

## SUMMARY

Among the products of the FT palette, the olefins in the range  $C_2$  to  $C_4$  are important raw materials for the chemical industry. In the Federal Republic of Germany, seven million tons of these are required annually. Up to now, they were fabricated from crude oil products or ethane-rich natural gases.

Within the framework of the R & D project, an attempt was made to use new catalysts and to vary the reaction conditions so as to increase the yield of  $C_2/C_4$  olefins.

The reaction took place in liquid phase reactors of various size and in small fixed-bed reactors. According to H. Klbel, liquid phase reactors are especially suitable for this purpose. They also can be operated nearly isothermally, are suitable for use of even carbon monoxide-rich gases, and permit varying experimental conditions over a wide range.

The make-up gas, the residual gas, the hydrocarbon condensate, and the organic oxygen compounds in the reactor water were all investigated by gas chromatography. An EDP program was set up for evaluating the experiments, and this program can be adapted to various requirements.

The melt catalysts of Sasol Company and the precipitation catalysts of Ruhrchemie Company, as well as iron whisker catalysts of Bonn University and manganese-iron catalysts, obtained from Berlin Technical University or produced in our own laboratory, were all tested.

By means of the new catalysts, yields of  $C_2/C_4$  olefins could be increased from a previous value of less than 40 g to more than 60 g per  $m^3$  ( $V_n$ ) hydrogen and carbon monoxide. The researches were continued within the framework of a new R & D project. The primary objective continues to remain the increase of  $C_2/C_4$  olefin selectivity.

### 1 Problem Definition

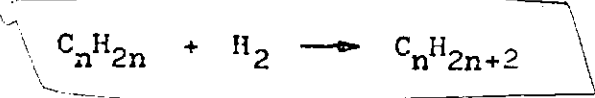
In the Fischer-Tropsch synthesis - below called the FT synthesis, hydrocarbons and oxygen-containing compounds are formed from synthesis gas, a carbon monoxide-hydrogen mixture, in the presence of a catalyst.

The reaction is exothermal. Aliphatic hydrocarbons generally dominate in the product palette.

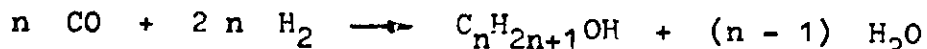
The following overall equation holds for the formation of the olefins:



By hydrogenation, paraffins can be formed from the olefins in a follow-up reaction.



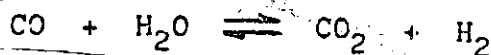
With the oxygen-containing organic compounds, whose fraction in the product palette generally is only small, the main components are alcohols. The formation equation reads as follows:



Aldehydes, ketones, carboxylic acids, and esters are generated as other oxygen compounds.

Side reactions are conversion and carbon formation.

The conversion is a reversible process.



In general, carbon dioxide and hydrogen are formed from the carbon monoxide and the reaction water of the synthesis. In the case of very hydrogen-rich synthesis gases, the reverse reaction can also predominate. As a rule, equilibrium is not reached during the reaction.

An excess of carbon monoxide generates carbon and carbon dioxide:



The quantity of the soot produced in this way increases with increasing carbon monoxide content in the synthesis gas and with increasing reaction temperature. This carbon can block portions of the catalyst surface and can thus reduce the lifetime of the catalyst.

The composition of the product palette depends on the catalyst and on the reaction conditions. The FT products can consist almost only of hydrocarbons or can also contain considerable fractions of oxygen compounds. The hydrocarbons can be rich or poor in olefins, the double bonds can be predominantly terminal bonds or can also, to a considerable extent, be centrally located. The chain length of the FT products is subject to a statistical distribution. The average C-number in the molecule, however, can vary over a wide range. The carbon chains can be essentially straight-chain or can also be predominantly branched.

Among the products of the FT palette, the lower olefins of the range  $\text{C}_2$  through  $\text{C}_4$  are important raw materials for the chemical industry. Seven million tons of these are needed annually in the Federal Republic of Germany. Of this demand, about 53 percent falls to ethylene, 36 percent to propylene, and 11 percent to butadiene and butene. The butenes occurring in the FT synthesis can be converted to butadiene by dehydrogenation.

Ethylene is a raw material for the production of polyethylene, vinyl chloride, ethylene oxide, acetaldehyde, ethanol, and ethylbenzene. From propylene, one makes polypropylene, propylene oxide, acrylonitrile, cumol, and isopropanol, and from butadiene one makes synthetic rubber.

Especially the unbranched olefins in the range  $\text{C}_8$  through  $\text{C}_{18}$ , which are likewise formed in the FT synthesis, are important starting products for the fabrication of softening alcohols and anion-active surface-active agents, of which several hundred thousand tons are annually consumed in the Federal Republic of Germany.

By means of the FT synthesis, it is therefore possible in principle to generate important raw materials for the chemical industry. Details concerning this are found in several studies which have been accomplished during the preceding years under contract with the Federal Ministry for Research and Technology (/1/ through /3/). For more extensive literature, special reference is made to the literature index listed in reference /3/.

The FT synthesis has previously been run primarily with the objective of fabricating motor fuels. The product palettes formed thereby, as expected, are not optimal for the production of chemical raw materials. For motor fuels, one strives for palettes which have maximum amounts of strongly branched hydrocarbons in the range  $C_6$  through  $C_9$ . For chemical raw materials, on the other hand, one desires products which have a high concentration of olefins in the range  $C_2$  through  $C_4$ .

In order to develop further the previous fuel synthesis into a chemical raw material synthesis, a change of the product palette composition is primarily required. To what extent the FT palette can be adapted to the raw materials needs of the chemical industry should be investigated in the FT laboratory systems that have been set up and operated by us. The reaction takes place preferably in a liquid phase reactor, which, according to H. K8ibel is especially suited for the desired objective.

Advantages of this reactor type:

- a) The excellent heat dissipation makes possible a nearly isothermal reaction. Local overheating, which changes the product palette and which especially increases the methane content, can be avoided.
- b) The reaction conditions can be varied over a wide range. Carbon monoxide rich gases, which yield olefin-rich palettes and which are thus especially important for chemical raw materials can also be reacted in this reactor. Precisely such gases will primarily arise in the future coal gasification, and will thus be very economical.

- /1/ Union Rheinische Braunkohlen Kraftstoff AG (Union of Rheinisch Brown Coal Fuels, Inc.), Wesseling; Generation of primarily petrochemical raw materials and basic materials by the Fischer-Tropsch process, January 1976.
- /2/ Ruhrchemie AG, Oberhausen; Status and development possibilities of the Fischer-Tropsch synthesis for producing chemical base materials and raw materials, May 1976.
- /3/ Schering AG, Berlin and Bergkamen; Synthesis of raw materials for the chemical industry by means of the Fischer-Tropsch process subject to further development, May 1977.

## 2 Structure of the Laboratory Installation

The dependence of the product palette on the catalyst and on the reaction conditions is to be investigated in the laboratory installations. For this purpose, several reactors of various size and type were available.

The component system that was set up first has a liquid phase reactor, which can accept a 3 liter catalyst suspension. In a second component system, a liquid phase reactor with 12 liter capacity has been installed. With both reactors, the dependence on the dimensions can be investigated within a narrow region.

For comparable investigations and for testing small amounts of catalysts, the system was first supplemented by a fixed-bed reactor with 1 liter capacity, at the end of 1977, and by three fixed-bed reactors, each with 50 ml useful capacity, by the middle of 1978.

## 2.1 Laboratory Systems with Liquid Phase Reactors

In these systems, the reaction conditions can be varied in the following ranges:

- the reaction temperature from 200 to 380° C
- the reaction pressure from 1 to 50 bar
- the CO/H<sub>2</sub> ratio arbitrarily, but preferably from 0.5 to 2
- the circulation ratio from 0 to 6
- the space velocity from 150 to 1000 h<sup>-1</sup>.

By the circulation ratio is understood the ratio of recycled residual gas to the inputted make-up gas.

The space velocity is the number of liters of make-up gas, relative to standard conditions, which is put through per hour and per liter of catalyst suspension.

These systems were planned, set up, and put in operation in 1975. The centerpiece on the liquid phase reactors were designed after H. K8lbel, and Figure 1 shows their shop drawings. The reactors differ as regards the inside diameter of the reactor tube, which is 25 mm for the smaller reactor and 50 mm for the larger one. With a total length of 6 m, the reactor is subdivided into three equally long component segments, which are connected together by flanges. The reactor is surrounded by a casing. In each component section, the internal temperature can be measured through a thermometer stud. At the bottom of the reactor tube there is a replaceable metal frit, through which the synthesis gas is supplied. The frit serves as a gas distributor and - on the basis of its small pore width - as a block against the catalyst which is present in finely suspended particles. At the upper end of the reactor, a tube expansion acts as a liquid separator. Further details can be seen in Figure 1.

Figure 2 shows the flow chart of the FT laboratory system with a liquid phase reactor. Hydrogen, carbon monoxide, and nitrogen are separately conducted into the system and can be mixed in any arbitrary ratio. Nitrogen is added so that the volume ratio of residual gas to make-up gas can be specified exactly. Carbon monoxide and hydrogen are present at the system boundary at a pressure of about 150 bar. After reducing the pressure and setting the desired volume stream, the two gases are conducted separately through the activated charcoal columns K 101 and K 102 respectively. At the activated charcoal, substances are adsorbed which would damage the catalyst - especially iron carbonyls.

By mixing the two flows, a synthesis gas with arbitrary CO/H<sub>2</sub> ratio can be produced. The precise CO/H<sub>2</sub> ratio, just like the N<sub>2</sub> content, is determined by gas chromatography. The gas chromatograph is connected directly to the synthesis gas line through a short connection line.

After the pressure is lowered to the desired synthesis pressure, the gas is heated to the synthesis temperature in a pre-heater W 101. It enters the bottom of the liquid phase reactor, flows through the catalyst suspension, whereby it is caused to react, and leaves the reactor on top, with the gaseous reaction products.

The initial filling with suspension takes place without pressure in the reactor, through the intake at the head. The height of the suspension in the reactor is determined while the reactor is running by means of a radioactive level measurement. If the suspension level falls while the reactor is operating, the liquid phase can be refilled from the heated liquid phase receiving flask B 102. This is done through an intermediate section, which contains a second frit, and which is situated in the center section of the reactor, by means of the dosing pump P 103. Outlets at the lower section of the reactor are used for emptying it. To temper the reactor and the synthesis gas, the thermally stable heat transfer medium is used, which is circulated.

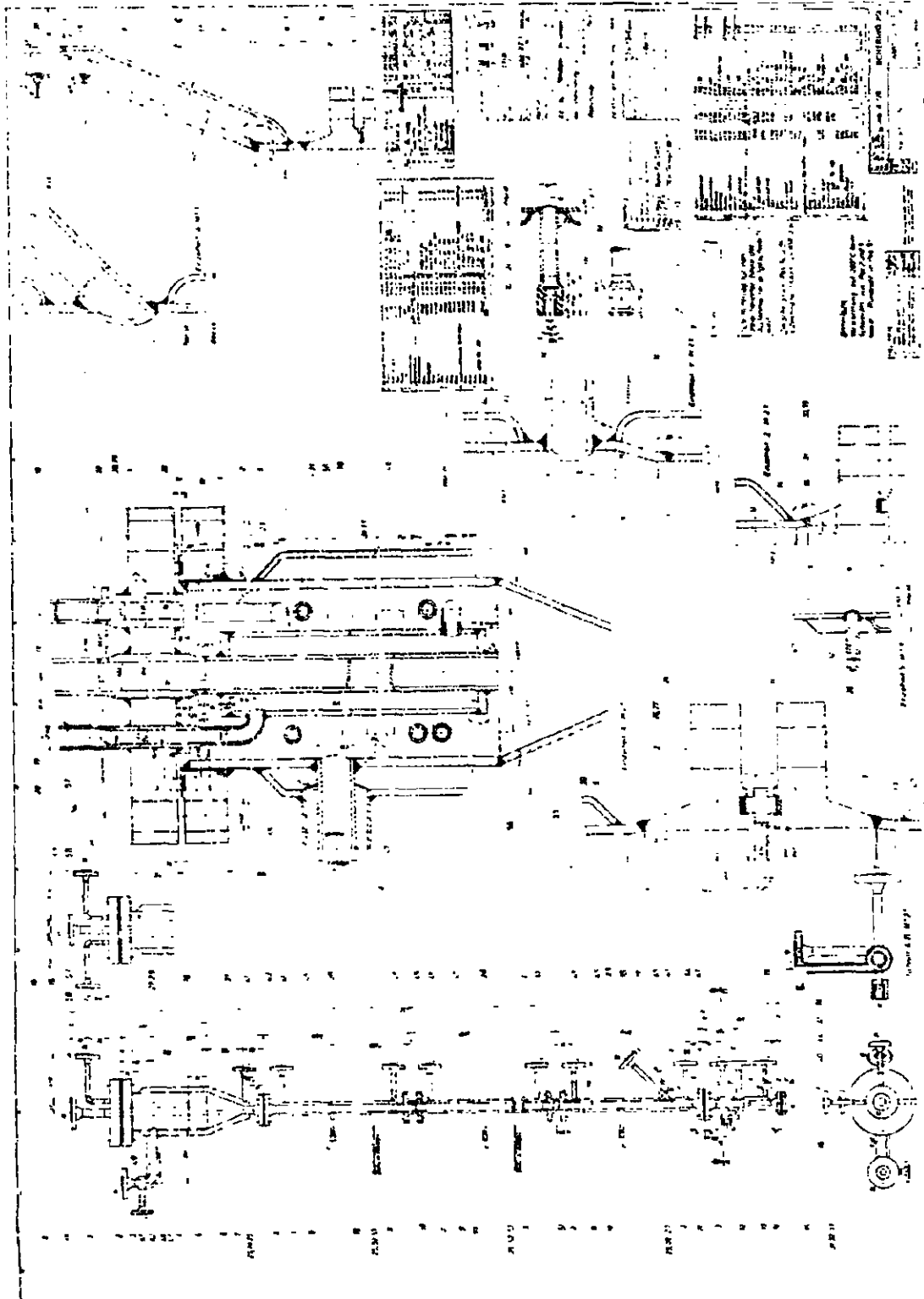
For reaction temperatures up to 320° C, Marlotherm S from the firm Chemical Works Hüls is suitable as a heat transfer medium. For higher reaction temperatures, up to about 380° C, the thermally more stable Gilotherm from the firm Rhone-Poulenc is used. However, with 20° C, this has a higher setting point than Marlotherm S (-35° C).

In the primary loop, which consists of an electric heater D 101 and a primary circulating pump P 101, the heat transfer medium is maintained at a temperature above the reaction temperature. The secondary loop comprises a liquid phase reactor C 101, the gas preheater W 101 which is run in parallel thereto, and the secondary circulation pump P 102. The synthesis temperature is maintained through a cascade control at the reactor, either by withdrawing a partial stream of the secondary loop from the primary loop for heating, or by running such a partial stream over the cooler W 102 for cooling. For safety reasons, this heating system is run as a closed system, i.e. the expansion vessel B 101 is not connected with the atmosphere. A certain system overpressure is produced by superimposing nitrogen. The heating system is controlled for an adequate cooling level by means of a viewing glass affixed below B 101.

The gas leaving the reactor consists of unused make-up gas, gaseous and vaporized reaction products and vaporized liquid phase. It is conducted to the hot condenser W 103. The hot condenser is tempered with low pressure steam so that as little as possible aqueous phase appears in the condensate, but, as much as possible, all the waxes will condense. If these waxes were not retained, they would deposit on the cooling surfaces of the cold condenser as a coating that inhibits heat transfer; less cold condensate will be generated, and the cold condenser would clog over the course of time.

The hot condensate is conducted in batches to the pressureless hot condenser container B 103. The view glass in the connection line between W 103 and B 103 is used for a level control; when the liquid level rises above the view glass, the valve situated beneath the view glass is opened, and thus

Figure 1. Shop drawing of the liquid phase reactor (text portions illegible)





overflow of the condenser is prevented. The gas liberated in B 103 during the pressure relief is conducted to the off-gas combustion system through the gas drainage line.

To prevent the hot condensate in the lines and in the hot condenser container from solidifying, a heating unit is provided. Since the liquid phase involves waxes with a melting point between 50 and 100° C, the liquid phase receiver flask B 102 and the connection lines B 102 - P 103 and P 103 - C 101 must also be heated.

The encased viewing glass for the .... (line missing)... heated by a transparent heat transfer medium, so that the liquid level both in the view glass and in the liquid phase receiver flask can be observed. If the melting point of the wax is at most 80° C, hot water is used as the heat transfer medium. With higher melting temperatures, hot paraffin oil is used. The connecting lines are heated electrically.

The gas leaving the hot condenser is cooled to room temperature in the cold condenser. The resulting cold condensate - hydrocarbons and reaction water - is released in batches into the cold condenser container B 104. The liquid level can be observed in the view glass. The gas that is liberated during this release is conducted to the off-gas combustion system through the gas drainage line. When the reaction conditions are changed, the condenser containers B 103 and B 104 are emptied. The condensate in the reaction water is investigated analytically.

A portion of the residual gas coming from the cold condenser can be admixed to the synthesis make-up gas via the circulation compressor V 101, and can thus be recycled into the reactor. Condensates which appear in the separation vessels B 105 and B 106 are combined with the cold condensate. The remaining residual gas is relieved of pressure and - after measuring the gas quantity - is conducted to the off-gas combustion system. A partial stream is conducted through a line to the laboratory, where its composition is determined by gas chromatography. The gas chromatographs are connected to a computer which evaluates the chromatograms. The synthesis gas and the residual gas are investigated every hour. Before start-up, the system is flushed with nitrogen.

## 2.2 Laboratory Systems with Fixed-Bed Reactors

Until October 1977, the FT synthesis with various catalysts and under changing reaction conditions was performed only with liquid phase reactors. Subsequently, ... (line missing)... The basis of the first fixed bed reactor was a 2 meter long component section of a liquid phase reactor with 25 mm inner diameter and a volume of 1 liter. Figure 3 shows the shop drawing of this reactor. In contrast to the liquid phase reactor, the synthesis gas flows through the fixed bed reactor from the top to the bottom, in order to avoid a build-up of products with a high boiling point in the reactor. The reaction heat is dissipated through a heat medium, which flows through the jacket space that surrounds the reactor tube. By means of a centrally disposed, moveable thermometer, the inner temperature can be measured over the entire reaction length. The height of the catalyst layer is about 1.8 m. Gas specimens can be withdrawn not only at the entry and exit end of the reactor but also through the specimen stud at half the reactor height. It is thus possible to determine the reaction and the product palette separately in the first and second reactor halves.



The reactor was built into a laboratory installation corresponding to Figure 2. During the runs that were performed with the reactor, there were problems with dissipating the reaction heat generated over the gas phase. A very unstable equilibrium existed between heat generation and heat dissipation. Small perturbations, such as fluctuations in the gas stream or gas composition, could cause a rapid rise of the interior temperature, especially in the first third of the reactor. Further use of this reactor was given up.

It was replaced by three significantly smaller systems, whose fixed bed reactors have a useful volume of only 50 ml. With these reactors, whose shop drawing is shown in Figure 4, there are no problems with maintaining the reaction temperature constant.

The interior tube of copper has a clear width of 15 mm. A thermometer tube is centrally disposed therein, in which the thermometer can be moved along the entire reactor length. The reactor tube is covered by an aluminum block, which is electrically heated... (line missing)... The reactor is heat-insulated. The temperature in the reactor pipe is controlled through the block temperature.

The synthesis gas is taken from pressurized bottles in premixed form. It flows to the reactor from the top to the bottom. The hydrocarbons with a high boiling point and the reaction water are separated from the emerging residual gas in a water-cooled condenser. After release, the remaining residual gas is directly conducted to gas chromatographs, the residual volume is measured with a gas gauge. Taking into account the pressure and temperature, the data are converted to standard conditions. All three fixed-bed reactors can be run in parallel with various pressures, temperatures, synthesis gas flows, and synthesis gases. A circulation of the gas has not been provided for at this time. At the beginning of the run, the catalyst is formed in the reactor. The fixed bed reactors are excellently suited for the rapid testing of catalysts.

### 3 Evaluation of the Experiments

For the evaluation, the reaction conditions must be known, and the conversion as well as the product palette must be calculated. Measured data are the reaction temperature, the reaction pressure, the circulation ratio, the residual gas volume relative to standard conditions, and the gas chromatographic areas of make-up gas and residual gas.

#### 3.1 Composition of Make-Up Gas and of Residual Gas

The make-up gas, i.e. the synthesis gas which enters the reactor, is a mixture with varying composition, containing hydrogen, carbon monoxide, and nitrogen. In the residual gas which remains after the reaction, after the condensate has been separated off, there are also contained the reaction products - carbon dioxide and hydrocarbons. Up to  $C_4$ , the hydrocarbons remain almost completely in the gas phase under the condensation conditions, and from  $C_5$  to  $C_8$ , they partially remain in the gas phase. While a gas chromatogram is sufficient for the analysis of the make-up gas, two gas chromatograms are required for the residual gas analysis.

The first gas chromatogram determines hydrogen, carbon monoxide, nitrogen, carbon dioxide, and methane. The mixture is separated at  $110^\circ C$  in a 2 m

Figure 3. Shop drawing of the fixed-bed reactor with 1:1 content  
(text portions illegible)

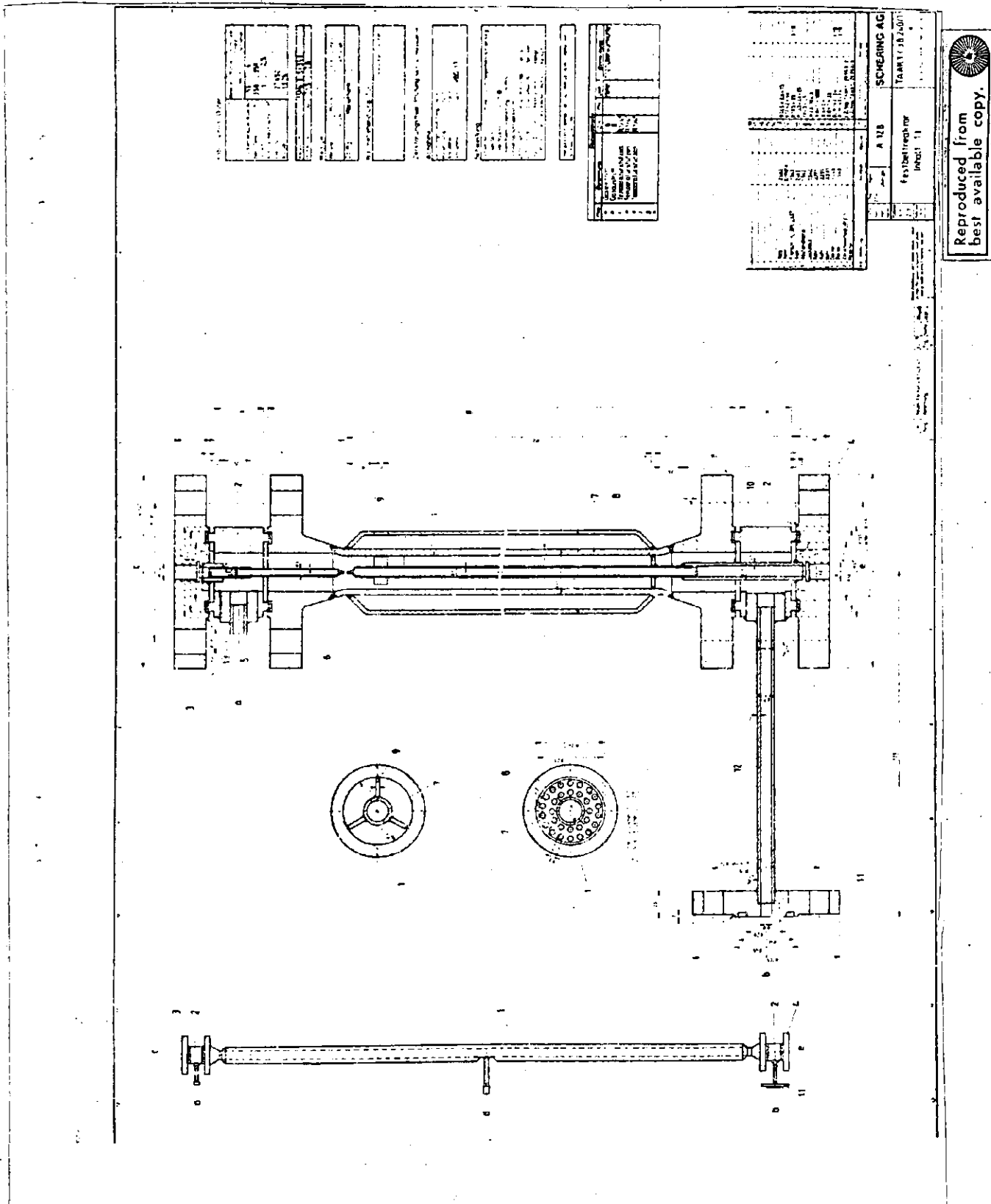


Figure 4. Fixed bed reactor with 50 ml content

- 1 gas entry
- 2 hard-soldered
- 3 hard-soldered on both sides
- 4 tight-soldered
- 6 hard-soldered
- 7 last soldering seam after sliding over the aluminum block
- 8 drilled open to  $\emptyset$  15 rotary surface milled into a cone
- 9 hard-soldered
- 10 gas exit
- 11 1/2 of the intermediate piece R 1/4" soldered on
- 12 1/2 of the intermediate piece R 1/4" soldered on
- 13 thermometer
- 14 hard-soldered on both sides
- 5 position of the thermometer tube



column, which is filled with a carbon molecular sieve B from Perkin Elmer Company. As an indicator, a heat conduction detector is utilized. A favorable carrier gas is argon, as became apparent from a series investigation with test gas mixtures. Figure 5 shows a gas chromatogram, which was obtained during the investigation of a residual gas. The direction of the paper transport is indicated by an arrow. The hydrogen peak is followed by peaks for nitrogen, carbon monoxide, methane, and carbon dioxide.

Since the peak areas are not proportional to the volume fraction of the components, calibration with gases of known composition is required. The required calibration gases were obtained from Messer-Griesheim Company. When comparing the results which were obtained with calibration gases of different composition, it appeared that the correction factor of hydrogen is concentration-dependent. The factor increases with increasing concentration. It can be represented as a linear function of the hydrogen area. The constants of this function were determined by investigating calibration gases with different hydrogen concentrations.

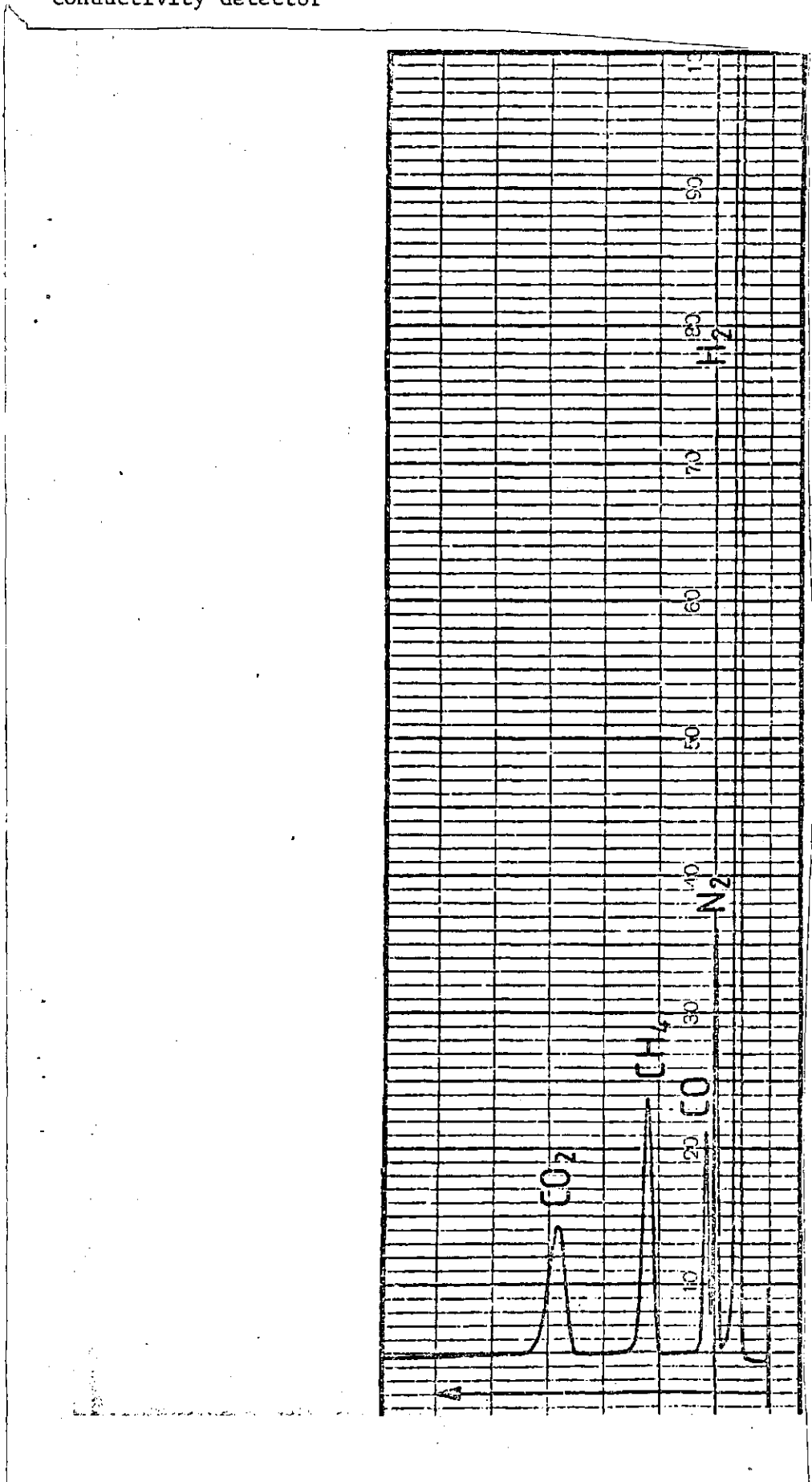
The integration of the peak areas and the calculation of the gas composition in volume percent was performed in a connected PEP 2 computer from Perkin Elmer Company. In the evaluation, no distinction is made between volume percent and mole percent, since the inaccuracies of the analysis are certainly greater than the differences between the two... (line missing)... The hydrocarbons of the residual gas, from methane to the C<sub>8</sub>-fraction are determined in the second chromatograph. This contains a 2.5 m long column, filled with Porapak S from Perkin Elmer Company. The indication takes place through a flame ionization detector. During the gas chromatography, the column temperature is increased from 50° C to 190° C with a heat up rate of 8 K/min.

Figure 6 shows the chromatogram of residual gas. Up to C<sub>3</sub>, the mixture is decomposed into individual hydrocarbons. The C<sub>4</sub> hydrocarbons, isobutene and butene-1 are not separated, also n-butane and trans-butene-2. From C<sub>5</sub> on, individual peaks are indeed resolved, but these always contain a series of individual compounds. Further decomposition is possible only with capillary columns.

Since we are primarily interested in hydrocarbons up to the C<sub>4</sub> fraction, a division into C-number fractions seems sufficient beginning with C<sub>5</sub>. With the C<sub>4</sub> hydrocarbons, the isobutene content is small, so that the common peak is primarily caused by butene-1. N-butane and trans-butene-2 are separated on other column materials. These chromatograms indicated that the trans- and cis-configuration of the butene-2 are formed in about the same amounts. The use of such column material, however, was disadvantageous for other reasons, so that it was given up.

In the evaluation of the gas chromatograms, equally large areas were presupposed for the trans- and for the cis-butene-2. Accordingly, the area which remains after subtracting the F 44 from the F 43 area corresponds to n-butane. As calibration measurements have shown, in this analysis with the flame ionization detector (FID), the peak area is proportional to the product of the mole fraction and the C-number in the molecule. This proportionality also is the basis for calculating the hydrocarbon contents in volume percent.

Figure 5. Gas chromatogram of residual gas separation column: carbon molecular seive B, carrier gas: argon. Indicator: heat conductivity detector



The gas chromatogram-(GC) obtained by the heat conductivity detector (WLD) and the gas chromatogram obtained with the FID have a methane peak in common. By using this peak, both gas chromatograms were related to one another and the composition of the residual gases was calculated.

### 3.2 Calculation of the Conversion and Product Palette

If the composition of the make-up gas and of the residual gas are known, the gas conversion and the product palette can be calculated therefrom by a balancing process.

The following relationship, important for balancing, exists between the nitrogen contents of the make-up gas and the residual gas and their volumes:

$$\frac{V_R}{V_F} = \frac{x_{N_2}}{y_{N_2}}$$

Here the symbols have the following meanings:

- $V_R$  = residual gas volume
- $V_F$  = make-up gas volume
- $x_{N_2}$  = mole fraction of nitrogen in the make-up gas
- $y_{N_2}$  = mole fraction of nitrogen in the residual gas

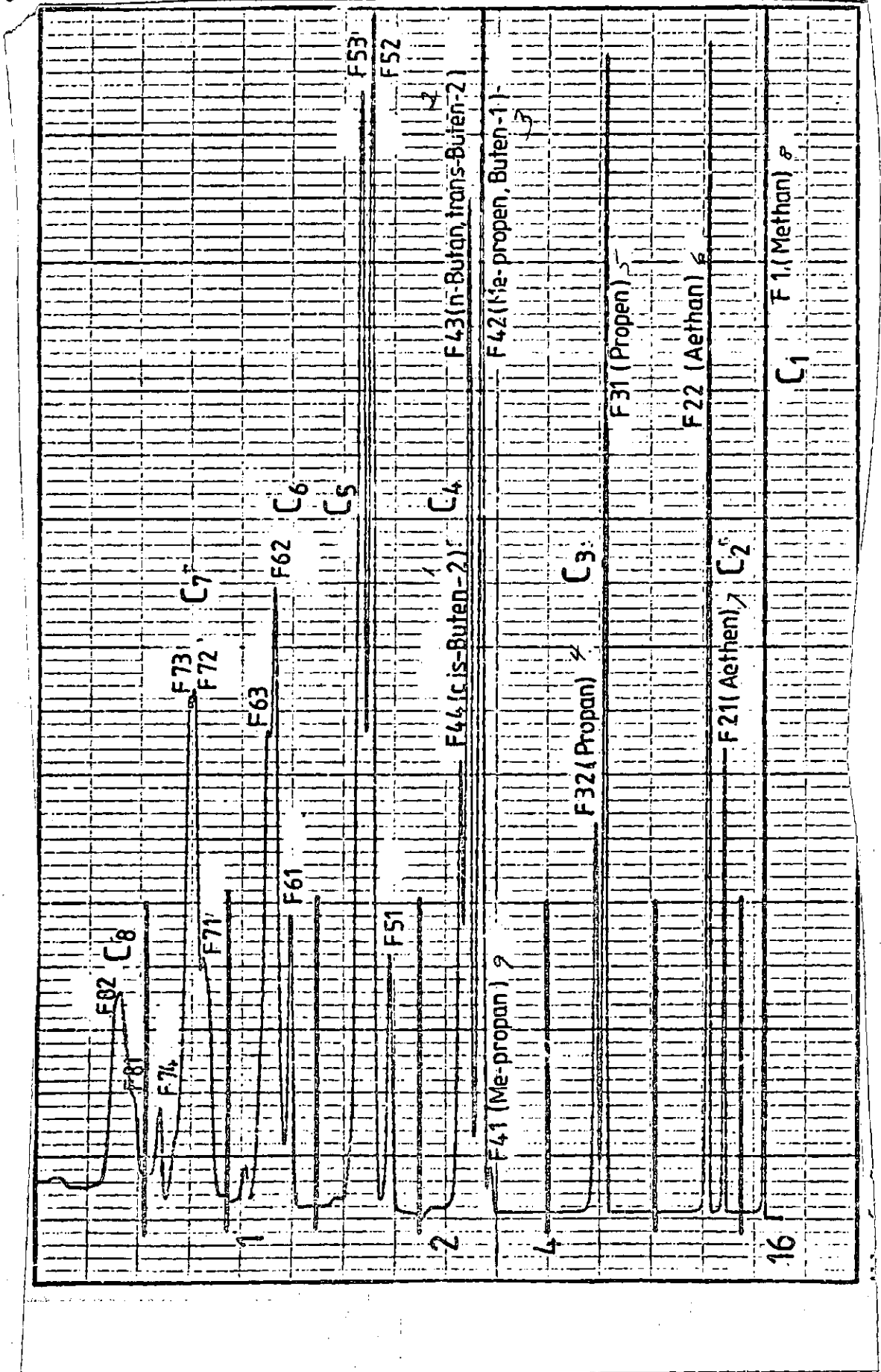
The important equations for the balance are collected in Table 1. The significance of the symbols can be taken from the lower portion of the table.

The reactions which take place per mole of utilized synthesis gas are described by the stoichiometric equations. The first equation includes all reactions in which olefins and paraffins are formed, which contain up to four carbon atoms per molecule. The formation of all hydrocarbons with at least five carbon atoms in the molecule regardless.... (line missing)... or whether they are still in the residual gas, is described by the second equation. The third equation takes into account the conversion from carbon monoxide with reaction water to carbon dioxide and

Figure 6. Gas chromatogram of a residual gas, separation column: Poropak S  
Indicator: flame ionization detector

- 1 cis-butene-2
- 2 n-butane; trans-butene-2
- 3 methylpropene, butene-1
- 4 propane
- 5 propene
- 6 ethane
- 7 ethene
- 8 methane
- 9 propane

Figure 6





hydrogen. The fourth equation summarizes the first three partial equations. This system of equations does not take into account the formation of oxygen-containing organic compounds, but these are included as C<sub>5+</sub> products. However, in our experimental runs, the product palettes contained only a few percent of these compounds. Consequently, the balancing error caused by this is so small that it lies within the analytical measurement accuracy.

Since the difference between the carbon monoxide and hydrogen quantity respectively in the make-up gas and residual gas must agree with the carbon monoxide and hydrogen conversion respectively in the fourth equation, the balancing equations listed in Table 1 must hold for carbon monoxide and hydrogen. From these equations, the quantity k can be eliminated. Thus results the last equation of the table, which contains only quantities which are accessible from analyses of the make-up gas and residual gas.

For these balancing equations to be fulfilled, the analytical values, which are subject to measurement error, are subjected to an equalization calculation. The equations for this mole fraction correction are collected in Table 2. The calculation presupposes that the relative measurement error is the same with all the gas components. The table shows the relationship between the corrected and measured mole fractions and the resulting equations for calculating the correction quantity. If this is known, the corrected mole fractions, which are the basis for further experimental evaluation, can be calculated.

The hydrogenated hydrogen fraction β in the C<sub>5+</sub> hydrocarbons can be determined approximately by the following empirical equation:

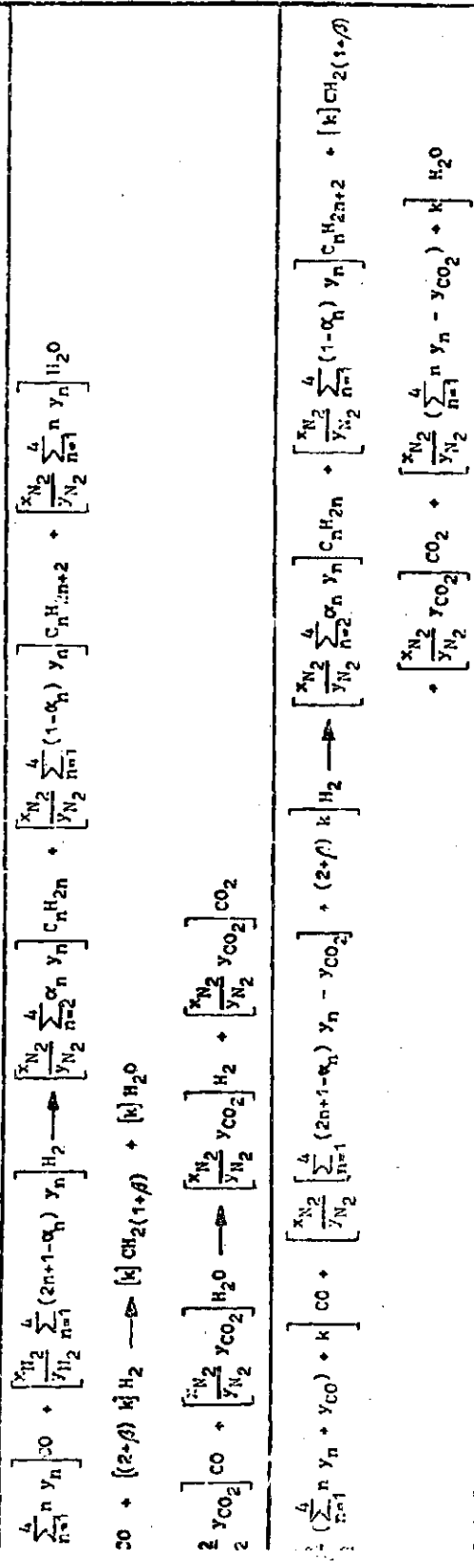
$$\beta = \frac{1 - \alpha_4}{\alpha}$$

Table 1 Balancing equations for the FT synthesis

1	stoichiometric equations for the reactions per mole of synthesis gas utilized
2	balancing equations for carbon monoxide and hydrogen
x <sub>N<sub>2</sub></sub>	mole fraction of N <sub>2</sub> in the make-up gas
x <sub>H<sub>2</sub></sub>	mole fraction of H <sub>2</sub> in the make-up gas
x <sub>CO</sub>	mole fraction of CO in the make-up gas
x <sub>N<sub>2</sub></sub>	mole fraction of N <sub>2</sub> in the residual gas
x <sub>H<sub>2</sub></sub>	mole fraction of H <sub>2</sub> in the residual gas
x <sub>CO</sub>	mole fraction of CO in the residual gas
y <sub>CO<sub>2</sub></sub>	mole fraction of CO <sub>2</sub> in the residual gas
y <sub>n</sub>	mole fraction of KW substances with n C atoms in the residual gas
n	number of C atoms in the molecule
α <sub>n</sub>	olefin component in the C <sub>n</sub> fraction
k <sup>n</sup>	moles C in C <sub>5+</sub> products per mole of synthesis gas
β	mole of hydrogenated hydrogen per mole C in C <sub>5+</sub> products

Table 1

Schlonstrische Gleichungen für die Umsetzungen pro Mol eingesetzten Synthesegases



Ionisierungsgleichungen für Kohlenoxid und Wasserstoff

$$0 - \frac{x_{N_2}}{y_{N_2}} y_{\text{CO}} - \frac{x_{N_2}}{y_{N_2}} \left( \sum_{n=1}^4 y_n + y_{\text{CO}_2} \right) + k$$

$$2 - \frac{x_{N_2}}{y_{N_2}} y_{\text{H}_2} - \frac{x_{N_2}}{y_{N_2}} \left[ \sum_{n=1}^4 (2n+1-\alpha_n) y_n - y_{\text{CO}_2} \right] + (2+\beta) k$$

$$+\beta) x_{\text{CO}} - x_{\text{H}_2} - \frac{x_{N_2}}{y_{N_2}} \left[ (2+\beta) y_{\text{CO}_2} + (2+\beta) y_{\text{CO}} - y_{\text{H}_2} - \sum_{n=1}^4 (1-\alpha_n) y_n \right]$$

- $x_{N_2}$  = Molbruch des  $N_2$  im Frischgas
- $x_{H_2}$  = Molbruch des  $H_2$  im Frischgas
- $x_{CO}$  = Molbruch des  $CO$  im Frischgas
- $y_{N_2}$  = Molbruch des  $N_2$  im Restgas
- $y_{H_2}$  = Molbruch des  $H_2$  im Restgas
- $y_{CO}$  = Molbruch des  $CO$  im Restgas
- $y_{CO_2}$  = Molbruch des  $CO_2$  im Restgas
- $y_n$  = Molbruch der  $KV$ -Stoffe mit  $n$  C-Atomen im Restgas
- $n$  = Zahl der C-Atome im Molekül
- $\alpha_n$  = Olefinanteil in der  $C_n$ -Fraktion
- $k$  = Mole  $C$  in  $C_{5+}$ -Produkten pro Mol Synthesegaseinsatz
- $\beta$  = Mole Hydrierwasserstoff pro  $K_{1,1} C$  in  $C_{5+}$ -Produkten

Thus all the data are known which are necessary for the experimental evaluation. The calculational equations can be taken from Table 3. Since the nitrogen contents of the make-up gas and residual gas are known, the stream of make-up gas can be calculated from the stream of residual gas. By the ideal gas is always understood the fraction of the synthesis gas which consists of hydrogen and carbon monoxide.

For the economy of the method, the gas conversion is of considerable significance, since the cost for the FT products are predominantly the costs for the synthesis gas, and since the process for residual gas, which is used as heating gas, lie far below the generation costs for purified synthesis gas. The conversions, relative to the charges, are generally higher with carbon monoxide than with hydrogen. The  $\text{CO}/\text{H}_2$  ratio is therefore generally higher in the case of conversion than with the make-up gas, so that it is reduced in the residual gas. The reaction ratio depends on the charge ratio, on the conversion, and - to a much smaller extent - on the resulting product palette.

One measure for the CO conversion is the  $\text{CO}_2$  component. This specifies the percentage in which the primarily generated reaction water, whose mole fraction corresponds to the resulting  $\text{C}_{1+}$  compounds, is converted into hydrogen and carbon dioxide by reaction with carbon monoxide.

The selectivities reflect the distribution of C atoms in the FT products. For our investigations, the  $\text{C}_2/\text{C}_4$  olefin selectivity is was especially significant. Also significant was the composition of this olefin mixture and the yield of these olefins, which was obtained per  $\text{m}^3$  ( $V_n$ ) of ideal gas utilized.

In addition, the table contains an equation for calculating the average molar mass per C atom in the molecule. This quantity is necessary for converting the selectivity into mass percent. By means of further relationships, the gas quantity required to produce 1 kg FT product .... (line missing)...

### 3.3 EDP Tables with Experimental Results

The EDP program FT 540 was developed to evaluate the experiments. It can be varied by inputting certain control quantities and thus can be adapted to various wishes.

The composition of the make-up gas and residual gas is first calculated from the input data. Under constant reaction conditions, average values Table 2. Equations for the mole fraction correction

- 1 make-up gas
- 2 residual gas

The symbols have the following meaning

- $x'$  measured mole fractions in the make-up gas
- $y'$  measured mole fractions in the residual gas
- $x$  corrected mole fraction in the make-up gas
- $y$  corrected mole fraction in the residual gas
- $\Delta$  correction quantity

Table 2

Frischgas 1	Restgas 2
$x_{CO} = x'_{CO} \frac{1 - \Delta}{SF}$ $x_{H_2} = x'_{H_2} \frac{1 + \Delta}{SF}$ $x_{N_2} = x'_{N_2} \frac{1 + \Delta}{SF}$	$y_{CO} = y'_{CO} \frac{1 + \Delta}{SR}$ $y_{H_2} = y'_{H_2} \frac{1 - \Delta}{SR}$ $y_{N_2} = y'_{N_2} \frac{1 - \Delta}{SR}$ $y_{CO_2} = y'_{CO_2} \frac{1 + \Delta}{SR}$ $y_n = y'_n \frac{1 - \Delta}{SR}$
$SF = 1 + (1 - 2 x'_{CO}) \Delta$	$SR = 1 - \left[ 1 - 2 (y'_{CO} + y'_{CO_2}) \right] \Delta$
$\Delta = \frac{\sqrt{4 a b + c^2} - a - b}{a - b - c}$	
$a = \frac{x'_{N_2}}{y'_{N_2}} \left[ (3 + \beta) y'_{CO_2} + (2 + \beta) y'_{CO} \right]$ $b = (2 + \beta) x'_{CO}$ $c = x'_{H_2} - \frac{x'_{N_2}}{y'_{N_2}} \left[ y'_{H_2} + \sum_{n=1}^4 (1 - \alpha_n - n \beta) y'_n \right]$	
<p>Es bedeuten:    <math>x'</math>    gemessener Molenbruch im Frischgas                    <math>y'</math>    gemessener Molenbruch im Restgas                    <math>x</math>    korrigierter Molenbruch im Frischgas                    <math>y</math>    korrigierter Molenbruch im Restgas                    <math>\Delta</math>    Korrekturgröße</p>	

Table 3. Equations for experimental evaluations

1	stream of make-up gas
2	stream of residual gas
3	ideal gas stream
4	reactions in percent of charge
5	CO conversion
6	H <sub>2</sub> conversion
7	CO + H <sub>2</sub> conversion
8	reaction ratio
9	CO <sub>2</sub> fraction
10	percent of C <sub>1+</sub>
11	selectivity for hydrocarbons with n C atoms (percent of C <sub>1+</sub> )
12	composition of the C <sub>2</sub> /C <sub>4</sub> olefin fraction
13	content of olefins with n C atoms
14	average mole mass through C-number
15	composition of the product palette in mass percent
16	olefins with n C atoms
17	paraffins with n C atoms
18	C <sub>5+</sub> products
19	yield in g per m <sup>3</sup> ideal gas charge under standard conditions
20	C <sub>1+</sub> products
21	C <sub>2</sub> /C <sub>4</sub> olefins
22	gas consumption m <sup>3</sup> - relative to standard conditions - per kg C <sub>1+</sub>
23	space-time yields in g product per h and l catalyst suspension <sup>1+</sup> (V <sub>K</sub> )
24	C <sub>1+</sub> products
25	condensate
26	reaction water A

Table 3

Frischgasstrom 1	$\dot{V}_{FG} = \frac{y_{H_2}}{x_{H_2}} \dot{V}_{RG}$	$\dot{V}_{RG} = \text{Reaktionsstrom in l (n)/h}$ 2	Idealgasstrom 3	$\dot{V}_{IG} = (x_{CO} + x_{H_2}) \dot{V}_{FG}$
Umsätze in % vom Einsatz: 4	CO-Umsatz $u_{CO} = 100 \left[ 1 - \frac{x_{N_2} y_{CO}}{y_{N_2} x_{CO}} \right]$ 5	H <sub>2</sub> -Umsatz $u_{H_2} = 100 \left[ 1 - \frac{x_{N_2} y_{H_2}}{y_{H_2} x_{H_2}} \right]$ 6		
	(CO+H <sub>2</sub> )-Umsatz $u_{IG} = 100 \left[ 1 - \frac{x_{N_2} y_{H_2} + y_{CO}}{y_{N_2} x_{H_2} + x_{CO}} \right]$ 7			
Umsatzverhältnis 8	$Z_{CO/H_2} = \frac{x_{CO} u_{CO}}{x_{H_2} u_{H_2}}$	CO <sub>2</sub> -Anteil 9	$CO_2-A = 100 \frac{\frac{x_{N_2}}{y_{N_2}} y_{CO_2}}{x_{CO} - \frac{x_{N_2}}{y_{N_2}} (y_{CO} + y_{CO_2})}$ (% vom C <sub>1+</sub> ) 10	
Selektivität für Kohlenwasserstoffe mit n C-Atomen (% vom C <sub>1+</sub> ) 11	$S_n = 100 \frac{\frac{x_{N_2}}{y_{N_2}} n y_n}{x_{CO} - \frac{x_{N_2}}{y_{N_2}} (y_{CO} + y_{CO_2})}$		$S_{S+} = 100 - \sum_{n=1}^4 S_n$	
Zusammensetzung der C <sub>2</sub> /C <sub>4</sub> -Olefinfraktion: 12	Gehalt an Olefin mit n C-Atomen 13		$O_n = 100 \frac{n \alpha_n y_n}{\sum_{n=2}^4 n \alpha_n y_n}$	
Mittlere Molmasse durch C-Zahl: 14	$\bar{M} = M_{CH_2} + \left[ \sum_{n=1}^4 \frac{1 - \alpha_n}{n} S_n + \beta S_{S+} \right] \frac{M_{H_2}}{100}$			
Zusammensetzung der Produktpalette in Massenprozent 15	<p>Olefine mit n C-Atomen <math>m_{n, o} = \alpha_n S_n M_{CH_2} / \bar{M}</math> <span style="margin-left: 100px;">18</span> 16</p> <p>Paraffine mit n C-Atomen <math>m_{n, p} = (1 - \alpha_n) S_n (M_{CH_2} + M_{H_2}/n) / \bar{M}</math> 17</p> <p>C<sub>5+</sub>-Produkte <math>m_{S+} = 100 - \sum_{n=1}^4 (m_{n, o} + m_{n, p})</math></p>			
Ausbeuten in g pro m <sup>3</sup> Idealgaseinsatz unter Normbedingungen 19	<p>C<sub>1+</sub>-Produkte <math>\epsilon_{1+} = \frac{1000}{22,414} \frac{x_{CO} - \frac{x_{N_2}}{y_{H_2}} (y_{CO} + y_{CO_2})}{x_{CO} + x_{H_2}} \bar{M}</math> <span style="margin-left: 100px;">20</span></p> <p>C<sub>2</sub>/C<sub>4</sub>-Olefine <math>\epsilon_0 = \epsilon_{1+} \sum_{n=2}^4 m_{n, o}</math> <span style="margin-left: 100px;">21</span></p>			
Gasverbrauch in m <sup>3</sup> - bezogen auf Normzustand - pro kg C <sub>1+</sub> 22	GV = 10 u <sub>IG</sub> /ε <sub>1+</sub>			
Raumzeitausbeuten in g Produkt pro h und l Katalysatorsuspension (V <sub>K</sub> ) 23	C <sub>1+</sub> -Produkte $A_{1+} = \frac{\epsilon_{1+}}{1000} \frac{\dot{V}_{IG}}{V_K}$ 24			
Kondensat $A_{KD}$ 25	Reaktionswasser $A_{H_2O}$ 26			
$A_{KD} = A_{1+} \left[ 1 - \frac{\frac{x_{N_2}}{y_{N_2}} \sum_{n=1}^4 n y_n}{x_{CO} - \frac{x_{N_2}}{y_{N_2}} (y_{CO} + y_{CO_2})} \right] \frac{M_{CH_2} + \beta M_{H_2}}{\bar{M}}$		$A_{H_2O} = A_{1+} \left[ 1 - \frac{\frac{x_{N_2}}{y_{N_2}} y_{CO_2}}{x_{CO} - \frac{x_{N_2}}{y_{N_2}} (y_{CO} + y_{CO_2})} \right] \frac{M_{H_2O}}{\bar{M}}$		

of the run and average values of time-sequential analyses are formed. Subsequently, the reactions and product palettes are determined by means of the equations given in Tables 1 through 3. The results are printed out in tabular form. Details concerning the EDP program FT 540 can be found in Chapter 6.

The following tables show examples of EDP printouts for an experimental run under constant reaction conditions.

As can be seen from Table 4, the EDP printout 1 contains data concerning the makeup gas composition, the gas streams, and the reactor temperatures at various levels. In the upper portion of the table, are listed the values measured at different clock times.

In the center portion follow the average values calculated from these. The first column specifies the time period over which the average was taken. The first line contains the average value of the run, the following lines the average values of three successive individual values. In the last line of this section, the finally remaining individual values - in Table 4 there are two of these - have been averaged.

The lower section of the table indicates the extremal values measured during the run and the calculated standard deviations.

The first two lines in the table header, which are identical with EDP printouts 1 and 2, provide information concerning the ... (line missing) ... through a number -, the beginning and duration of the run, the number of analyses, and the reaction conditions.

Table 5 shows EDP printout 2. Here, in analogous fashion, data are summarized concerning the composition of residual gases and the olefin contents of the  $C_2$  to  $C_4$  fractions. Individual values, average values, extremal values, and standard deviations are again listed.

Table 6 is an example of EDP printout 3. It contains data concerning the reaction conditions, the gas composition, the reactions, the yields, and the product palettes.

The lines with running number 1 give average values for the run, the following lines give averages of three individual values. The averages show whether systematic changes occurred during the run.

The specified streams of ideal gas, make-up gas, and residual gas, have, in the case of liquid phase reactors, been referred to the suspension volume and, in the case of fixed-bed reactors, to the catalyst volume.

The C number distribution is the sum of the selectivities. With the  $C_4$  fraction, the  $\alpha$  component indicates how high is the  $\alpha$ -olefin content of the butenes. This is a measure for the terminal position of the olefin double bond.

In the lowermost section of the table are given the compositions of the make-up gas and residual gas which result after performing the equalization calculation, as well as the calculated correction quantity, in percentages of the measured value.

As can be seen from Table 7, the EDP printout 4 is limited to the most important data of printout 3. In particular, the corrected values for the gas composition are missing.

For further compression, the data of several individual runs with different reaction conditions can be summarized in one printout. Each individual line then contains the results of an individual run, which have been calculated from the average values.

The printout can correspond to Table 6 or Table 7. In a printout corresponding to Table 6, a maximum of ten individual runs can be summarized. If one chooses the form shown in Table 7, the results of even 15 individual runs can be concentrated in one printout.

This form has been chosen in the following chapter to present the experimental results, so as to attain a good overview and to facilitate comparison of results under different reaction conditions.



Table 4. EDP printout 1; composition of the make-up gas, gas streams, reaction temperatures

1 reactor 1  
2 cat. no. 41  
3 experiment no. 138  
4 o'clock  
5 duration 24 hours  
6 analyses  
7 experimental conditions  
8 pressure 11 bar  
8a temperature 324 deg C  
9 space velocity  
10 circulation "VEPH" (abbreviation unknown)  
11 clock time  
12 composition of the make-up gas  
13 make-up gas  
14 residual gas  
15 reactor temperature (deg C)  
16 maximum value  
17 minimum value  
18 spread  
19 standard deviation  
20 standard deviation  
21 average values  
22 extremal values and standard deviations  
23 bottom  
24 middle  
25 top

4 EDV-Ausdruck 1; Frischgaszusammensetzung, Gasströme, Reaktionstemperaturen

KAT.NR. 41		VERS.NR. 136 3	ABGANG 25.10. 14.00 UHR 4	DAUER 24. STD. 5	8 ANALYSEN 6				
VORBEREITUNGEN 7		DRUCK 11.00 BAR 8	RAHM-DESCHW. 9	CO/H2 1.0357	KREISL.VERH. 1.50				
UHRZEIT	FRISCHGAS-ZUSAMMENSETZUNG	CO/H2	FRISCHGAS 73	REACTORTEMP.	REACTORTEMP.				
% H2	% CO	% H2	NL/H	UNTEREN 23	MITTE 24				
			REACTORTEMP.	OBEN 25					
14.00	43.56	45.78	11.26	1.0371	591.655	265.351	320.0	321.0	329.0
15.00	43.57	45.09	11.34	1.0351	607.556	369.767	321.0	321.0	329.0
20.00	43.72	46.22	12.00	1.0113	602.095	367.861	321.0	321.0	329.0
21.00	44.01	46.24	11.71	1.0040	601.533	364.527	321.0	321.0	329.0
1.00	43.26	45.74	11.00	1.0572	622.016	369.936	321.0	321.0	329.0
2.00	42.93	45.61	11.66	1.0630	621.087	373.901	322.0	323.0	330.0
6.00	43.23	45.06	11.74	1.0429	567.669	349.555	321.0	322.0	329.0
7.00	43.53	46.07	11.60	1.0345	632.182	384.323	322.0	322.0	330.0
M I T T E L W E R T 2 /									
14. / 7.	43.56	45.02	11.52	1.0357	605.664	367.035	321.1	321.5	329.2
14. / 20.	43.67	46.93	11.55	1.0278	600.456	367.659	320.7	321.0	329.0
21. / 2.	43.41	45.20	11.39	1.0416	614.992	366.475	321.3	321.7	329.3
6. / 7.	43.32	45.91	11.67	1.0592	599.738	366.939	321.5	322.0	329.5
E X T R E M W E R T E U N D S T A N D A R D A B W E I C H U N G 2 2									
MAXIMALE WERT 16	44.03	45.74	12.06	1.0630	637.188	384.323	322.0	323.0	330.0
MINIMALE WERT 17	42.93	46.22	11.00	1.0040	567.669	349.555	320.0	321.0	329.0
SPEZIFISCHE WERT 18	1.10	1.52	1.06	0.0582	64.600	34.768	2.0	2.0	1.0
STANDARDABW. 19	0.14	0.56	0.23	0.0200	20.384	10.049	0.6	0.8	0.5
STANDARDABW. 20	0.78	1.24	2.06	1.9348	3.365	2.738	0.2	0.2	0.1



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Table 5. EDP printout 2, composition of residual gas and olefin contents of the C-number fractions

1 reactor 1  
2 cat. no. 41  
3 experiment no. 138  
4 o'clock  
5 duration 24 hours  
6 analyses  
7 experimental conditions  
8 pressure 11 bar  
8a temperature 234 deg C  
9 space velocity  
10 circulation "VEPH" (abbreviation unknown)  
11 clock time  
12 composition of residual gas  
13 olefin contents (percent)  
14 maximum value  
15 minimum value  
16 spread  
17 standard deviation  
18 standard deviation  
19 average values  
20 extremal values and standard deviation

ab. 5 EDV-Ausdruck 2; Restgaszusammensetzung und Olefingehalte der C-Zahl-Fractionen

REACTOR 1./	KAT.NR. 41 2	VFPS.NR. 138 3	BEGINN 25.10.	14.00 UHR 4	Dauer 24. STD. 5	8 ANALYSEN 6								
VORSUCHSERIENUNGEN 7	DRUCK 11. BAR 8	TEMP. 324. GRD.C 9	RAUN-GESCHW. 200. ML/LEH	CO/H2 1.0357	KREISL.VERH. 1.50 10									
UHR- ZEIT //	% H2	% N2	% CO	% CO2	% C1	% C2	% C3	% C4	% C5	% C6	% C7	% C8	CO/H2	OLEFIN-GEHALTE (18) 12 C2-EP. C3-FR. C4-FR.
14.00	30.14	18.24	19.93	23.33	2.46	1.51	1.43	1.01	0.95	0.64	0.29	0.08	0.6612	82.63 91.39 90.51
16.00	30.10	18.23	20.06	22.08	2.48	1.52	1.44	1.00	0.95	0.63	0.26	0.07	0.6784	83.56 91.50 90.74
20.00	30.41	19.73	19.02	22.16	2.49	1.50	1.41	0.98	0.94	0.91	0.36	0.09	0.6256	81.56 91.50 90.49
21.00	30.99	19.35	19.38	21.99	2.48	1.49	1.39	0.97	0.93	0.66	0.20	0.08	0.6251	83.53 91.50 90.73
1.00	29.51	18.26	19.94	23.26	2.48	1.50	1.41	0.97	0.92	0.67	0.29	0.09	0.6755	83.47 91.43 90.40
2.00	29.78	19.03	20.75	23.10	2.44	1.49	1.40	0.97	0.91	0.62	0.28	0.07	0.6897	83.55 91.47 90.45
6.00	29.95	19.06	19.86	22.99	2.46	1.50	1.40	0.96	0.88	0.59	0.27	0.07	0.6633	83.50 91.51 90.48
7.00	30.23	19.78	19.92	22.95	2.44	1.48	1.38	0.94	0.85	0.52	0.26	0.06	0.6587	83.41 91.44 90.45
19 M I T T E I L U N G E N														
14. / 7.	30.09	19.01	19.79	22.83	2.47	1.50	1.41	0.97	0.91	0.65	0.29	0.07	0.6578	83.51 91.47 90.53
14. / 20.	30.21	18.07	19.67	22.79	2.48	1.51	1.43	1.00	0.95	0.73	0.30	0.08	0.6510	83.58 91.46 90.58
21. / 2.	30.96	19.11	19.95	22.80	2.46	1.50	1.40	0.97	0.92	0.65	0.29	0.08	0.6624	83.48 91.47 90.52
16. / 7.	30.29	19.07	19.89	22.72	2.45	1.49	1.39	0.95	0.86	0.55	0.26	0.07	0.6510	83.46 91.48 90.47
20 EXTREMPUNKTE UND STANDARDAUFWEICHUNG														
14/ ARITHMET	30.99	19.73	20.25	23.33	2.48	1.52	1.44	1.01	0.95	0.91	0.36	0.09	0.6592	83.63 91.53 90.74
15/ STATISCH	29.38	18.24	19.02	21.99	2.46	1.48	1.38	0.94	0.84	0.52	0.26	0.06	0.6251	83.41 91.39 90.40
16/ BEF. ZUNG	1.61	1.49	1.22	1.34	0.06	0.04	0.05	0.07	0.11	0.39	0.19	0.02	0.0648	0.22 0.13 0.34
17/ TART. ABW.	0.57	0.45	0.63	0.50	0.07	0.01	0.02	0.02	0.04	0.11	0.03	0.01	0.0224	0.17 0.05 0.13
18/ TEMP. ABW.	1.68	2.34	2.00	2.18	0.84	0.77	1.37	2.30	4.00	17.25	10.56	8.96	3.4065	0.09 0.05 0.14

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Table 6. EDP printout 3; reaction conditions, gas composition, reactions, yields, and product palettes

1 program FT 540  
2 liquid phase reactor no. 1  
3 catalyst number 41  
4 experiment number 138  
5 suspension volume  
6 type of calculation  
7 beginning  
8 duration  
9 analysis  
10 pressure  
10a H<sub>2</sub> + CO charge  
11 make-up gas  
12 residual gas  
13 circulation  
14 make-up gas  
15 residual gas  
16 reaction  
17 make-up gas  
18 measured  
19 measured minus theoretical  
20 residual gas  
21 C-number distribution, percent of C<sub>1+</sub>  
22 olefin contents of the fraction  
23 C<sub>4</sub> fraction  
24 alpha-component  
25 C<sub>2</sub>/C<sub>4</sub> olefins content of  
26 composition of the FT product, mass percent  
27 yield  
28 consumption  
29 gas reactions, percent of charge  
30 correction  
31 make-up gas  
32 residual gas  
33 volume percent (corrected)  
34 day  
35 hour  
36 number  
37 deg C

6 EDV-Ausdruck 3; Reaktionsbedingungen, Gaszusammensetzung, Umsätze, Ausbeuten und Produktpaletten

PROGRAMM FT 540 / FLUENSTICHPHASE-REAKTOR-NR. 1.2		KATALYSATOR-NR. 3.41		VERSUCHS-NR. 130		SUSPENSIONNS-VOL. 3.000 L														
ZEIT	TEMP. DRUCK	HAUER ANA- LVS.	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100									
1	8.2	25.10	14	7	3	324	11	177	210	172	1.50	1.0277	0.6533	1.2902	43.46	11.52	45.02	3.20	1.24	3.41
2	8.2	25.10	14	7	3	324	11	176	199	172	1.50	1.0239	0.6535	1.2967	43.62	11.55	44.83	3.39	1.24	3.46
3	8.2	25.10	14	7	3	324	11	179	202	172	1.50	1.0255	0.6779	1.2720	43.41	11.39	45.20	3.39	1.24	3.39
4	8.2	26.10	6	2	2	324	11	176	199	172	1.50	1.0346	0.6639	1.3786	43.32	11.67	45.01	0.11	1.24	3.37

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Table 7. EDP printout 4; reaction conditions, reactions, yields, and product palettes

1 program FT. 540  
2 liquid phase reactor no. 1  
3 catalyst no. 41  
4 experiment no. 138  
5 suspension volume  
6 beginning  
7 duration  
8 analysis  
9 temperature  
10 pressure  
10a H<sub>2</sub>+CO charge  
11 make-up gas  
12 residual gas  
13 circulation  
14 make-up gas  
15 residual gas  
16 conversion - VEPH (abbreviation unknown)  
17 gas conversion, percentage of charge  
18 selectivities percent of C<sub>1+</sub>  
19 olefin contents of the fractions  
20 composition of the C<sub>4</sub> fraction  
21 composition of the FT product mass percent  
22 composition of the C<sub>2</sub>/C<sub>4</sub> olefins  
23 yields  
24 date  
25 hour  
26 number  
27 deg C

ib. 7 EDV-Ausdruck 4; Reaktionsbedingungen, Umsätze, Ausbeuten und Produktpaletten

PROGRAMM FT 540 / FLIESSICHPHASE-REAKTOR-NR. 1. 2		KATALYSATOR-NR. 3 41		VEFSUCHS-NR. 4 12A		SUSPENSIONSVOL. 5 3.000 L							
NR.	REGIM 24 TAG	DAUER 25 STU	TEMP. 324	ANFA- LYS. ZARL 820	DRUCK 10 10a		FRISCH -GAS NE/L*H	PEST- GAS NE/L*H	KREIS- LAUF VERH.	CO/H2 FRISCH -GAS	CO/H2 FEST- GAS	CO/H2 UNSATZ -VERH.	17 GAS-UMSATZ % VOM EINSATZ CO H2 CO+H2
					BAR	MPA							
1	25.10.14.	24.	324.	3.	11.	177.	20%	122.	1.50	1.0772	0.6633	1.2502	72.91
2	25.10.14.	7.	324.	3.	11.	176.	19%	123.	1.50	1.0239	0.6535	1.2367	72.93
3	25.10.21.	6.	324.	3.	11.	179.	20%	122.	1.50	1.0255	0.6729	1.2720	73.01
4	26.10.6.	2.	224.	2.	11.	176.	19%	122.	1.50	1.0346	0.6639	1.3386	72.73
<p>EFFEKTIVPALETTEN 78</p> <p>SELEKTIVPALETTEN 78</p> <p>FRAKTIONEN 79</p> <p>FRAKTIONEN 79</p> <p>ZUSAMMENSETZUNG DER C4-FRAKTION 20</p> <p>ZUSAMMENSETZUNG DER C4H8-2 C4H10 C4H12 &amp; V. C4H8</p>													
NR.	CP/C4	CL	C2	C3	C4	C5+	C2	C3	C4	TRANS	CIS	N-	AUTEN-1
1	22.25	8.03	9.77	12.77	12.69	55.73	81.51	91.47	90.53	85.24	2.60	2.60	8.36
2	30.15	8.17	9.06	14.12	13.14	56.60	83.58	91.46	90.58	85.32	2.63	2.63	9.31
3	31.41	7.95	8.53	13.40	12.37	56.75	83.48	91.47	90.52	85.38	2.57	2.57	9.37
4	32.17	9.10	9.85	13.80	12.52	55.73	83.46	91.48	90.47	85.28	2.59	2.59	8.41
<p>ZUSAMMENSETZUNG DES FT-PRODUKTES 21</p> <p>ZUSAMMENSETZUNG DER C2H6 C2H4 C3H6 C4H8 C4H10 C5+</p>													
NR.	CP/C4	CL	C2	C3	C4	C5+	C2H6	C2H4	C3H6	C4H8	C4H10	C5+	AUSREUTEN G/M3(19) 23
1	31.77	9.05	8.04	1.77	12.41	1.21	11.32	1.23	55.05	25.30	39.06	35.64	47.6
2	32.04	9.21	8.20	1.73	12.72	1.24	11.72	1.26	53.92	25.12	38.97	35.91	43.6
3	30.05	8.35	7.84	1.66	12.78	1.13	11.03	1.20	56.16	25.32	39.03	35.64	41.8
4	31.69	9.13	8.10	1.72	12.44	1.21	11.16	1.22	55.04	25.55	39.24	35.21	42.3

