor had to be smaller.

The results obtained during the operation of the demonstration plant, and the collection of process and reaction data essential for designing large-scale plants along with economically important consumption data, formed the basis for the offer made by Heinrich Koppers GmbH, Essen to the Indian government to erect a complete liquid-phase synthesis plant with an annual production of 250,000 t in 1955. As is well known, because of the switch from coal to petroleum, the plans for constructing a F-T plant in India did not materialize.

3.3.1. Composition and properties of the products

As already mentioned, the production goal for the demonstration plant was to make gasoline. An analysis of such a synthetic "gasoline" product according to boiling range and properties is shown in Table 3. The product analyzed was a sample from large storage tanks which contained the products from one of the longer operating periods. The operating conditions under which this product was made are listed in Table 2. The olefin content, which is of importance for petrochemical processing, is given as 70-85% for the C_3-C_4 fraction. It fluctuated between these limits because of a change in operating conditions over the long period of operation to which the analyses are referred. Worth noting is the high olefin content (70%) of the 40-180°C fraction, which is of interest as raw material for the Oxo process. Almost one-half of the 180-220°C fraction important for the production of surface-active agents consists of olefins.

Gasoline, the production goal of the demonstration plant, was obtained in the proportion of 85% in the C_3-synthesis products. The raw primary gasoline (25-190°C), with a Reid vapor pressure of 0.55 atm, had an intermediate octane rating (IOR) of 73 which, after thermal treatment with Al_2O_3, rose to 83. Mixing with polymer gasoline without adding lead gave an octane rating of 93. About 12% of the liquid products were diesel fuels (190-310°C) with a solidification point of -13°C and an ignition value of over 70 (cetane number). As products of the F-T synthesis, the materials were free of sulfur and thus ideally met present requirements for environmentally safe automotive fuels.

3.4. Flexibility and Selectivity of the Process

The construction and operation of plants for the production of chemical raw materials from coal will always carry economic risks because of the competition of petroleum. These risks will increase if the processes are geared toward a specific, narrow production spectrum which, in the presence of a change in market demand, does not permit one to face this change and to readjust the production. The liquid-phase process does not involve this risk because, in contrast to other processes, the composition of its products and the composition of the synthesis gas give it a high flexibility.

The product composition can be controlled by changing such important reaction variables as temperature, pressure, CO/H_2-content of the synthesis gas, space velocity, etc., over a relatively wide range, something that cannot be done in fixed bed processes or in fluidized bed or dust processes. These processes are necessarily very limited as regards the gas composition (fixed bed) and operating temperature (fluidized bed and flying dust process), resulting in a rather inflexible product spectrum. The reason for the confinement of the last two processes solely to low-boiling products is the high flow velocities of the synthesis gas or circulating gas required to maintain the flying-dust or fluidized state. Obtaining a sufficient yield for these very brief residence times requires a reaction temperature in excess of 300°C, so that a sufficiently high reaction rate can be achieved. However, since high temperatures promote the formation of carbon from the decomposition of carbon monoxide, causing the catalyst granules to burst and disintegrate in the indicated processes. The decomposition of the carbon monoxide must be curbed by means of a high proportion of hydrogen in the synthesis gas. Both high temperatures and a high hydrogen content of the synthesis gas necessarily lead to the formation of large amounts of undesirable methane and therefore to a low selectivity.[59]

In order to make the synthesis economically attractive, over 80% of whose cost is accounted for by the synthesis gas, a high selectivity and yield are of essential importance, since the synthesis gas must be converted into valuable petrochemicals, a class to which methane does not belong. The high selectivity of the liquid-phase process, characterized by a low methane yield amounting to only about 3% of the total products, can be attributed, on the one hand, to the impossibility of overheating of the catalyst, and on the other hand, to the preferable use of CO-rich gases with a low partial pressure of hydrogen.

3.4.1. Flexibility in product composition

Next to the type of catalyst of particular importance is the choice of the operating temperature, which determines the equilibrium position between the synthesis of molecules prevailing at low temperatures and the decomposition of molecules at high temperatures.[60,61] The flexibility thus achieved will be demonstrated with the results of small-scale experiments (reactors with daily outputs of 4-20 kg hydrocarbons).

3.4.1.1. *Preparation of Low-Molecular Products*

A low-molecular, olefin-rich product containing more than 80% of hydrocarbons boiling below 200°C with an olefin content of 80% was obtained by use of high temperatures (274-278°C) and a regenerated catalyst. Another way of producing low-boiling olefins consists in splitting the synthesis fractions of the 290-320°C boiling range at high operating temperature by recycling into the liquid-phase reactor during the synthesis over suitable iron catalysts to form products rich in olefins.[62] The operating conditions, results, product range and olefin content of the fraction are shown in Table 4.

The application of high operating temperatures to the production of low-boiling olefins is normally limited by the increased formation of methane and carbon. These undesirable side reactions can be inhibited if the temperature in the liquid-phase reactor from the gas inlet to the gas outlet, that is, from the bottom to the top, is allowed to rise by 30-60°C. This can be achieved by the use of appropriate cooling surfaces which decrease from the bottom toward the top[59,63] In this way, the temperature in the reactor increases - which is logical from the standpoint of reaction kinetics - as the synthesis gas becomes increasingly depleted of reactants from the bottom to the top. The formation of carbon and methane in the upper, warmest reactor zone is inhibited by the low CO and H_2 concentrations prevailing there, so that for a high gas conversion and high yield, a low-boiling product very rich in olefins is obtained. Without any loss of good selectivity, Table 5 gives the composition of a product obtained by this method, along with the operating conditions and results of a small-scale experiment that was discontinued after 1,644 hours.

3.4.1.2. *Preparations of Higher-Molecular Products*

The formation of higher-molecular products is favored by low operating temperatures and a high alkali content of high-activity iron precipitation catalysts, and also by the chain-extending molecular structure of the hydrocarbons present in the catalyst suspension or recycled into it.[61] In this operating mode, enough filtrate is continuously removed from the reactor through a pressure filter to keep the filling level of the reactor constant in proportion to the quantity of higher-boiling hydrocarbons which do not escape freely with the residual gas. In the example cited, the filtrate would be distilled, and the fraction boiling up to 320°C together with 33% of a synthesis fraction boiling between 260°C and 320°C would be fed back into the reactor. Thus, 244 g of total product per Nm^3 and $CO + H_2$ was recovered, 177 g of which was formed from $CO + H_2$, and 67 g consisted of paraffin and hard wax synthesized from the fraction recycled into the reactor. About 80% of the recycled fraction is involved in this molecule enlargement.

Table 6 shows the remaining operating conditions and results as well as the composition of the total reaction products.

If during the sequence just described, water gas ($CO/H_2 = 0.84$) is used instead of carbon monoxide-enriched gas, the proportion of hard wax (450°C) is increased at the expense of that of paraffin slack wax (320-450°C). Thus the yield is 96 g of hard wax per Nm^3 of $CO + H_2$ used.[63]

3.4.1.3. *Preparation of Oxygen-Containing Products*

For the sake of completeness it must be mentioned that the synthesis in a liquid medium can also be steered in the direction of oxygen-containing products.[64] This can be done by feeding potassium carbonate into the catalytic suspension. At a conversion of about 85%, the total yield was 172 g of products per Nm^3 of $CO + H_2$. The product contained C_2-C_5 alcohols, 75 g/Nm^3, and C_6-C_{21} alcohols, 25 g/Nm^3 of $CO + H_2$.

3.4.2. Flexibility of gas composition

The F-T synthesis in the liquid phase can be performed with hydrogen-enriched gases just like in fixed-bed or flying dust reactors. However, as in the above-mentioned techniques, the yield for a one-step procedure or without gas circulation is lower, because of the CO consumption in the conversion reaction, than when carbon monoxide-enriched gases are used. As in the fixed-bed process, the conversion reaction which adversely affects the yield can be limited in the gas-phase process by lower operating temperatures and short gas residence times. For this purpose, the process is carried out in several steps and/or by recirculating the gas with intermediate removal of the water of reaction.

Because of the lower operating temperatures and the higher alkalization of the iron catalysts which is therefore required, it has become more difficult to synthesize preferentially low-boiling hydrocarbons from the hydrogen-rich gas. Also, because of the higher partial pressure of the hydrogen in the synthesis gas, the olefin content of the other products must be less than when gases rich in carbon monoxide are used. For this reason, hydrogen-rich gases (H_2/CO = 1.25-2) were used in experiments at Rheinpreussen mainly when the desired products were slack and hard paraffins. Table 7 shows the operating conditions and results of small-scale experiments using water gas and synthesis gas $H_2/CO = 1.95$. In the experiments here described, the gas leaving the reactor was cooled to 15°C under pressure before it was fed into the second stage or circulation. A large portion of the water of reaction was thereby separated from the gas, but the carbon dioxide was not removed.

The effect of these measures and of the stepwise or circulation process on the improvement of the synthesis conditions can be seen in the limitation of the secondary conversion reaction. Noteworthy is the total suppression of methane formation, due to a high degree of alkalization of the catalysts and to the relatively low reaction temperatures. Thus the yield of C_2+ hydrocarbons is also relatively high for water gas and synthesis gas with $H_2/CO = 1.95$, despite the fact that the synthesis gas is not quite of the "right type."

3.5. Synthesis of Hydrocarbons From Carbon Monoxide and Water

(Kölbel-Engelhardt Synthesis)

The flexibility of the liquid-phase process with respect to the gas composition is further demonstrated by the fact that gases can be used in the synthesis which besides carbon monoxide contain not hydrogen, but steam.[66-69] Iron-cobalt-nickel and ruthenium catalysts are suitable in this case.

This process is especially suited for the utilization of carbon monoxide-containing waste gases (blast-furnace gas, carbide furnace gas, phosphorus furnace oven gas) or of inexpensive generator lean gas from coal, the use of which in gas turbines generating electric power is under discussion at the present time. Best suited are iron precipitation catalysts as described for use in the F-T synthesis. Their optimum temperature range is 250-300°C. The pressure is adjusted to the CO-content of the gas; for a gas having about 35% CO, it is approximately 20 atm, and at 90% conversion of CO, the yield of C_2+ hydrocarbons is 160-170 g per m^3 of CO supplied. Because of a total absence of methane formation, a yield of 198 g is obtained with cobalt catalysts.[70] High-molecular polymethylenes are obtained with ruthenium catalyst suspended in water.[71]

The operating conditions and results of small-scale experiments with original blast-furnace gas, which because of the absence of sulfur compounds did not require any purification, and the composition of the synthesis products, are given in Tables 8 and 9. In composition, the products are similar to those of the liquid-phase F-T synthesis. The selectivity is high - methane + ethane amounted to only 5% of the total products - and so is the flexibility in the product spectrum, as can be seen from column (a) primarily for low-boiling products and from column (b) primarily for high-boiling products. Seventy-six percent of the usable C_2+ products can be obtained as the C_2-C_{10} fraction. The olefin content of the products is very high, due to the absence of hydrogen from the synthesis gas. It amounts to 80-90% of the C_2-C_5 fraction and 70% of the C_5+ fraction. The alcohol content of the products increases with pressure amounting to 30% at 100 atm.

3.6. Developments Abroad

3.6.1. Work at the British Fuel Research Station in Greenwich and at the Warren Spring Laboratory, Stevenage

Work related to liquid-phase synthesis was started at the Fuel Research Station in Greenwich, England, in 1949 under the direction of C. C. Hall.[72] The work was started on a "pilot plant" scale at the Fuel Research Station, Greenwich, and after being interrupted in 1958, was continued at the Warren Spring Laboratory, Stevenage, supported by the Department of Scientific and Industrial Research. The work was stopped in 1961.

The plant was designed for a gas throughput of 70 m^3/h and a production of 310-450 ℓ of products/day, for a pressure range of 1-20 atm and a temperature range up to 300°C. The layout and mode of operation were essentially the same as those of the Rheinpreussen demonstration plant, and modifications are described below. The reactor had a diameter of 24.8 cm and a total height of 8.53 m. The reaction chamber for the expanded suspension was 6 m high and was cooled by four water pressure pipes 2.54 cm in diameter. The free reaction chamber had a volume of 276. The heat of reaction was removed from the reactor by means of a pressure water - thermosiphon system through cooling pipes with a surface area of 2.6 m^2. The level of the suspension in the reactor was kept constant by means of an overflow pipe. Gas was supplied to the suspension through a single jet with a bore diameter of 19 mm, which was designed to operate as a nonreturn ball valve.

From the standpoint of process technology, the performance of the pilot plant at Stevenage was completely satisfactory. In particular, the removal of the heat of reaction was so effective that the temperature at a reactor height of 6 m could be kept constant within ±1°C. The coefficient of heat transfer (suspension-cooling surface-cooling water) was determined as 1400 J/m^2 h deg.

The catalyst used was prepared according to the specifications of Peter Spence Company, Ltd. According to Ref. 88, it was precipitated with ammonia from a solution of ferriferrous sulfate which had been obtained by "partial oxidation" of iron sulfates (copperas). X-ray analysis showed the presence of hematite and spinel structures present in about equal proportions. The high content of potassium promoter, 2.76%, referred to iron, and the SO_3 content, 0.1%, are noteworthy. The SO_3, which is a catalyst poison, may be responsible for the low activity of the catalyst, whereas the pronounced formation of carbon observed during the synthesis is attributable to the unusually high potassium content. The formation of the catalyst took place in the liquid phase with the synthesis gas over a period of 37 hours. In this state, chemical analysis of the catalyst gave 56% of iron and 12.5% of carbon.

It was acknowledged in the discussion section of Ref. 73 that the catalyst employed was unsuitable. This accounts for the very bad CO + H_2 conversion rate, which dropped from 59.4% at the beginning of the experiment to 35.4% after 418 hours. To achieve this conversion, the operating temperature had to be raised from 20°C to 280°C over a period of 430 hours. Because of the high alkali content of the catalyst and an operating temperature above 274°C, this resulted in such abundant carbon formation that the viscosity of the suspension increased from about 2 cP at 185°C to 230 cP. At such high temperature, the relative gas content of the suspension declined so greatly, from 40% to 10%, that because of the markedly reduced interfacial surface area, the gas transport to the catalyst was able to adversely influence the overall reaction rate For this reason, Calderbank's[74] description of the synthesis results and discussion of the theoretical kinetics, based on a system employing an unsuitable catalyst, is unnecessary.

3.6.2. Work at the US Bureau of Mines

The liquid-phase process was investigated on a pilot scale[75-78] at the US Bureau of Mines laboratories, Bruceton/Pittsburgh, Pa., in the years 1948-1953.

The reactor consists of a pressure pipe of 76 mm inside diameter and 3.1 m height, and a reaction chamber of 13.5 liter capacity. The reactor bottom is cone-shaped and contains the gas injection jet. The reactor top forms an expansion container to prevent the suspension from foaming over. Welded into the reactor wall is a porous pipe made of sintered bronze (of the same diameter as the reactor pipe) and surrounded by a pressure sleeve. This circular space permits the withdrawal of a filtered, catalyst-free product from the reactor. The catalyst collecting at the interior wall of the filter pipe during filtering is washed by the turbulent suspension. From the reported space velocities of the gas, 130 - 500, an hourly gas throughput of 1.75-6.7 m^3 is obtained.

In addition to precipitation, fusion, sintering and ammonia catalysts, the investigation also covered various iron ores, chiefly alkalized magnetites. It was shown that formation, which was mostly performed in the liquid phase, was of decisive importance for the activity and lifetime of the catalysts.

As a rule, water gas or synthesis gas with a CO/H_2 ratio of 1 was used. The yields obtained were correspondingly modest, and the olefin content of the products was relatively low. Since no detailed descriptions are given in the research reports cited,[75] it was not possible to tabulate the experimental results. Some of the data which appear important include the following items. With iron precipitation catalysts, a synthesis gas conversion of 90% at temperatures between 230 and 260°C and a pressure of 10.5 atm was obtained. A 2000-hour run yielded 476 kg of hydrocarbons and 28 kg of oxygen-containing compounds per kg of iron. Seventy-nine percent of the liquid products consisted of hydrocarbons in the boiling range of gasoline (50-190°C), and 13% consisted of hydrocarbons in the diesel oil range (220-320°C). The solid paraffins obtained amounted to only 2%.

With the use of an inexpensive catalyst prepared very simply by impregnating magnetite (Alan Wood) with potassium carbonate, a 71% conversion of synthesis gas with a CO/H_2 ratio of 1:1 was achieved by circulating the gas at a pressure of 21 ata, a space velocity of 300, and a temperature of 260°C. Eighty percent of the products consisted of hydrocarbons of C-number 3 and higher, boiling below 200°C; the other 20% consisted of methane, ethylene, and ethane. Raising the temperature by 10°C increased the gas conversion to 82%, while the increase in the proportion of C_1 and C_2 hydrocarbons was insignificant. The yield of this fraction was reduced by 13% by performing the synthesis in two consecutive steps.

Nitrided iron fused catalysts[78] were subsequently also used. Because of their greater resistance to carbon formation, these catalysts have a longer lifetime and a special tendency to short-chain olefins and oxygen-containing compounds. The catalysts were reduced with hydrogen to the point where X-ray analysis revealed that at least 90% of the iron had been converted to the metallic bonding state. After the reduction, the catalysts were treated with ammonia gas until the atomic ratio N/Fe became 0.45, and X-ray analysis at that point showed the hexagonal nitride to be prevalent. The reduction and nitriding can be performed in a fixed bed as well as in the liquid phase. The best formation method consisted in treating the suspension (14% Fe) with synthesis gas ($CO/H_2 = 1$) at a pressure of 21 atm and a space velocity of 200/h. The temperature and duration of the formation were not reported.

A fused catalyst formed in this manner produced the results shown in Table 10. Because of the deviation of the consumption ratio H_2/CO of 0.81 as compared to the supply ratio of 1, the conversion referred to $CO + H_2$ and the corresponding yield had to be relatively low. The proportion of C_1 and C_2 hydrocarbons was surprisingly high; the proportion of ethylene was not reported. The proportion of oxygen-containing compounds (45% of the water-soluble products consisted of ethanol) amounted to about 46% of the total C_3+ products up to an operating temperature of 240°C, corresponding to a $CO + H_2$ conversion of 45%. Above this temperature, the proportion of oxygen-containing products drops markedly. The olefin content of the hydrocarbons increases with the space velocity of the synthesis gas; the following limiting values are given for this case: C_2 fraction, 7-43%; C_3, 47-84%; C_4, 60-80%. The olefin content of the "oil" was reported with bromine numbers of 8-46 depending on the operating conditions.

3.6.3. Work at the Indian Institute of Technology, Kharagpur

A distinctive feature of the Dowtherm-heated reactor (length, 3 m; Ø 0.05 m) employed at this institute[79] was the use of an injector nozzle at the reactor bottom, which provided for a good distribution of the gas and a fast circulation of the suspension from the top to the bottom of the reactor. A precipitated iron support catalyst of the following composition was used: 100 Fe : 10 Cu : 4 MgO : 3.5 CaO : 50 diatomaceous earth.

The synthesis gas contained CO and H_2 in the ratio 0.7 (water gas). The optimum reported yield was 174 g of liquid product per m^3 of CO + H_2 used; it was obtained at 260°C, 10.5 bar, and a space velocity of 100 h^{-1}. The yield seems very high, and the small extent of the secondary water gas reactions is surprising. Both are attributable to the special characteristics of the catalyst.

3.6.4. Work at the Department of Synthetic Chemistry of Tokyo University[80]

The reactor was based on the design of the bubble column used for small-scale experiments by Rheinpreussen. Its inside diameter was 50 mm, and its height, 5.5 m. The reactor pipe was surrounded with a heating jacket and heated with Dowtherm liquid. The gas throughput was 1.2-3 m^3/h. An iron catalyst of the composition 100 Fe : 0.3 Cu : 0.6 and 1.2 K_2CO_3 was used; it was formed under pressure with CO-rich synthesis gas.

Results of the synthesis are given in Table 11. The English abstract reports yields of 10-45 g of gaseous and 110-170 g of liquid hydrocarbons per Nm^3 of synthesis gas. The very high content of carbon monoxide in the synthesis gas accounted for the remarkably high olefin content of the products. (The C_3-C_5 fraction contained 90 wt.%, and the C_6-C_{15} fraction, 75 wt.% of olefins).

3.7. Selective Liquid-Phase F-T Synthesis

Since 1973, attempts have been made in the Federal Republic of Germany to replace petrochemical products with products obtained from coal.[42,81-83] Of greatest current interest is selective synthesis aimed at short-chain

C_2-C_4 olefins and other chemical raw materials like α-olefins with C-numbers in the C_8-C_{14} range for the production of detergents,[84] and oxygen-containing materials (aldehydes).

While the adjustment of the operational parameters for the production of medium-chain olefins does not present any problem, the operational mode aimed at a sufficient selectivity for C_2-C_4-α-olefins depends on the development of new catalysts. These catalysts must be less active in hydrocarbon chain propagation. Their hydrogenating effect must not be too strong, or it would lead to higher proportions of methane and to further hydrogenation of the olefins initially formed. These catalysts also must be better suited for higher operating temperatures than the traditional iron and cobalt catalysts, especially so that short-chain products can be obtained. At the same time, they must exert only a weak catalytic influence on the Boudouard reaction, so that the liberated carbon will not influence the lifetime of the catalyst.

The search for selective catalysts has led to the discovery of new contacts whose synthesis properties are shown schematically in Fig. 7. Whereas the classical iron and cobalt catalysts produce a wide spectrum of hydrocarbons, the newly developed contacts are characterized by a selectivity in the direction of formation of short-chain hydrocarbons.

These new contacts can be divided into four groups:

(a) The first group includes iron catalysts modified by additions of oxides of titanium, vanadium, molybdenum, and manganese.[86] They are produced as multicomponent precipitation or sinter catalysts.

(b) In the second group, selectivity of the contacts is obtained by partially poisoning the catalyst surface with sulfur. Franz Fischer recognized as early as 1932 that such poisoning leads to a shifting of the product spectrum in the direction of short-chain hydrocarbons. Newly initiated studies in this area have led to the discovery of selective catalysts based on partially poisoned iron whiskers with added promoters (K, Au, Co).[87]

(c) The third group includes iron-base catalysts developed by the Sasol Company in Sasolburg, South Africa. Data on their composition have not been published.

(d) The fourth group consists of manganese catalysts[88] developed by Kölbel and Tillmetz at Berlin Technical University in 1974 and containing 10-20 wt.% of iron. They act selectively both as precipitation contacts and alloy catalysts. These catalysts can be used, in particular, for the processing of carbon-monoxide-rich gases which yield a product rich in olefins, since the liberation of carbon on the new catalyst is only very slight. The composition of these products can be influenced by varying the Mn-Fe ratio over a wide range. A higher iron content leads to a more hydrogenated product with a longer chain.

The yields which can now be obtained in laboratory fixed-bed reactors without circulation are around 100 g of C_2-C_4 hydrocarbons per 1 Nm^3 of synthesis gas with an olefin content of about 70%. A reduction in selectivity was observed in the selective liquid-phase synthesis, wherein the yield of C_2-C_4 olefins amounted to only about 60% of that obtained in the laboratory fixed-bed reactor.[89] This fact can be accounted for by the subsequent hydrogenation of the initially formed olefins as a result of back mixing in the liquid phase, and hence by their wide residence time distribution.

With the aid of statistical experimental plans and the regression models derived from them, the tendencies leading to the optimum selectivity toward short-chain olefins were determined by use of manganese catalysts (synthesis pressure: 11 bar).[90] The selectivity of C_2-C_4 olefin formation and that of C_2-C_4 hydrocarbon formation (olefins + paraffins), expressed in g of products per 1 Nm^3 of converted synthesis gas, was chosen as the target function. An assessment of the optimization process showed that the selectivity of C_2-C_4 olefin formation in the technologically relevant range of the process variables increases with increasing CO/H_2 ratio, falling synthesis temperature, and increasing linear velocity of the synthesis gas. The same results were obtained by the optimization, when the selectivity of formation of C_2-C_4 olefins plus paraffins was studied as the target quantity. Thus, the two target quantities are symbatic.

However, other groups of catalysts behave differently.[91] "Sasol" catalysts, for example, lead to increased linear velocities in the reactor and thus to a better C_2-C_4 selectivity, but the C_2-C_4-olefin yield declines with rising CO content of the synthesis gas.

Reducing the average residence time by increasing the gas load or the linear gas velocity has its limits, since a marked decrease in conversion must be reckoned with. In this case, the products present in the residual gas in only very low concentrations can be isolated only with a considerable expenditure of energy and at high cost.[91] This makes it necessary to perform the process at high gas velocities in stages.

3.8. Notes on the Development of Large-Scale Reactors

The target for large-scale reactors is as large a diameter or cross section as possible at a suspension layer height of 5.8 m. However, an increase in cross section makes a uniform gas distribution of the suspension more difficult. At points of low resistance and favored gas outflow, the gas moves more quickly through the liquid. The hydrostatic equilibrium is disturbed, the residence time of the gas becomes nonuniform, and this results in a rolling motion of the liquid with vigorous back mixing. Other factors which will have to be reckoned with include the tendency of the gas to move to the center and of the liquid to move along the walls. In cases where these phenomena are strongly influenced by the cooling pipe bundle, they should be considered in the further development of reactors with large cross sections.

The uncontrollable rolling movement of the liquid can be avoided by building-in vertical shafts open at the top and bottom and having a honeycombed cross section. They are located at a sufficient height above the gas distributor so that the suspension can commute freely, and they open into a common gas chamber in the upper part of the reactor (Fig. 8). The gas is introduced either into each shaft individually, or by a gas ejector centrally mounted in the cone-shaped bottom of the reactor. The cooling pipes can be arranged centrally around the shafts or in corners, as shown in Fig. 8. The cooling surfaces of such shaft reactors can be reduced in the direction from the bottom to the reactor head in such a way that the suspension temperatures from the gas inlet to the gas outlet will increase by 30-60°C,[17,92] this being essential for catalyst efficiency and the preferential formation of low-boiling olefins.

Notation:

a	gas-liquid interfacial area per unit volume of 3-phase system, cm^2/cm^3 (bzw m^2/m^3)
c_p	specific heat capacity, J/gK
c	concentration
D	diffusion coefficient, cm^2/s
d_B	mean bubble diameter, cm
d_R	reactor diameter, cm
d_S	mean diameter of solid particle, cm
E	dispersion coefficient, cm^2/s
Fr	Froude number, $u_{Go}^2/(d_S)$
g	gravitational acceleration, cm/s^2
h	heat transfer coefficient, $J/m^2\ s\ K$
k_L	liquid side mass transfer coefficient, cm/s
k_S	liquid-solid mass transfer coefficient, cm/s
p	pressure, kPa (bzw bar)
Pr	Prandtl number, $\eta c_p/\lambda$
Re	Reynolds number, $u_{Go} d_S \rho/\eta$
Sc	Schmidt number, $\eta/D\rho$
Sh	Sherwood number, $k_L d_B/D$ bzw $k_S d_S/D$
St	Stanton number, $h/(\rho c_p u_{Go})$
T	temperature, °C
u	superficial velocity, cm/s
u_t	terminal rise velocity of single bubble, cm/s
X	conversion

Greek symbols:

α	dimensionless constant
ε	holdup
η	dynamic viscosity, Pa s
λ	heat conductivity, J/msK
ρ	density, g/cm^3

Indices:

o	inlet
G	gas
L	liquid
S	solid

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Table 1. Summary of relations for estimation of hydrodynamic properties of a Fischer-Tropsch slurry reactor. Liquid phase: molten paraffin, temperature: 250-290°C, pressure: 400-1100 kPa, Gas velocity: <4 cm/s, solid contents: >5 wt.%

Gas holdup	$\varepsilon_G = 0.053\, u_{Go}^{1.1}$ $\varepsilon_g (1 - \varepsilon_G)^{2.22} = u_{Go}/u_t$
Bubble diameter, cm	$d_B = 0.07$
Gas-liquid interfacial area per unit volume of 3-phase suspension, cm^{-1}	$a = 4.5\, u_{Go}^{1.1}$
Gas-liquid mass transfer coefficient, k_L	$Sh = 0.0187\, (\beta Re^{0.484} Sc^{0.339})^{1.61}$ $\beta = (d_B g^{1/3}/D_L^{2/3})^{0.072}$ (Hughmark[35]) $k_L Sc^{2/3} = 0.31\, (\rho_L \Delta\rho g/*_L^{2})^{1/3}$ (Calderbank, Moo-Young[29])
Liquid-solid mass transfer coefficient, k_S	$Sh_S = 2$
Liquid-solid interfacial area per unit volume of 3-phase suspension, cm^{-1}	$a_S = \dfrac{6(1-\varepsilon_G)\rho_L}{d_S \rho_S}\, \bar{c}_S$
Heat transfer coefficient h	$St = 0.1\, (ReFrPr^2)^{-1/4}$

*symbol missing in original [translator]

Table 2. Operating data and results of liquid-phase synthesis (14) for one-step operation with a single passage of the gas over iron catalysts. (a) pilot plant
(b) laboratory plant

	a	b
Effective reaction space (volume suspension including dispersed ,), (l)	10,000	6
Catalyst (kg Fe)	800	0.4
Synthesis gas pressure (bar)	12	11
Synthesis gas (volume ratio, $CO:H_2$)	1.5	1.5
Quantity of synthesis gas (Nm^3/h)	2700	1.3
Linear velocity of the compressed gases at operating temperature referred to the free reactor cross section (cm/s)	9.5	3.5
Total $CO + H_2$ used (Nm^3/h)	2300	1.1
per m^3 of reaction chamber (Nm^3/h)	230	183
per kg of Fe (Nm^3/h)	2.6	2.45
Average synthesis temperature, °C	268	266
CO conversion, %	91	90
$CO + H_2$ conversion, %	89	88
Synthesis products referred to $CO + H_2$ used		
Hydrocarbons C_1+ (g/Nm^3)	178	176
$C_1 + C_3$ (g/Nm^3)	12	11
C_3+ (g/Nm^3)	166	165
O-containing products in the synthesis water (g/Nm^3)	3	2
Space-time yield of C_3+ products incl. O-products in 24 hours (kg/m^3 of reaction chamber)	930	740

Table 3. Composition and properties of a product from the demonstration plant
(Mode of operation adjusted for gasoline production)

	G/Nm^3 CO+H$_2$	Weight % of total product C$_1$+	% Olefin	Av. molec. weight	Density, 20°C	OH number mg KOH/g	Acid number mg KOH/g	Ester nmb. mg KOH/g
Methane + ethane	5.7	3.2	0	-	-	-	-	-
Ethylene	613	3.6	100	-	-	-	-	-
C$_3$	40.3	22.6	75-85	-	-	-	-	-
C$_4$	9.1	5.1	70-80	-	-	-	-	-
40-180°C fraction	95.5	53.6	70	93.9	0.683	19.4	0.38	3.25
180-220°C	7.1	4.0	48	139.4	0.760	4.6	0.25	1.26
220-320°C	10.7	6.0	37	218.0	0.781	2.3	0.16	0.65
> 320°C	3.3	1.9	7	300.5	0.811	0.0	0.45	1.05
Total	178.0	100.0						

Table 4. Conditions, results, and product composition of a liquid-phase synthesis with simultaneous cleavage of recycled products[62]

Synthesis	
Temperature, °C	270°
Pressure, bar	12
Synthesis gas CO/H_2	1.5
Space velocity, vol. gas/vol. susp. h	180
Circulation ratio, fresh gas:final gas	1:1
Iron precipitation catalyst ($\sim$0.1 wt.% K_2CO_3)	
Yield, g C_1 HC + Nm^3 ($CO + H_2$)	170
Yield, methane + ethane/Nm^3 ($CO+H_2$)	16
Yield, g C_2 HC + Nm^3 ($CO + H_2$)	163
Cleavage yield, g low-boiling HC/Nm^3 ($CO + H_2$)	39
Total yield C_2+ HC from synthesis and cleavage, g/Nm^3 ($CO + H_2$)	218

Product composition		
Fraction	Weight %	Olefins, %
C_1	10.6	-
C_2	4.2	86
C_3	6.5	85
C_4	8.3	85
15-150°C boil.	51.0	86
150-200°C boil.	7.1	85
200°C	10.6	76
alcohols	1.2	-

Table 5. Operating conditions and results of a synthesis in the liquid-phase reactor with temperature increasing from top to bottom[59]

Temperature, °C	
at gas inlet	270
at gas outlet	305
Pressure, bar	12
Synthesis gas CO/H_2	1.5
Catalyst load m^3 gas/kg Fe h	2.7
Catalyst from large-scale production, 0.2% Cu; 0.5% K_2CO_3 (referred to Fe)	
CO conversion, %	
After 1400 h of operation	90
Yield after 1400 h of operation	
C_2 HC + g/Nm^3 $(CO + H_2)$	169.0
C_3 HC + g/Nm^3 $(CO + H_2)$	163.0
Methane + ethane g/Nm^3 $(CO + H_2)$	7.7

Composition of C_3+ HC products

Fraction	Portion, %	Olefins, %
$C_3 + C_4$	34.0	86
C_5	25.1	90
C_6	9.2	85
C_7	6.9	83
C_8	6.4	86
C_9	4.5	83
C_{10}	2.3	79
C_{11-12}	3.1	-
C_{13-15}	3.2	-
C_{16-17}	1.8	-
C_{17}	2.5	-
Alcohol	1.0	-

HC = hydrocarbons

Table 6. Operating conditions, results and product composition of a synthesis of high-boiling products[63]

Temperature, °C	216-230
Pressure, bar	11
Synthesis gas, CO/H_2	1.3
Space velocity, vol. gas/vol. susp. h	116
CO-conversion, %	>90
Catalyst, Iron precipitation catalyst K_2CO_3, 1 wt.%	
Yield from synthesis, g/Nm^3 $(CO + H_2)$	177
Yield of HC >320° from Molecule building g/Nm^3 $(CO + H_2)$	67
Total yield of C_3 HC + g/Nm^3 $(CO + H_2)$	244

Composition of total products from synthesis and molecule building

Fraction	Portion in wt.%
$C_3 + C_4$	2.9
26-120°C	7.1
260-320°C	2.2
320-450°C	52.4
Hard wax >450°C	22.6
F_p 102°C	
Alcohols from synthesis water	1.2

Table 7. Operating conditions and results of liquid-phase synthesis with hydrogen-rich gases and precipitated alkalized Fe-catalysts[65]

Type of gas	Water gas			H_2-Enriched gas
H_2/CO ratio	1.1	1.2	1.2	1.95
Temperature, °C	247	238	230	226
Pressure, bar	16	13	13	13
Gas flow	1 step without circulation	2 steps	circulation 2.5:1 + 2nd step without circulation	circulation 1.5:1
Space velocity, vol. gas/vol. susp. h	130	105	245	240
CO conversion, %	93	93	95.5	95
Consumption ratio H_2:CO	0.76	0.89	1.05	1.43
Yield, g C_2+ HC/Nm^3 (CO+H_2)	140	157	168	163
Yield, g CH_4/Nm^3 (CO+H_2)	6	0	0	0

Table 8. Operating conditions, results and product composition for liquid-phase synthesis using carbon monoxide and steam[67]

Operating conditions	
Average composition of top gas used, %	7 CO_2 34 CO 2 H_2 57 N_2
Amount of top gas used, Nm^3/h	20
Effective reaction chamber (volume of suspension in operating state incl. gas), liter	9
Amount of catalyst (iron contact), g Fe	384
Synthesis pressure, bar	16
Synthesis temperature, °C	240-280
Contact load Nm^3 CO/kg Fe h	1.8
CO/H_2O ratio in entering gas	3:1.15

Results	
CO-conversion, %	92
Yield of hydrocarbons, g/Nm^3 CO	182
Yield of C_3 and higher (C_3+) hydrocarbons, g/Nm^3 CO	160
Total catalyst efficiency (total amount of C_3+ hydrocarbons obtained during the operating time of the catalyst in kg/kg iron)	405
Space/time yield of C_3+ hydrocarbons (kg hydrocarbons per m^3 reaction chamber in 24 h)	272

Table 9. Composition of synthesis products from top gas

(a) synthesis of low-boiling materials

(b) synthesis of high-boiling materials

Fraction	Carbon number	Boiling range, °C	Wt. % of total products (a)	(b)
Methane + ethane	$C_1 + C_3$	-	8.6	8.1
Ethylene	C_3	-	3.5	2.1
Gas oil	$C_3 + C_4$	-	29.8	15.1
Gasoline	$C_5 - C_{10}$	to 190	43.1	17.8
Kogasin I	$C_{11} - C_{14}$	190 to 260	8.1	3.2
Kogasin II	$C_{15} - C_{18}$	260 to 320	4.0	9.7
Slack wax	$C_{10} - C_{27}$	320 to 450	1.7	15.0
Hard paraffin	$> C_{27}$	> 450	1.2	29.0
Total yield of hydrocarbons, g/Nm^3 CO			174	136

Table 10. Operating conditions and results of liquid-phase synthesis using nitrided iron fused catalyst[78]

Temperature, °C	252
Pressure, bar	21.5
Synthesis gas, H_2/CO	1
Space velocity, vol gas/susp. h	200
Conversion of $CO + H_2$, %	69
Consumption ratio, H_2/CO	0.81
Yields, g/m^3 of converted $(CO + H_2)$	
$C_1 + C_2$	46
C_3 and higher	123
O_2-containing products in water of reaction	12.8
Weight % of O_2-containing products in oil	13.1

Table 11. Operating conditions and results of a liquid-phase synthesis at Tokyo University[80]

Synthesis	
Operating hours, h	96.1
Temperature, °C	266
Pressure, bar	10.3
Synthesis gas, CO/H_2	1.7
Gas flow, Nm^3/h	1.5
Catalyst load, Nm^3/kg Fe h	10.0
Concentration of suspension, weight % Fe	3.2
CO-conversion	80.8
Yield, g HC/Nm^3 $(CO + H_2)$	
Methane	6.6
Condensate I	31.6
Condensate II	98.4

TEXT TO FIGURES

Fig. 1. Reactor for liquid-phase synthesis (Rheinpreussen Process)

1 reactor cylinder

2 cooling pipe register

3 liquid level regulator

4 steam drum

Fig. 2. Operational range diagram for a bubble column reactor with suspended solid matter (particle size: 30 μ, $\rho_S \sim 2$, $\rho_L \sim 1$)

Fig. 3. Comparison of experimental and theoretical conversions for the case of mass exchange limitation

F-T synthesis using iron precipitation catalysts[14]

F-T synthesis using selective manganese catalysts[90]

Methanization[30]

CO conversion[34]

Fig. 4. Flow diagram of the large-scale demonstration plant (Rheinpreussen Process)

A freely separated initial products

B final gas for production of low-boiling hydrocarbons

C high-boiling initial products

a compressor

b gas meter

c diaphragm

d sampling intake

e bubble column reactor

f steam collector

g heat exchanger
h separator
i container for separated substances
k pump
l condenser
m CO_2 expulsion unit
n pressure filter
o contact stirring container and container for materials removed from furnace
p centrifuge
q "Anmaisch" oil

Fig. 5. Partial view of the pilot plant

Fig. 6. Diagram of the synthesis of iron and manganese catalysts and selective catalysts

Fig. 7. Construction of the zone reactor for the continuous precipitation of catalysts

a pH and temperature measuring site
b overflow for removing the precipitate
c inlet for metal salt solution
d inlet for precipitant

Fig. 8. Honeycombed inserts with cooling pipes

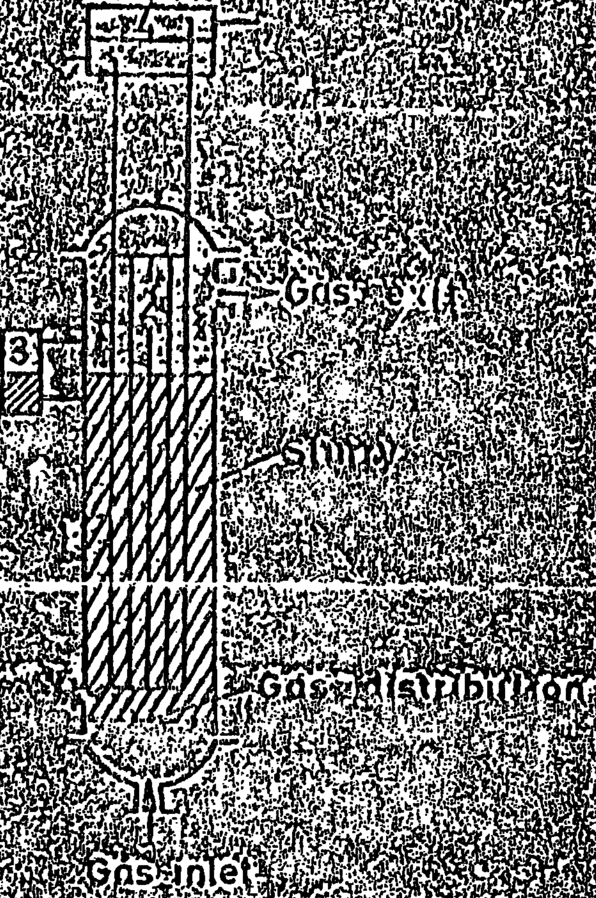

Fig. 1

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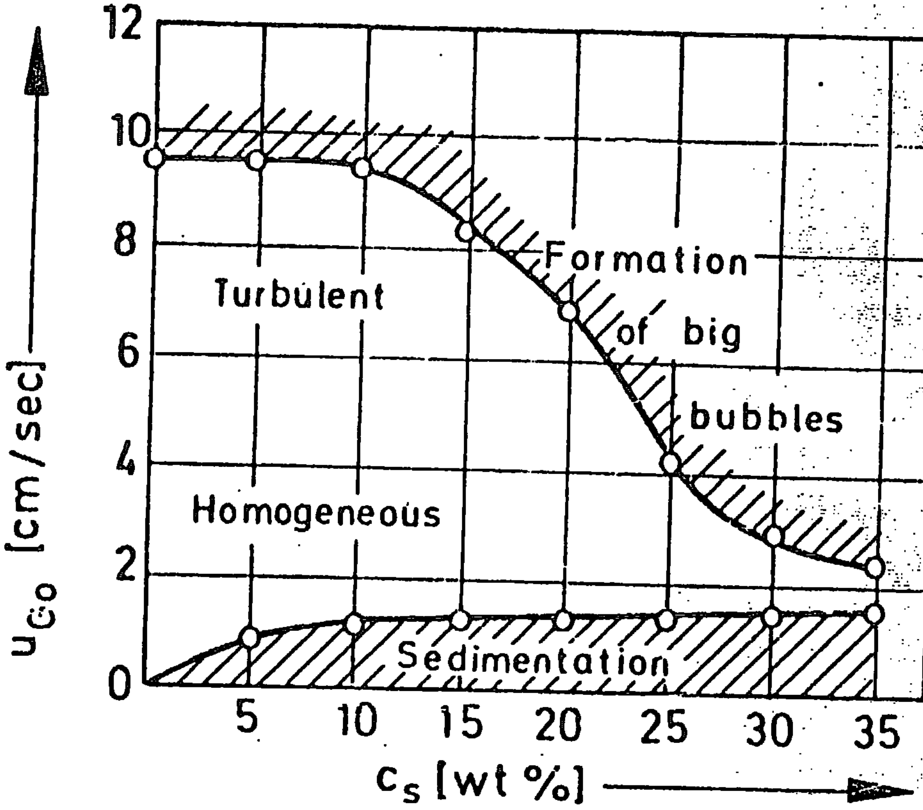
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30
35
c_s [wt %]
Turbulent
Homogeneous
Formation of big bubbles
Sedimentation

Fig. 2.

Figure 3 was not included with the original [translator]

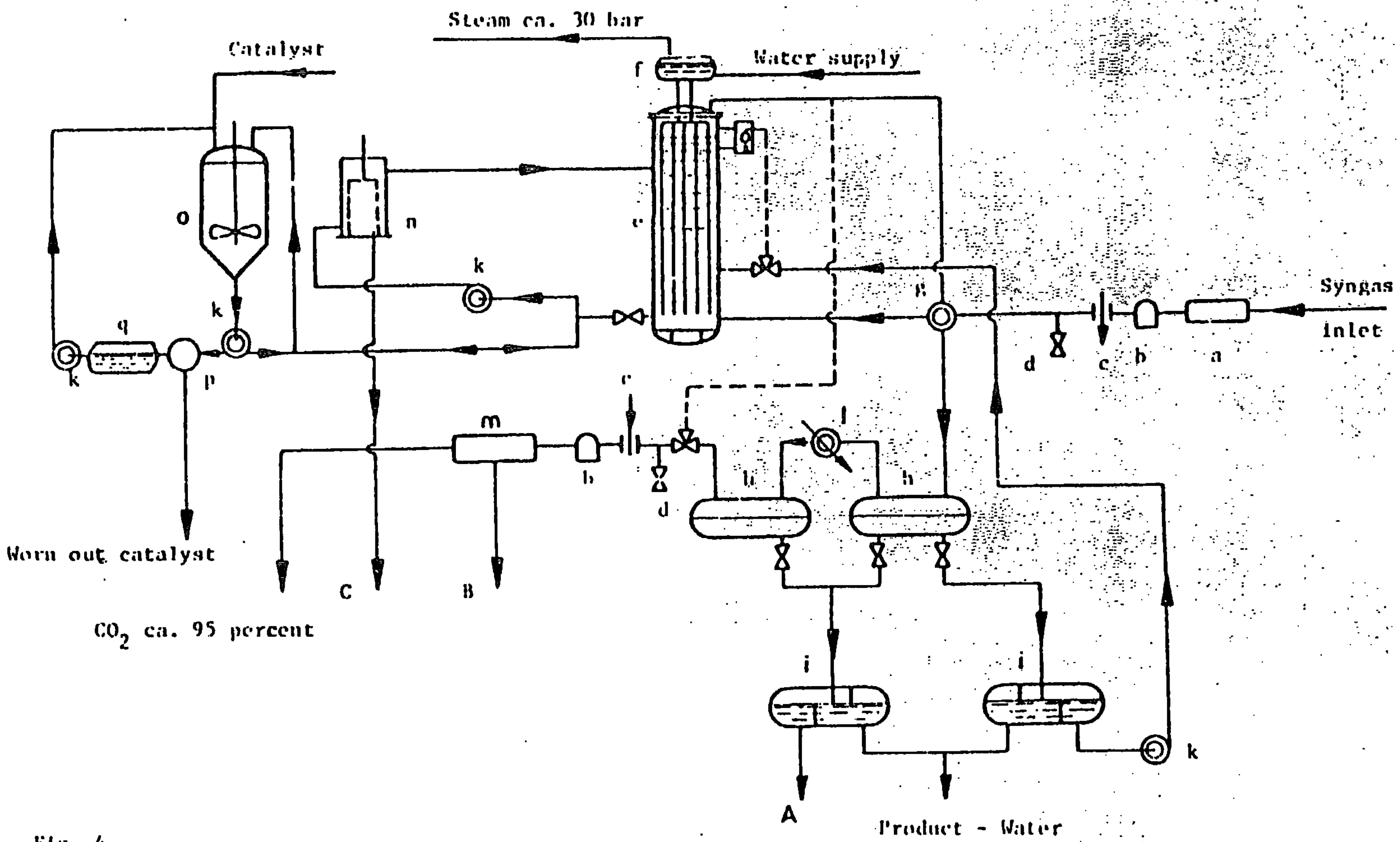

Steam ca. 30 bar
Catalyst
Water supply
f
o
n
e
k
g
Syngas
inlet
a
b
c
d
q
p
k
k
m
b
c
d
h
l
h
Worn out catalyst
C
B
CO2 ca. 95 percent
i
i
A
Product - Water
k

Fig. 4.

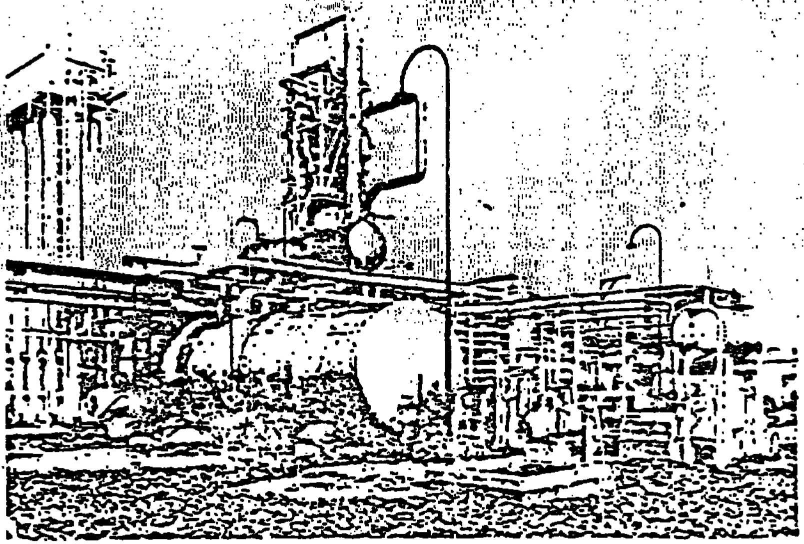


Fig. 5

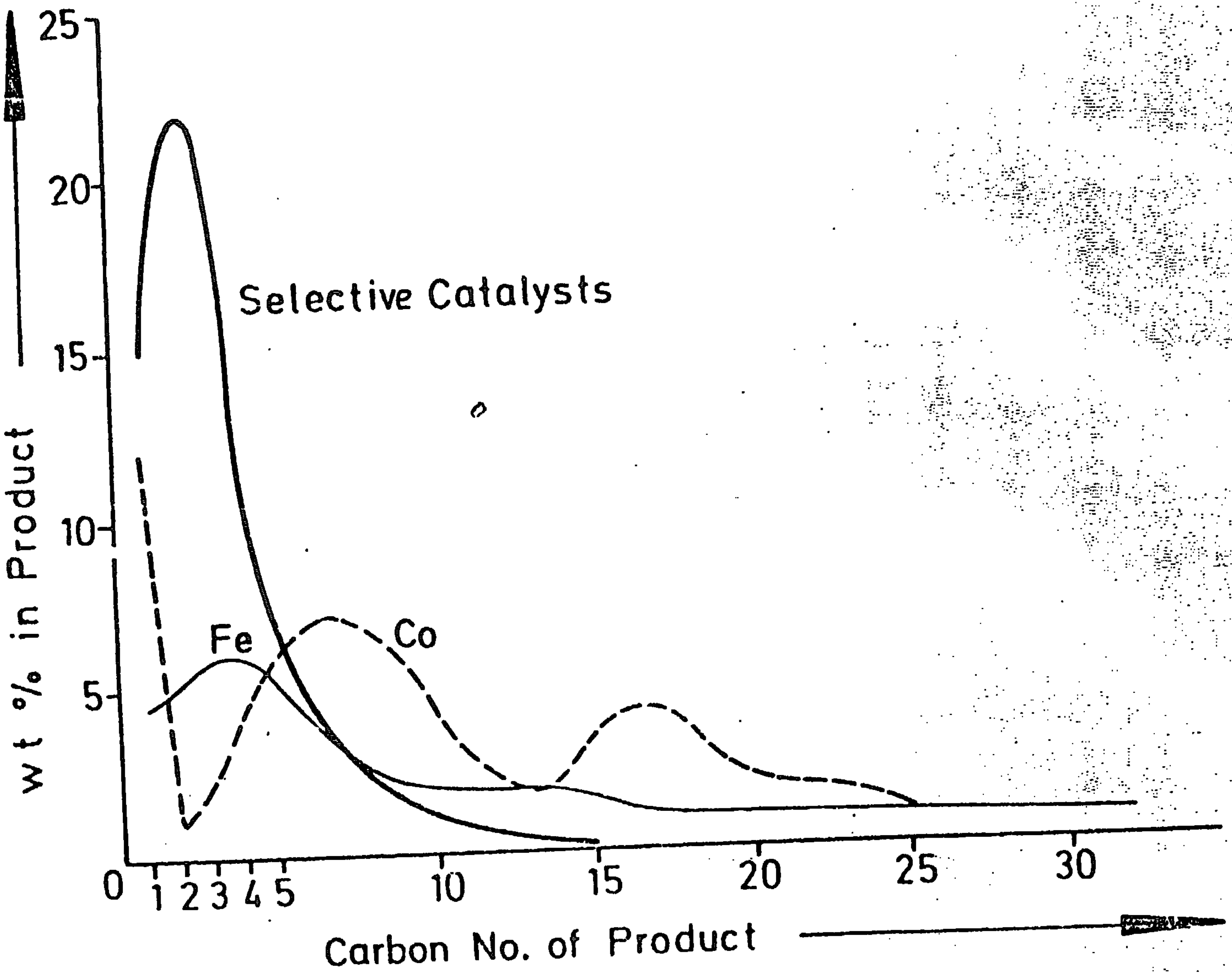

25
20
15
10
5
wt % in Product
Selective Catalysts
Fe
Co
0
1
2
3
4
5
10
15
20
25
30
Carbon No. of Product

Fig. 6

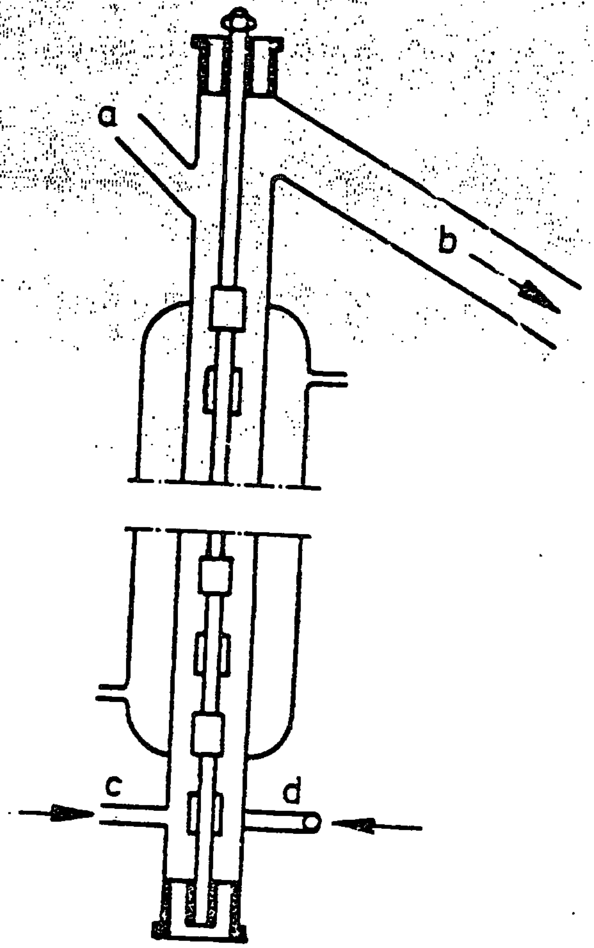
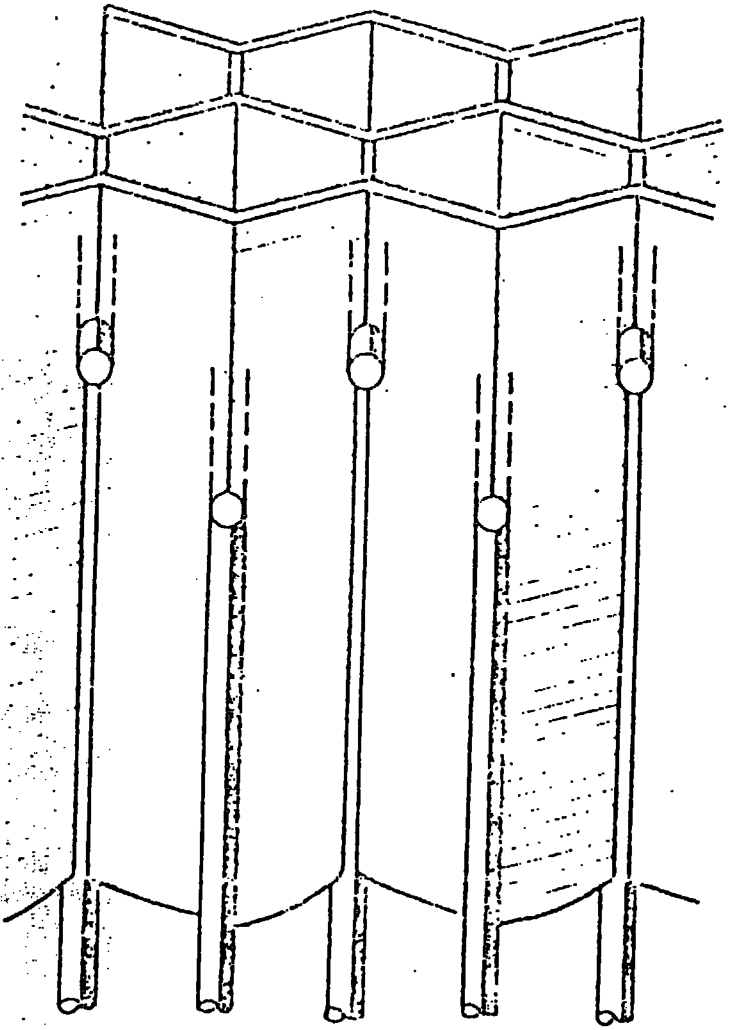


Fig. 7



All. 5

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