4 Experimental Results when using Different Catalysts

During the past years, the laboratory system was set up and test runs were completed, and then a series of catalysts were investigated by varying the experimental conditions in different reactors. The results obtained thereby are listed and discussed below, organized according to the type of catalyst. Iron precipitation catalysts, special catalysts of Sasol Company, iron whisker catalysts from the Institute for Physical chemistry of Bonn University, catalysts from Ruhrchemie and manganese-iron catalysts, which first were made available to us by the Institute for Physical Chemistry of Berlin Technical University, and which we subsequently fabricated in our own laboratory, were all used.

The catalysts were generally delivered in unreduced form. They were then formed in the synthesis reactor. The results obtained with the catalyst and a reactor were summarized, in dependence on the chosen reaction conditions, in generally one but sometimes two EDP printouts. Each line specifies the average results for one reaction condition. The number of basic individual values is specified as the analysis number. As a rule, the results are printed out in their time sequence. In individual cases, the arrangement is by reaction conditions, to increase clarity.

4.1 Iron Precipitation Catalysts after H. Kölbel

At the beginning of the investigation in the liquid phase reactor, iron precipitation catalysts were tested, which were fabricated in our own laboratory according to a prescription partly under the supervision of H. Kölbel. They correspond to catalysts for the conventional FT synthesis. Investigation of these catalyst represent the connection to older researches on the liquid phase reactor.

In the smaller liquid phase reactor (diameter 25 mm), 3 l suspensions were always utilized which contained 700 g unreduced, powdered catalyst. The formation was performed in the reactor at 320° C through 24 hours treatment with hydrogen. The experimental results from 1976, which were obtained with catalysts 15 through 17, are shown in Tables 8 through 10. These catalysts were reduced according to the same prescription. The liquid phases were FT waxes of the Sasol Company. The catalysts 15 and 17 were suspended in soft wax, and the catalyst 16 in hard wax. Under the reaction conditions, the soft wax escapes in considerable quantities in vapor form jointly with the FT products. Consequently, because of its much lower vapor pressure, the usefulness of hard wax was to be investigated.

The results achieved with catalyst 15 are summarized in Table 8. In this experiment, CO-rich gas (CO/H_2 = 1.4) was always used. The pressure was 11 bar, the space velocity about 390 h^{-1}, the circulation ratio 0. The temperature was increased during the run from 270 to 294° C. During the run, the total reaction was nearly constant. The temperature increases compensated the aging deactivation of the catalyst. At most, 29 g C_2/C_4 olefins per m^3 (V_n) utilized ideal gas were obtained with a total yield of 118 g C_{1+} products. These olefins contained 11 mass percent ethylene. The selectivity for these olefins was 25 percent.

Table 9 contains the results obtained with catalyst 16 in hard wax, and Table 10 contains the results obtained with catalyst 17 in soft wax. In

both experimental runs, the pressure was 11 bar, the space velocity about 330 h^{-1}, the circulation ratio 1.08, and the CO/H_2 ratio about 0.7. Hydrogen-enriched synthesis gas was therefore utilized. During the runs, the temperature was increased from 269 to 286 and respectively 290° C.

In these experiments, too, the conversions remain practically constant during the run. Somewhat higher conversions were here obtained in soft wax than in hard wax. With the subsequently cited figures, the first one always refers to catalyst 17 (Table 10) and the second one, in parentheses, refers to catalyst 16 (Table 9). Per m^3 (V_n) of utilized ideal gas, a maximum of 14 (12) g C_2/C_4 olefins were obtained with a total yield of 119 (96) g C_{1+} products. These olefins contain 8 (7) mass percent ethylene. A C_2/C_4 olefin selectivity of 12 (13) percent was obtained. The C_2/C_4 olefin yield, composition, and selectivity is thus practically the same with hard wax and soft wax. The low C_2/C_4 olefin selectivity is a consequence of the low olefin contents in the C_2 through C_4 fractions. The C_2/C_4 selectivity is more than 60 percent. A comparison with the results of Table 8 shows that, with these conventional catalysts, it is more favorable to use CO-rich synthesis gases if the C_2/C_4 olefins selectivity and yield are to be increased.

The results obtained in a small fixed-bed reactor with an iron precipitation catalyst are shown in Table 11. During the entire run, the gas was not run in circulation and the pressure was 11 bar. The temperature was raised from 270 to 300° C, the space velocity was varied in the range from 150 to 430 h^{-1}. Two different synthesis gases were used. The gas conversions lay between 62 and 85 percent. When using the CO-rich gas, the product palette contained a higher portion of C_{5+} products. Per m^3 (V_n), the highest C_2/C_4 olefin yields were 31 g with a total yield of 151 g of C_{1+} products. These olefins contained 9 mass percent ethylene. The C_2/C_4 olefin selectivity here reached 21 percent. The maximum C_2/C_4 olefin yield was obtained with a CO/H_2 ratio of about 1 and a temperature of 300° C.

4.2 Special Catalysts from Sasol

In 1976, Sasol made available to us three catalysts. They are identified by the digits 1, 2, and 3. We obtained them in synthesis-active form, melted into wax. About 500 g of the reduced catalyst were always inserted in the liquid phase reactor with 3 liter useable capacity. Soft wax was the liquid phase for some experimental runs and hard wax with others. The results are summarized in Tables 12 through 17.

4.2.1 The Sasol Catalyst 1

The results achieved with this catalyst are shown in Tables 12 and 13. In experiment number 53 (Table 12), the catalyst is suspended in soft wax and is identified by the number 18. In experiment number 70 (Table 13), the same catalyst is surrounded by hard wax as the liquid phase and is designated by number 22. In the tables, the cross-lines indicate a change of the CO/H_2 ratio. But for one exception (Table 12, number 6), the results are given in their time sequence.

The reaction conditions are quite similar and thus the results are comparable with numbers 4 through 6 in Table 12 and numbers 1 through 6 in Table 13. The like holds for numbers 7 through 12 in Table 12 and numbers 7 through 12 in Table 13. Under comparable conditions, somewhat higher conversions are attained with soft wax as the liquid phase than with hard wax.

The highest C_2/C_4 olefin yields and selectivities are obtained with very hydrogen-rich synthesis gases ($CO/H_2 = 0.4$). As the CO content rises, these olefin yields and selectivities decline. This is a consequence of the low hydrogenating action of the catalyst, so that even with a very high hydrogen content, the C_2- through C_4-fractions still contain much olefin. The rise of the carbon oxide content extends the average chain length in the (line missing) and thereby reduces the C_2/C_4 selectivity. this reduction cannot be compensated by increasing the olefin contents.

Per m^3 (V_n), the maximum C_2/C_4 olefin yield was 43 g with a total yield of 136 g of C_{1+} products. These olefins contained 25 mass percent ethylene. The C_2/C_4 olefin selectivity is 33 percent, which was quite high. This favorable yield was obtained only after a longer running time.

4.2.2 The Sasol Catalyst 2

This catalyst, too, was suspended in both types of wax. In combination with soft wax, it was used in experiment number 57 (Table 14), and distributed in hard wax it was used in experiment number 72 (Table 15). The experimental conditions differ only slightly, and consequently the experimental results are comparable, with numbers 1 through 4 and respectively numbers 5 through 8 in Table 14 and numbers 1 through 3 and respectively 4 through 8 in Table 15. With this catalyst, the conversions are practically independent of the medium of the liquid phase. The C-number distributions also differ only little from one another. However, the olefin contents of the C_2 to C_4 fractions were greater with hard wax than with soft wax, and thus the C_2/C_4 olefin selectivities and yields in hard wax exceeded those in soft wax. The C_2/C_4 olefin yields depend only slightly on the CO/H_2 ratio of the make-up gas. When using carbon monoxide-rich gas (CO/H_2 ratio about 1.36), however, the catalyst is rapidly deactivated, which leads to a quick drop of the gas conversion.

With both types of wax, a maximum of 41 g C_2/C_4 olefins are formed per m^3 (V_n) utilized ideal gas. The C_2/C_4 olefin selectivity with hard wax is 27 percent as compared to 24 percent for soft wax, and the ethylene content is 20 percent as compared to 15 percent with soft wax. However, this result was obtained with catalysts of different age - the hard wax had a fresher catalyst - and thus this may also be the reasons for the differences.

4.2.3 The Sasol Catalyst 3

Tables 16 and 17 summarize the results obtained with this catalyst in soft wax and in hard wax respectively. On the basis of the very similar experimental conditions, the results of numbers 1 through 4 of Table 16 should more or less agree with those of numbers 1 through 3 of Table 17. However, this does not happen. The palettes obtained in soft wax are poorer in olefins and the C_2/C_4 olefin yields and selectivities are lower. With the butenes, the double bonds tend much less to occupy the terminal positions. With experiment number 59 (Table 16), therefore, the catalyst was probably damaged rather early on. The reason for this has remained unknown. Consequently, the results obtained in hard wax are to be regarded as characteristic for this catalyst. Per m^3 (V_n) utilized ideal gas, a maximum of 40 g C_2/C_4 olefins was obtained, containing 20 mass percent ethylene. The C_2/C_4 olefin selectivity was 26 percent.

4.3 Catalysts from Ruhrchemie

From 1976 through 1978, the Ruhrchemie supplied us with several catalysts for testing. They were investigated in the liquid phase reactor and one also in the fixed-bed reactor. High temperatures during formation and synthesis were required for adequate catalyst activity. In the liquid phase reactor, they could only be reached after converting the system and changing the heat medium. Thus, only the last delivered catalyst was tested under the temperatures which were designated as optimal by the Ruhrchemie. In particular, the following results were obtained.

4.3.1 Ruhrchemie Catalyst LP 5/76

500 g of the unreduced delivered catalyst, suspended in soft wax, were used in the liquid phase reactor with 3 l useful capacity. The catalyst was formed

by 24 hour treatment with hydrogen at 320° C - the maximum reactor temperature of that time. The temperature of 340° C, which was proposed by Ruhrchemie, could not be obtained.

During the six weeks run in August and September 1976, the temperature was increased weekly by 10 K. All other conditions were kept constant. As Tables 18a and 18b show, the pressure was 15 bar, the space velocity was about 330 h^{-1}, the circulation ratio was 0.37, and the CO/H_2 ratio in the make-up gas was about 1.0. The synthesis was started at a temperature of 268° C, and the run was completed at 316° C.

Table 18a shows the results obtained during the first three weeks, Table 18b the results obtained during the last three weeks. Up to the fourth week, there was a slight rise of conversion from 60 to about 74 percent. Subsequently, the slight reduction of conversion, which was observed at constant temperature, was compensated by increasing the temperature. With rising temperature, both the olefin content and the selectivities...(line missing) ... the C_2 through C_4 fractions and thus also the C_2/C_4 olefin selectivities.

The highest C_2/C_4 olefin content, with 37 g per m^3 (V_n) ideal gas utilization, was reached at the maximum temperature of 315° C. Under these conditions, these olefins contained 24 mass percent ethylene. The C_2/C_4 olefin selectivity was 25 percent.

4.3.2 The Ruhrchemie Catalyst LP 5/77

This catalyst was delivered in pieces in synthesis active form. It had to be disintegrated before use in the liquid phase reactor. It was ground in a ball mill, whereby the catalyst was suspended in an FT heavy gasoline fraction, to prevent oxidation.

During the grinding, and filling into the reactor, the catalyst suspension was protected by being covered with carbon dioxide.

Nevertheless, only a low conversion was obtained with this catalyst, as can be seen from Table 19. At the end of February, an attempt was made to improve the activity of the catalyst by 24 hours treatment with hydrogen at 320° C. Subsequently, higher but still unsatisfactory conversions were obtained at a reduced space velocity. Details can be found in Table 19.

Because the activity was too low, the results achieved are not to be regarded as optimal for this catalyst. At most 29 g C_2/C_4 olefins with 22 percent ethylene were obtained per m^3 (V_n) of utilized ideal gas. The selectivity of these olefins was here 28 percent. In this particular run, 51 percent of the utilized ideal gas was converted.

4.3.3 The Ruhrchemie Catalyst LP 14/77

This catalyst was again delivered in pieces in reduced form and had to be ground in the same fashion as described for catalyst LP 5/77. As can be seen in Table 20, the gas conversions for this catalyst were a maximum of 18 percent, which is still smaller. The results therefore need not be discussed.

4.3.4 The Ruhrchemie Catalyst LP 8/78

The previous results have shown that it does not always make sense to grind already synthesis-active catalysts. On the other hand, an adequate catalyst reduction and a satisfactory gas conversion are possible only at higher temperatures in the liquid phase reactor. Before testing the next Ruhrchemie catalyst, the reactor was therefore converted to higher temperatures. The previous heat medium, Marlotherm S, was replaced by the thermally more stable Gilotherm. The higher temperatures also made necessary the replacement of the pumps for the heat medium circulation. After this system conversion, the reactor could be heated to 380° C.

The catalyst was tested both in the liquid phase and in the fixed-bed reactor. It was delivered in pieces and unreduced and had to be ground before being used in the liquid phase reactor. After this, its particle size was less than 0.05 mm. A five liter catalyst-hard wax suspension was used, containing 800 g of the ground, unreduced catalyst. The larger liquid phase reactor was utilized, in which the non-expanded suspension column was 2.5 m high. The catalyst was activated by 20 hours hydrogen treatment at a maximum temperature of 380° C.

Table 21 shows the experimental results. The gas was not circulated. The pressure and the make-up gas composition was nearly constant during the entire run. It was begun in August 1978 and was continued after a pause at the end of August. Despite the high reduction temperature, the gas conversions were again unsatisfactory. Therefore, the temperature was raised from 320 to 370° C during the run, and the space velocity was lowered from 430 to 150 h^{-1}. Nevertheless, at the highest temperature and the lowest space velocity, only a conversion of 54 percent was obtained.

Under constant reaction conditions, the conversion already declined noticeably within a few hours. This rapid deactivation was surely the consequence of the high reaction temperature, at which carbon is formed to an increasing extent and the hard wax is cracked, at which short-chain waxes vaporize and the viscosity of the suspension rises, both the carbon separation and the velocity increase influence the gas conversion. The wax cracking changes the product palette.

Because of experience gained during this run, it can be said that the liquid phase reactor should not be operated at such a high temperature, at least not with hard wax, since, under these conditions, the stability of the catalyst is also low. But even these temperatures are too low to obtain a sufficiently synthesis-active catalyst during forming.

A maximum C_2/C_4 olefin yield of 40 g per m^3 (V_n) with a high ethylene content (34 mass percent) was obtained. The C_2/C_4 olefin selectivity was 39 percent, a very high value.

For comparison, the catalyst was also investigated in the small fixed-bed reactors. In experiment number 4, 55 g of the catalyst was used, with grain sizes between 2 and 3 mm. It was reduced by 20 hours treatment with hydrogen at about 420° C. The results shown in Table 22 make clear that the catalyst was much more synthesis active after this than in the liquid phase reactor, in which the formation took place at a 40 K lower temperature.

During the run, the pressure was kept at 11 bar and the CO/H_2 ratio in the make-up gas was held constant at 1.2. The temperature was increased step

by step from 292 to 331° C. The space velocity was first run 100 h^{-1}. It was first raised to 534 h^{-1} and then was again lowered at constant temperature. At 331° C, a maximum of 90 percent of the utilized ideal gas was converted.

Up to the 8th of September, no activity change of the catalyst could be observed. After this, the flow resistance in the reactor increased so strongly within a few hours that the experiment had to be terminated. With a gas conversion of 81 percent, a maximum of 54 g C_2/C_4 olefins per m^3 (V_n) were formed, containing 19 mass percent ethylene. A C_2/C_4 olefin selectivity of 34 percent was achieved here.

Investigations with this catalyst were concluded with experiment number 14, during which formation at 400° C was performed. The synthesis activity observed after this lay above that which was obtained in the liquid phase at 380° C and below that which was obtained in the fixed bed at 420° C. Evidently, temperatures above 400° C are required for this catalyst if a sufficient activation is to be achieved.

During the experimental run, the CO/H_2 ratio in the make-up gas was 1.0, corresponding to that in the experiment in the liquid phase reactor, as can be seen in Table 23. Initially, the catalyst activity increased under constant reaction conditions (numbers 1 through 6). The gas conversion rose from 39 percent to 75 percent. With increasing conversion, the methane content rose, and the C_2/C_4 olefin specificity as well as the ethylene content of these olefins declined. During this run, too, the flow resistance in the reactor finally increased so strongly that the experiment had to be terminated.

The maximum C_2/C_4 olefin yield was 54 g per m^3 (V_n), the C_2/C_4 olefin selectivity was 38 percent. These olefins had an ethylene content of 15 mass percent.

The investigations have shown that, by means of this catalyst in the small fixed-bed reactors, at least 54 g C_2/C_4 olefins per m^3 (V_n) ideal gas utilization can be formed. With more active catalysts than previously, this should also be possible in the liquid phase reactor. For temperatures above about 330° C, hard waxes are unsuitable as the liquid phase. The catalyst stability at high temperatures is unsatisfactory.

Interestingly, the C_2/C_4 olefins formed in the liquid phase reactor contain more ethylene than those formed in the fixed-bed reactor. Whether this is caused by the reactor type, or whether it is a consequence of the lower gas conversion and thus the lower olefin concentration in the residual gas, or whether the higher reaction temperatures is responsible for this, or whether a portion of the ethylene has been generated by hard wax cracking, cannot be decided on the basis of the present data material. The experiments should therefore be supplemented by testing more active liquid phase catalysts.

4.4 Iron Whisker Catalysts

Two iron whisker catalysts were made available to us by W. Vielstich and D. Kitzelmann of the Institute of Physical Chemistry of Bonn University, for testing in the liquid phase and fixed-bed reactors.

4.4.1 The Iron Whisker Catalyst for the Liquid Phase Reactor

800 g of the powdered catalyst, suspended in hard wax and without forming, were directly charged with synthesis gas in the 3 l-capacity liquid phase reactor. Within the first days, the gas conversion rose slowly even though the space velocity was increased from 410 to 760 h^{-1}. This indicated that the heavy catalyst was suspended more uniformly in the liquid phase as the gas flow increased. During the following week, the residual gas was recycled into the reactor with the high circulation ratio of 6, in order to increase the gas flow. With a reduced space velocity, the conversion here discontinuously rose from 21 percent to 74 percent. Surprisingly, despite the circulation, the ethylene content of the C_2 fraction increased only slightly.

Details concerning the reaction conditions and the results obtained can be found in Tables 24a and 24b. They are arranged in temporal sequence. As the circulation ratio declined, the conversion also was reduced. The conversion was increased only slightly by increasing the pressure at the end of the run. The double bond of the butenes had terminal positions in more than 90 percent of the cases.

A maximum of 48 g C_2/C_4 olefins with 24 mass percent ethylene was obtained per m^3 (V_n) ideal gas utilization. The C_2/C_4 olefin selectivity was 31 percent.

4.4.2 The Iron Whisker Catalyst for the Fixed-Bed Reactor

The whisker catalyst for the fixed-bed had a diameter of 2 mm and a length of 3 mm. They were formed in the reactor by 20 hours treatment with hydrogen at 380° C. The results obtained during the synthesis are shown in Table 25 in their temporal sequence. The temperature, pressure, space velocity, and CO/H_2 ratio in the make-up gas were varied. With a CO/H_2 ratio of barely 1.3, a catalyst deactivation, presumably caused by carbon segregation, led to a rapid decline of conversion. With a reduced CO content, the conversion rose again. The pressure rise from 11 to 21 bar increased gas conversion only slightly. At 11 bar, the olefin contents of the C_2 fraction exceeded 80 percent, that of the C_3 and C_4 fractions exceeded 90 percent. Upon an increase to 21 bar, the C_2 fraction became poorer in olefins.

The maximum C_2/C_4 olefin yield at 11 bar was 49 g per m^3 (V_n) with 26 percent ethylene and a C_2/C_4 olefin selectivity of 35 percent. 69 percent of the ideal gas was converted here. At 21 bar, a somewhat higher C_2/C_4 olefin yield was reached, namely 54 g per m^3 (V_n), which is a consequence of the higher ideal gas conversion of 80 percent. The C_2/C_4 olefins, however, contained only 18 percent ethylene. The C_2/C_4 olefin selectivity was 34 percent, which is about the same.

The results obtained in the two reactor types agree quite well. The somewhat lower ethylene content and the olefin selectivity which is less by a few percent in the liquid phase reactor probably is a consequence of the considerable circulation of the residual gas.

Characteristic for this catalyst is the low hydrogenation effect, so that even when using hydrogen-rich gases and considerable olefin recycling in the circulating gas, the very easily hydrogenatable ethylene is scarcely converted into ethane. Up to now, a disadvantage with this catalyst is the high C_{5+} fraction. If this can be reduced, considerable improvements in the C_2/C_4 olefin selectivity and thus also in the yield should be possible.

4.5 Manganese-Iron Catalysts

The manganese iron catalysts was made available to us by H. Kölbel and K.D. Tillmetz from the Institute for Technical Chemistry of Berlin Technical University. Later, we fabricated them ourselves according to the Berlin recipe.

4.5.1 Manganese-Iron Catalysts from Berlin Technical University

From the Berlin Institute we obtained seven catalysts. They were numbered in their time sequence and were identified by the supplement "(Berlin)". The catalysts were tested in the liquid phase reactors and partly also in the fixed-bed reactors. The liquid phase was always hard wax from Sasol.

4.5.1.1 The Mn-Fe Catalyst 1 (Berlin)

This catalyst, which we obtained in March 1977, had already been formed in Berlin in a fixed bed reactor. Consequently, after being inserted in the liquid phase reactor, it could be directly charged with synthesis gas.

Table 26 shows the reaction conditions and experimental results. The pressure was constant at 11 bar, and the space velocity was about 340 h^{-1}. What was varied were the temperature, from 286 to 314° C, and the CO/H_2 ratio in the make-up gas, from 1.0 to 1.4. The individual runs are not listed in their time sequence, but according to increasing CO/H_2 ratio and ....(line missing)

The activity of the catalyst was unsatisfactory, at most 50 percent of the ideal gas was converted. According to expectation, the conversion increased with increasing temperature. The molecules became more short-chain on the average. The selectivities of the C_2 through C_4 fractions, but also of the C_2/C_4 olefins increased, but the ethylene content of these olefins declined.

A maximum of 41 g C_2/C_4 olefins per m^3 (V_n) ideal gas, with an ethylene content of 12 mass percent, was obtained. The C_2/C_4 olefin selectivity was here 43 percent. The butene-1 content of the butenes was 63 percent.

4.5.1.2 The Mn-Fe Catalyst 2 (Berlin)

The catalysts 1 and 2 originated from the same production charge. In contrast to catalyst 1, the catalyst 2 - as all catalysts subsequently delivered by Berlin Technical University - was delivered unreduced and was formed in Bergkamen. To convert the catalyst into the synthesis-active state, successive treatments with carbon monoxide and hydrogen at 320° were performed in a liquid phase reactor, each treatment taking 24 hours.

The results are shown in Table 27. During the run, the temperature remained constant (315 to 317° C). The pressure was varied from 11 to 36 bar, and the space velocity from 330 to 1136 h^{-1}, and the CO/H_2 ratio in the make-up gas from 0.7 to 2.0. The individual runs are again arranged independent of their time sequence according to associated reaction conditions.

In this experiment, too, the gas conversions were not satisfactory. With the smallest space velocity and the highest pressure, the maximum attainable was 65 percent . One can see in the table that the C_{5+} selectivity became

larger with increasing pressure and increasing CO/H_2 ratio. The C_2/C_4 olefin selectivity was reduced with increasing pressure and depended only slightly on the CO/H_2 ratio in the make-up gas. A maximum of 40 g C_2/C_4 per m^3 (V_n) with 16 percent ethylene were obtained with a gas conversion of 50 percent. The C_2/C_4 olefin selectivity was 41 percent. Sixty-five percent of the butene double bonds occupied terminal positions.

As a comparison with Table 26 indicates, the maximum yields and their reaction conditions are very similar for catalysts 1 and 2. Despite different activation, both catalysts thus must have had the same properties.

4.5.1.3 The Mn-Fe Catalysts 3 (Berlin)

This catalyst was formed in the liquid phase reactor at 300° C. Carbon monoxide and then hydrogen was conducted through the reactor, each for 20 hours.

Table 28a and Table 28b show the results. Between the runs, the temperature was changed from 284 to 314° C, the pressure from 11 bar to 21 bar, and the space velocity from 258 to 646 h^{-1}, and the CO/H_2 ratio in the make-up gas from 0.8 to 1.5. These tables are also arranged by comparable reaction conditions and not according to time sequence.

With this catalyst, the gas conversion increased with increasing CO content in the synthesis gas, while the C_2/C_4 olefin selectivity decreased. As the temperature rose, the gas conversion also rose. The palette became more short-chained, without changing the C_2/C_4 olefin selectivity. The ethylene content of these olefins became somewhat less. The tendency of the double bonds to occupy the terminal positions also declined in the butenes. An increase in the space velocity lowered the gas conversion, as expected.

A maximum of 37 g C_2/C_4 olefins per m^3 (V_n) ideal gas, with an ethylene content of 18 mass percent were formed. With a gas conversion of 74 percent, the C_2/C_4 olefin selectivity was 25 percent.

The results of Table 28b followed in time those of Table 28a. They indicate that the pressure rise from 11 to 21 bar surprisingly led to a decline of conversion. This is probably the consequence of damage to the catalyst, caused by the pressure change, since even after reducing the pressure to the old value, the gas conversion remains small. The experimental run therefore had to be terminated.

4.5.1.4 The Mn-Fe Catalyst 4 (Berlin)

The catalysts 4 through 7 were formed in the same fashion as described for catalyst 3. Here the temperature, however, was only 280° C. During the run, the pressure was kept constant at 21 bar. The remaining reaction conditions and the experimental results obtained can be found in Table 29. The runs are again arranged by reaction conditions, but these generally coincide with the temporal sequence.

The first part of the table (numbers 1 through 7) shows the effect of temperature. Corresponding to the conversion increase, the C_2/C_4 olefin yield also increases. The C_2/C_4 olefin selectivity remains constant, and the ethylene content of these olefins declines.

The second part of the table (numbers 8 through 13) shows the dependence on the composition of the make-up gas. The conversion and C_2/C_4 olefin yield are hardly changed at all. The ethylene content of the C_2/C_4 olefins increases slightly with increasing CO/H_2 ratio, and the average chain length of the molecules increases. The maximum C_2/C_4 olefin yield was 34 g per m^3 (V_n). These olefins had 24 mass percent ethylene. With this yield, 69 percent of the ideal gas was converted. The C_2/C_4 olefin selectivity was 24 percent. Terminal positions were occupied by 97 percent of the butene double bonds.

4.5.1.5 The Mn-Fe Catalyst 5 (Berlin)

The catalyst was tested both in the liquid phase and in the fixed-bed reactor.

The results of the liquid phase reactor are shown in Table 30. The activity of the catalyst was low, so that at most only 37 percent of the utilized ideal gas were converted. A discussion of the results can therefore be omitted.

In the fixed-bed reactor, much higher conversions were attained as can be seen in Table 31. During the entire run, the pressure and the CO/H_2 ratio of the make-up gas were constant. At first (numbers 1 through 13), the space velocity remained constant and the temperature was step-by-step increased from 262 to 315° C. Subsequently, at constant temperature, the space velocity was increased from 280 to 520 h^{-1}.

The maximum C_2/C_4 olefin yield was 43 g per m^3 (V_n), and the C_2/C_4 olefin selectivity was 25 percent. Of these olefins, 16 percent was ethylene, and of the butenes, 72 percent were α-olefins.

As the temperature rose, the conversion rose and the ethylene content of the C_2/C_4 olefins declined. The tendency of the double bond in the butenes to occupy terminal positions also declined. With increasing space velocity, the reverse trends were observed.

4.5.1.6 The Mn-Fe Catalyst 6 (Berlin)

This catalyst, too, was tested in both reactors. Two experimental runs were performed in the liquid phase reactor and one in the fixed-bed reactor. In all cases, the conversions were unsatisfactory.

During experiment number 123 in the liquid phase reactor, the results of which are shown in Table 32, the temperature was first raised to 320° C. Since the conversion was low, the space velocity was then reduced, and finally the pressure was increased. At most, 59 percent of the ideal gas were converted and 25 g C_2/C_4 olefins per m^3 (V_n) with only 8 percent ethylene were obtained, and only 36 percent α-olefins in the butene fraction were obtained. Under these conditions, the C_2/C_4 olefin selectivity was only 22 percent.

The results of experiment number 125 in the liquid phase reactor are summarized in Table 33, and are arranged in their time sequence. During the entire run, the pressure was constant. Beginning with run number 3, the space velocity was no longer changed, and from number 7 on the composition of the make-up gas was not changed. The temperature also was no longer

changed beginning with number 12. At the final temperature, the catalyst was deactivated, which led to a rapid decline of the conversion rate.

During this experiment, the maximum conversion was 85 percent. Here, 28 g C_2/C_4 olefins per m^3 (V_n) were produced, with 12 percent ethylene. The butene fraction contained 53 percent α-olefins. With a maximum yield, a C_2/C_4 olefin selectivity of 25 percent was achieved. The results of the two experiments are quite similar.

Experiment number 12 (Table 34) was performed in the large fixed-bed reactor. This reactor could be operated stably only within a narrow range of parameters, since the dissipation of the reaction heat over the gas phase is difficult. It can be facilitated by circulating the gas. However, we could not do this, because, with this catalyst, recycling the gas would hydrogenate a considerable portion of the resulting olefins into paraffins. It is here especially easy to convert ethylene into ethane.

Gas samples could be withdrawn at the entry, at the middle, and at the end of the reactor. It was thus possible to have data concerning partial and total conversions.

In Table 34, the lines with an odd number always give the results of the first reactor half, and those with an even number give the results of the total reactor. The palettes formed in the first and second reactor halves differ only slightly. As expected, the gas conversion is higher in the first reactor half than in the second one.

A maximum of 31 g C_2/C_4 olefins per m^3 (V_n) ideal gas utilization, with an ethylene content of 23 percent, was obtained. Here, the gas conversion was 65 percent and the C_2/C_4 olefin selectivity was 24 percent. α-olefins made up 94 percent of the butenes. In the liquid phase reactor and in the fixed-bed reactor, the C_2/C_4 olefin selectivities were about the same. The C_2/C_4 olefins, however, were more ethylene-rich in the fixed-bed reactor.

4.5.1.7 The Mn-Fe Catalyst 7 (Berlin)

This catalyst was again used in both reactor types.

During experiment number 128 (Table 35), the smaller liquid phase reactor with 3 liter useful capacity was used. The pressure was varied from 8 to 15 bar, the temperature from 285 to 325° C, the space velocity from 165 to 365 h^{-1}, and the CO/H_2 ratio in the make-up gas from 1.03 to 1.65.

A maximum of 66 percent of the ideal gas was converted. During the run, the palettes became more short-chained (reduction of the C_{5+} selectivity), the olefin content, especially of the C_2-fraction, became less, and the initially nearly completely terminal double bonds of the butenes occupied central positions to an increasing extent.

A maximum of 33 g C_2/C_4 olefins per m^3 (V_n), with 23 percent ethylene were obtained, and 88 percent α-olefins in the butenes were formed. With a conversion of 64 percent, the C_2/C_4 olefin selectivity was 26 percent.

During experiment number 134 (Table 36), the conversion was performed in the larger liquid phase reactor. Here, the CO/H_2 ratio was constant at 1.0, and the pressure was constant at 11 bar beginning with run number 2. The temperature was varied from 275 to 335° C and the space velocity was varied from 360 to 184 h^{-1}. The maximum conversion was 64 percent. During this experiment, too, the C_{5+} selectivity and the ethylene content of the C_2 fraction, as well as the butene-1 content of the butenes, declined during the run.

The maximum C_2/C_4 olefin yield was 34 g per m^3 (V_n) with an ethylene content of 16 percent and 73 percent butene-1 fraction in the butenes. Here, a C_2/C_4 olefin selectivity of 27 percent was found.

The smaller fixed-bed reactor was used during experiment number 3 (Table 37). During this run, the pressure and gas composition were not changed, but the temperature and space velocity were raised step-by-step. The maximum gas conversion was 85 percent, which exceeded that of the liquid phase reactors. The C_{5+} selectivity and the ethylene content of the C_2 fraction declined less severely during the run than was the case in the liquid phase reactor.

With a conversion of 77 percent, and a C_2/C_4 olefin selectivity of 26 percent, a maximum of 40 g C_2/C_4 olefin per m^3 (V_n) with 18 percent ethylene content was obtained, and a maximum of 84 percent butene-1 in the butenes was obtained.

The C_2/C_4 selectivity, the ethylene content of these olefins, and the tendency of the butene double bonds to occupy terminal positions were not observed to depend on the reactor type.

4.5.2 Manganese-Iron Catalysts of Our Own Production

Catalyst 1 was produced beginning in 1977 according to the specification in the patent disclosure DT 2507647. At this time, we did not yet have available a catalyst from the Berlin Institute. The catalyst was tested in the liquid phase reactor.

The remaining catalysts were fabricated in the middle of 1978, in a special apparatus, according to the recipes of H. Kölpel and K.D. Tillmetz. They were investigated in the small fixed-bed reactors. The manganese content declines from catalyst 2 to catalyst 4. The catalysts of our in-house production are identified by the supplement "(Bergkamen)".

4.5.2.1 The Mn-Fe Catalyst 1 (Bergkamen)

This catalyst was activated by 30 hours treatment with hydrogen at 320° C.

During the entire experimental run, which lasted six weeks, the space velocity was nearly constant at 303 to 334 h^{-1}. The temperature was varied from 279 to 325° C, the pressure from 11 to 21 bar, and the CO/H_2 ratio in the make-up gas from 1.1 to 1.6.

The results are listed in their time sequence in Tables 38a and 38b. At the beginning of the run, the pressure was increased, which led to an increase of the gas conversion and thus also of the C_2/C_4 olefin yield.

The ethylene content of the C_2/C_4 olefins, however, declined severely. The subsequent temperature increases increased the conversion, as expected, while the C_2/C_4 olefin selectivity decreased. The C_2/C_4 olefin yield at first remained constant and then declined. The C_2/C_4 olefins were very poor in ethylene.

The maximum C_2/C_4 olefin yield was 33 g per m^3 (V_n) ... (line missing)... 66 percent were converted here. With this maximum yield, there was a C_2/C_4 olefin selectivity of 26 percent, and 55 percent of the butenes had terminal double bonds.

4.5.2.2 The Mn-Fe Catalyst 2 (Bergkamen)

Catalysts 2 through 4 were activated in the fixed-bed reactor at 280° C, in each case by 20 hours treatment with carbon monoxide and then with hydrogen.

Table 39 shows the results in their temporal sequence. During the entire run, the pressure was 11 bar. The remaining parameters were varied.

With the individual runs number 3, number 6, and number 9, the same gas conversion of barely 80 percent was achieved. Here, the constant CO/H_2 ratio of the make-up gas was 1.2, the temperature was 285, 300, and 310° C, and the space velocity was 105, 244, and 401 h^{-1}. With constant conversion, but with increasing temperature, the palettes became more short-chained. The selectivity and yield of C_2/C_4 olefins increased, while the ethylene content of these olefins and the tendency of the butene double bonds to occupy terminal positions decreased. At the same temperature and same conversion, but at different CO/H_2 ratio (run number 9 and number 12), the gas with more hydrogen yielded a higher C_2/C_4 olefin selectivity and yield with a reduced content of ethylene and terminally positioned double bonds.

A maximum of 60 g C_2/C_4 olefins per m^3 (V_n) of utilized ideal gas, with 12 percent ethylene, was obtained. The C_2/C_4 selectivity was 39 percent, and the butenes contained 63 percent α-olefins.

4.5.2.3 The Mn-Fe Catalyst 3 (Bergkamen)

The results of the runs, in their time sequence, are found in Table 40. The pressure was 11 bar and was not changed during the run.

With the individual runs number 3, 7 and 11 through 15, the gas conversion lay between 79 and 80 percent. With runs 3 and 7, the CO/H_2 ratio was about 1.2. The temperature and space velocity differed. The yield of C_2/C_4 olefins was the same, at 43 g per m^3 (V_n). The ethylene content of these olefins and the butene-1 content of the butenes was somewhat less at the higher temperature (run 7).

During the runs 11 through 15, the make-up gas was poorer in carbon monoxide. With the same conversion, higher C_2/C_4 olefin yields were obtained, which lay between 52 and 56 g per m^3 (V_n). However, these olefins had a reduced ethylene content.

A maximum of 56 g C_2/C_4 olefins per m^3 (V_n) with 10 percent ethylene was obtained. With a gas conversion of 80 percent, this corresponds to a C_2/C_4 olefin selectivity of 36 percent. The butenes still contain 59 percent butene-1.

4.5.2.4 The Mn-Fe Catalyst 4 (Bergkamen)

This catalyst was utilized twice in the fixed-bed reactor since, during the first experimental run, a plugging occurred already after a short time, which forced premature termination.

Table 41 shows the results of the first experiment and Table 42 those of the second experiment. In Table 41, the results are arranged in their time sequence, and in Table 42 according to reaction conditions. With both experiments, the pressure was 11 bar. During the first experiment, only the temperature and space velocity were varied. With the second experiment, the CO/H_2 ratio in the make-up gas was also varied.

At constant temperature and space velocity, the gas conversion increased with increasing CO/H_2 ratio, (Numbers 5, 10, and 11 in Table 42). The C_2/C_4 olefin selectivity and yield rose at first with increasing CO content and then dropped again. The C_2/C_4 olefins that had the most ethylene were obtained with the make-up gas that contained the most CO.

A maximum of 55 g C_2/C_4 olefins per m^3 (V_n) utilized ideal gas were formed with a gas conversion of 81 mass percent. This contained 12 mass percent ethylene. The butenes contained 56 mass percent butene-1. The C_2/C_4 olefin selectivity was 34 percent.

4.6 The Influence of the Reaction Parameters on Conversion, Yield, and Product Palette

The experimental results depend on the catalyst and on the reaction conditions. The most important parameters are the CO/H_2 ratio in the charging gas, the temperature, the pressure, the space velocity, and the catalyst age. These influences have already been described for the individual catalysts. The present results show that the trends scarcely depend on the catalyst, but their strengths depend strongly on the catalyst.

Such generally valid influences of the reaction parameters on the conversion and on the palette are summarized in Table 43. The product palette is identified in the table by the average C number in the molecule, the ethylene content of the C_2 fraction, and of the C_2/C_4 olefins, the C_2/C_4 olefin selectivity - here called the C_2/C_4 olefin content of the product palette - and the butene-1 content of the butenes, as a measure for the tendency of the olefin double bonds to occupy terminal positions. The C_2/C_4 olefin yield depends on the C_2/C_4 olefin selectivity and on the conversion. The selectivity and conversion can have different trends if the parameters are changed, and so the influence on the yield depends on the - catalyst-dependent - strength of individual trends. As a rule - especially with Mn-Fe catalysts - the trend given in the table has been observed. However, in individual cases, the trend can also change. The table indicates a rising trend by a plus and a falling trend by a minus, while a zero indicates values which tend to remain constant. The trends hold for increasing parameter values in the investigated ranges.

In the last column of Table 43, the desired trend is always specified. The product palettes accordingly should become more short-chained by the parameter change, the ethylene in the C_2/C_4 olefin content should rise; the tendency of double bonds to ocupy terminal positions in the longer-chained olefins should also increase, as should the synthesis conversion and the C_2/C_4 olefin yield.

As can be seen from the table, the influences of the reaction parameters are quite different. However, in no case can only desirable trends be observed with a parameter change. When using gases rich in carbon monoxide, the ethylene content does indeed increase in the individual fractions; nevertheless, the C_2/C_4 olefin content in the product palette decreases, since the increase of the average C number, i.e. the growth of the average chain length, reduces the C_2/C_4 hydrocarbon fraction. Despite reduced C_2/C_4 olefin content, the increased gas conversion leads to an increase of the C_2/C_4 olefin yield relative to the amount of charging gas. Consequently, there are important relationships between the individual trends.

With a temperature rise, the increased C_2/C_4 olefin yield must be valued especially positively. This is a consequence of the increased gas conversion and the stable C_2/C_4 olefin content. However, a decrease of the ethylene content ...(line missing)...A determining factor for the effect of pressure is the increase of the average C number. As a consequence of this, one observes a decrease of the C_2/C_4 olefin content, and this cannot be compensated by increased gas conversion, so that the C_2/C_4 olefin yield decreases.

The influence of pressure is hard to determine, since a pressure change generally leads to more rapid catalyst aging. Product palettes which are formed at variously damaged catalysts are not comparable. The trends in Table 43 are based on experiments during which such damage was not observed.

With an increase of the space velocity, the reduced gas conversion, despite increasing C_2/C_4 olefin selectivity, causes the C_2/C_4 olefin yield to drop, and the ethylene content to increase.

The trends observed as the catalyst ages are in every way to be valued negatively.

It should be noted that catalyst aging covers the influence of all other reaction parameters. Under otherwise equal conditions, a fresh catalyst will yield different results than an older one. The time sequence of the parameter change is thus of considerable significance. The aging rate strongly depends on the conditions. Rapid damage occurs with carbon monoxide rich gases, high temperatures and pressures and with low space velocities and frequent change of conditions, which is necessary to optimize the parameters. Meaningful statements concerning the lifetime of a catalyst can therefore be made only if the parameters have not been changed during the experiment.

During the optimization, a high C_2/C_4 olefin yield should primarily be striven for. In addition, the ethylene content of these olefins is very important.