Table 2.7
Reaction conditions of run 1 - 4.

		Conditions			
		Run 1	Run 2	Run 3	Run 4
Temperature	[°C]	230,250,270	250	250	190-270
Pressure	[bar]	1.5-17	1.5-9.0	4.0-13	1.1-9.0
$(H_2/CO)_{feed}$	[-]	0.67	0.67-3.0	0.67-3.0	0.57-1.0
Flow	[ml/min]	50-300	100-250	150-250	100-360
Catalyst conc.	[wt%]	13.0	13.0	9.1	2.6

[1] measured at 20°C and 1 bar

2.8.2 Experimental

All measurements were carried out in the stirred autoclave reactor (see section 2.3) using the potassium promoted fused iron catalyst C73 (see section 2.2), and in the absence of mass transfer limitations. Four runs were carried out of which the conditions are presented in Table 2.7.

To investigate the influence of the pressure of H_2O on the synthesis gas conversion rate CO_2 was co-fed. Addition of either CO_2 or H_2O can be applied to attain a certain H_2O concentration in the reactor because the H_2O and CO_2 concentration are practically in equilibrium via the water-gas shift reaction (see section 2.6). The H_2O/CO_2 concentration ratio in the reactor can be adjusted only by changing the H_2/CO ratio.

2.8.3 Results and discussion

The rate of the Fischer-Tropsch synthesis at a low conversion level is considered first. When the conversion of CO was lower than 30%, the rate of the Fischer-Tropsch synthesis approximately obeyed first order H_2 pressure, as shown in Figure 2.16. Figure 2.17 shows that the activity of the iron catalyst increased in the usual way when the temperature rises. It is interesting to note that both data points at p_{H_2}=0.5 bar in this figure lie somewhat beyond the curve. Futhermore, the catalyst was not stable at these reaction conditions in contrast with all other experiments. Additional experiments have demonstrated that the height of the hydrogen pressure is important as will be pointed out below. It appears that increasing the hydrogen pressure above a certain value can cause an unexpected increase in the conversion of CO and H_2 as shown in Figure 2.18. This figure indicates that the first order dependency on H_2 is only valid over a small range of hydrogen pressure values . The non-linear increase of the synthesis gas conversion rate was not caused by a decrease in water vapour or CO_2 pressure. This has been shown by the values of the CO conversion in parentheses (since the H_2O pressure increases with increasing CO conversion). In addition, it was also not

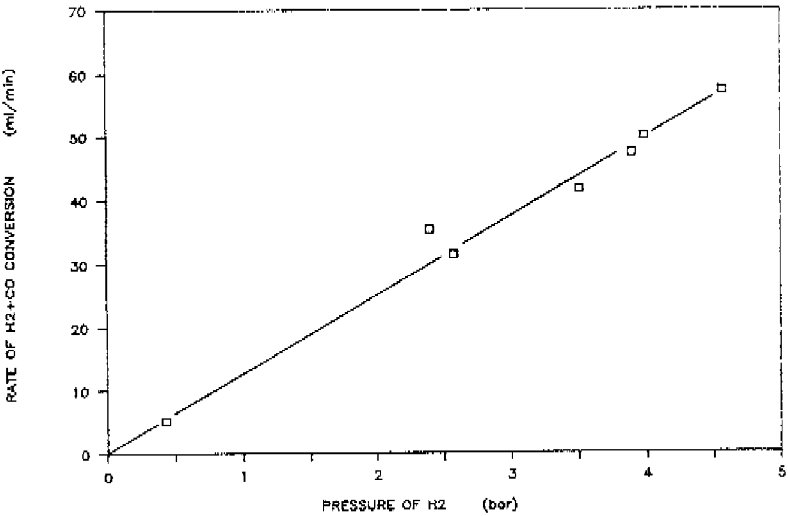

Fig. 2.16 Synthesis gas conversion rate as a function of the pressure of hydrogen at 250°C (run 4)

caused by the sequence in which the experiments were carried out. Fig. 2.19 demonstrates that the sequence of the experiments (shown by the numbers) is not related to the non-linear increase of the conversion of synthesis gas. Thus, *two different "regimes"* can be distinghuished depending on the value of the absolute H_2 pressure.

The inhibition of the rate of the Fischer-Tropsch synthesis by water or CO_2 does not play a significant role when the CO conversion is kept below 70% and the inlet H_2/CO ratio is lower then 1.0 (see Fig. 2.16). However, at a higher conversion and/or a higher H_2/CO ratio, the increased water vapour and CO_2 pressure can reduce the rate of the Fischer-Tropsch synthesis, as can been seen from model 2 and 3 of Table 2.6.

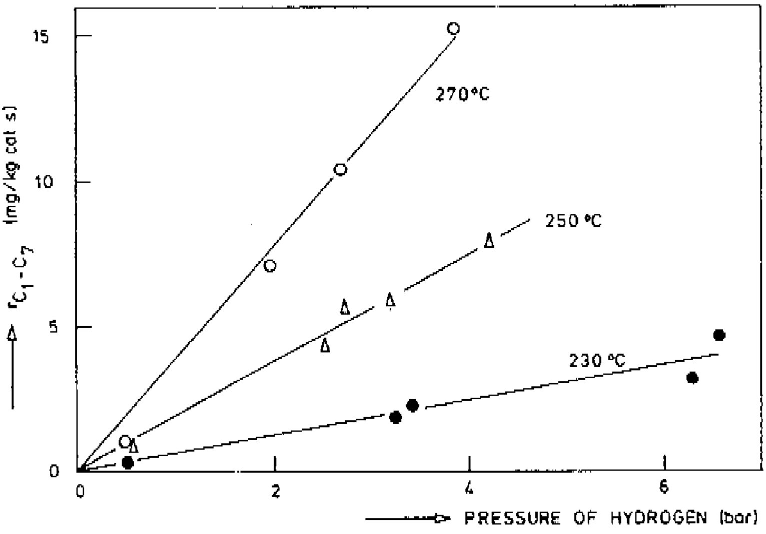

Fig. 2.17 Rate of hydrocarbon production as a function of the pressure of hydrogen at various temperatures (run 1)

The inhibition by water vapour and CO_2 can be investigated by the addition of CO_2. As mentioned before, the inhibition by H_2O generally is (much) more important than the inhibition of CO_2 but the influence of the latter cannot be excluded. Due to the high rate of the water-gas shift reaction, the pressure of CO_2 and H_2O are related in this investigation. Therefore, it is not possible to distinguish between the influence of water and CO_2. Thus, the addition of CO_2 increases both the CO_2 and H_2O concentration, the latter as a result of the water-gas shift reaction. The higher CO_2 concentration causes a decrease of the conversion of H_2O, produced by the Fischer-Tropsh synthesis, into CO_2. This results in a lower CO_2 production with respect to the CO conversion as shown in Figure 2.20.

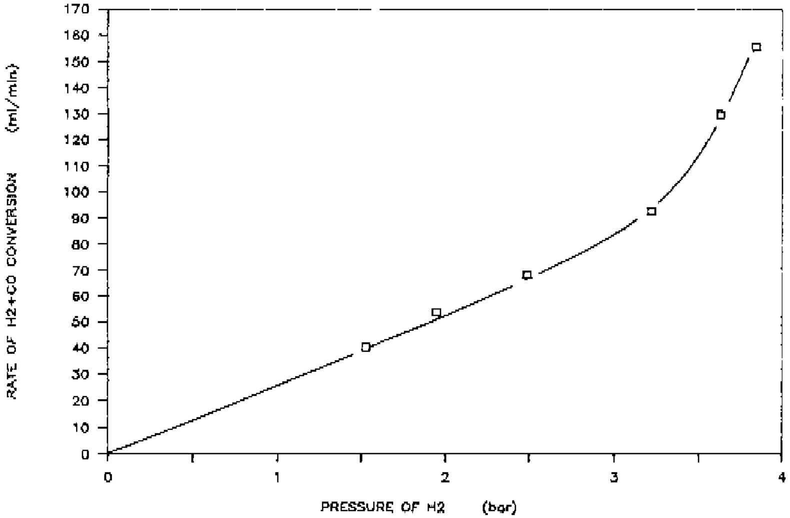

Fig. 2.18 Synthesis gas conversion rate as a function of the pressure of hydrogen at 250°C (run 3)

The co-feeding of CO_2 appeared to have only a moderate effect on the synthesis gas conversion rate. The activity decreases very little, even when the synthesis gas contained 40% CO_2, as shown in Figure 2.21, despite the high H_2O/CO and CO_2/CO pressure ratio as shown in Figure 2.22.

It follows from literature that two models are available which express the rate of synthesis gas conversion over iron catalysts in the slurry phase. First, the model of Ledakowicz will be discussed. Next, the model of Huff and Satterfield will be compared with the experimental data. Ledakowicz [34] reported that using a precipitated alkali-promoted iron catalyst, CO_2 is one of the most abundantly available components due the high water-gas shift activity of that catalyst. He suspected that the lower synthesis gas consumption rate with respect to the first order rate

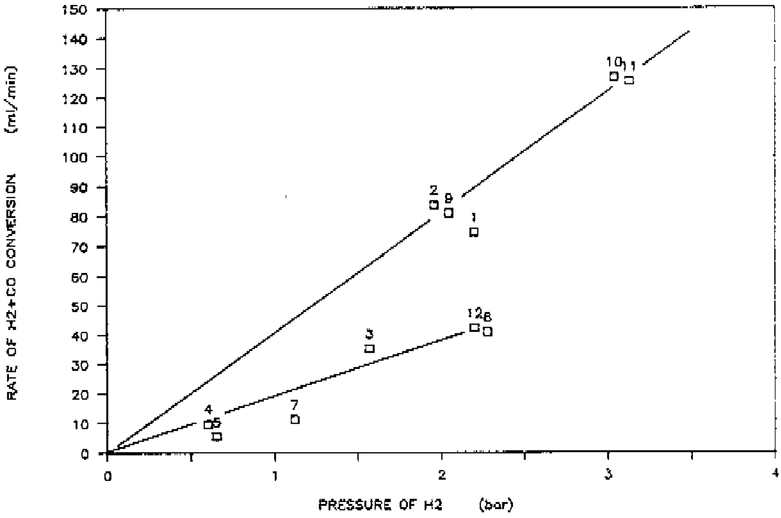

Fig. 2.19 Synthesis gas conversion rate versus pressure of hydrogen at 250°C (run 2). The sequence of the experiments is indicated in the figure

in hydrogen could be attributed to competitive adsorption between CO and CO_2. The argumentation was twofold. First, the water concentration was very small compared with the CO_2 concentration, because of the high rate of the water-gas shift reaction and the low H_2/CO inlet ratio. The water concentration should therefore be neglected. Secondly, there was no correlation between the calculated H_2O concentration and the deviation of the first order rate. Some values of the water concentration calculated even appeared to be negative.

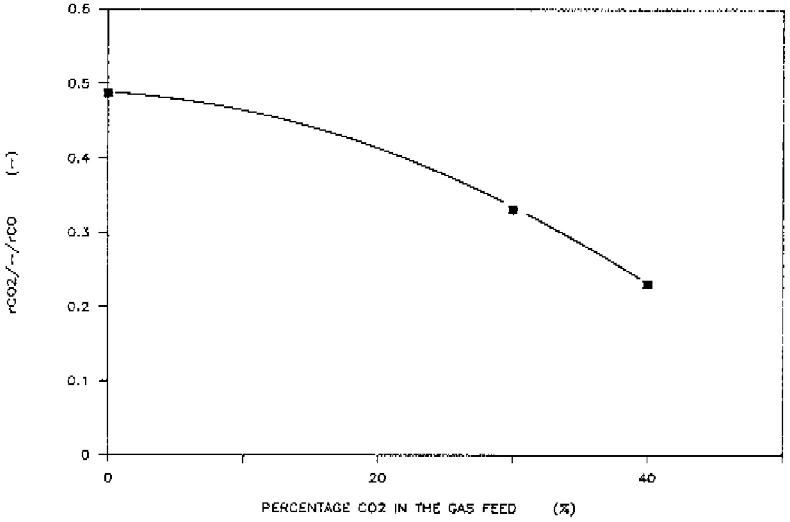

Fig. 2.20 CO_2 production rate with respect to the CO conversion as a function of the percentage of CO_2 in the gas feed (run 3)

Neither argument, however, is satisfactory. With regard to the first argument: a small H_2O concentration can be significant when the adsorption coefficient is high. With regard to the second one: in case of such low water vapour pressures and a high water-gas shift rate, the water mole fraction can be calculated more accurately via the water-gas shift equilibrium than via the usage ratio (as done by Ledakowicz [34]) (see section 2.6.3 Eq.(2.15)). Therefore the water vapour pressure has been recalculated, using the report of Ledakowicz [34] in order ascertain whether his model, Eq.(2.28), gives a better fit than the model of Huff and Satterfield [35], Eq.(2.30). The first step was, therefore, to rewrite Eq.(2.30). Under the assumption that the water-gas shift reaction has reached the equilibrium, the model of Huff, Eq.(2.30), can be written as follows:

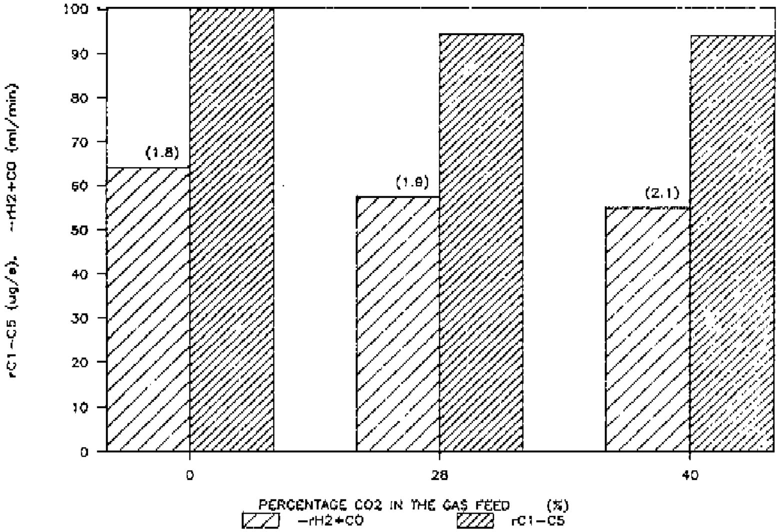

Fig. 2.21 Effect of the addition of CO_2 on the hydrocarbon production rate and conversion of synthesis gas (run 3). The pressure of hydrogen is shown in parentheses

$$- r_{CO+H_2} = k\, p_{H_2}/(1 + a\, K_S\, p_{CO_2}/p_{CO}^2) \qquad (2.35)$$

After rearrangement of Eqs.(2.35) and (2.28) both models can be written in a comparable form:

$$p_{H_2}/-r_{CO+H_2} = 1/k + (a/k)(p_{CO_2}/p_{CO}) \quad \text{(Ledakowicz)} \qquad (2.36)$$

$$p_{H_2}/-r_{CO+H_2} = 1/k + (K_S\, a/k)(p_{CO_2}/p_{CO}^2) \quad \text{(Huff \& Satterfield)} \qquad (2.37)$$

Figure 2.23 is obtained from the answers from these equations. This figure shows that, based on this data, it is hardly possible to discriminate between the two models. With the knowledge that Eq.(2.36) is only valid at a low water vapour concentration, Eq.(2.37) is preferred

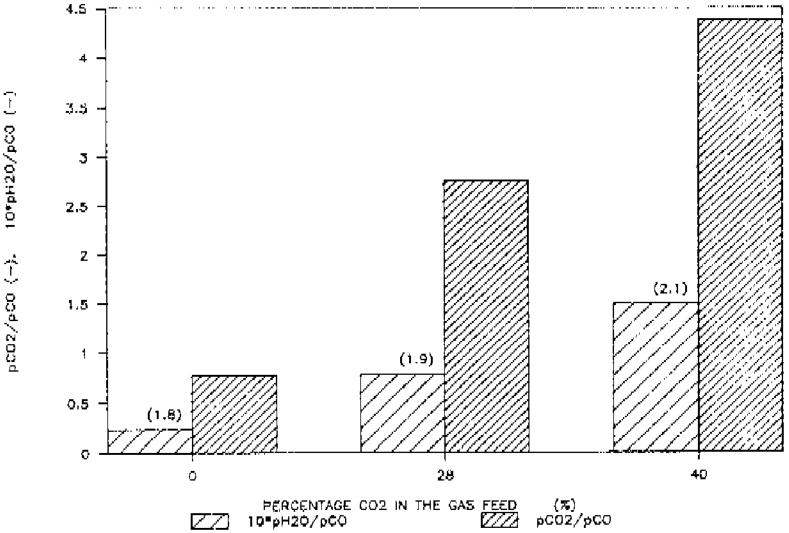

Fig. 2.22 The pressure of CO_2 and H_2O with respect to the CO pressure at various percentages of CO_2 in the gas feed (run 3). The hydrogen pressure is shown in parentheses

for calculating the conversion rate of $CO+H_2$ over iron catalysts in slurry reactors. Therefore the p_{CO_2}/p_{CO}^2 ratio (see Eq.(2.37)) is chosen as the parameter which might explain the deviation of the first order rate law in the experiments of this study.

A part of the experimental data is shown in Table 2.8. The data is arranged according to a decreasing $-r_{CO+H_2}/p_{H_2}$ ratio. This ratio should be constant if the reaction is first order in hydrogen. Clearly, the decreasing synthesis gas conversion rate per hydrogen pressure unit does not correlate at all with the CO_2/CO^2 pressure ratio which is shown in the last column. Moreover, it turns out to be difficult to find other parameters that can explain the decrease of the activity over such a wide range of reaction conditions as is shown in Table 2.8. Therefore, two series of experiments were carried out wherein the variation of the reaction conditions was limited.

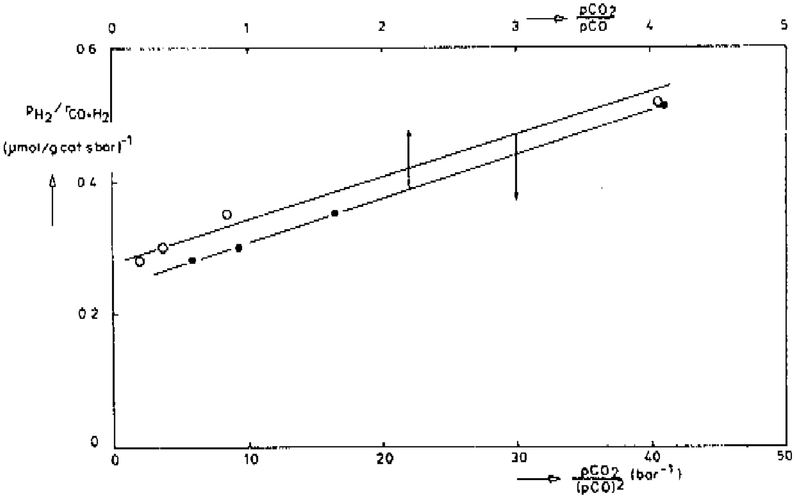

Fig. 2.23 The hydrogen pressure/synthesis gas conversion ratio as a function of both the CO_2/CO and CO_2/CO^2 pressure ratio at 250°C. The data are originated from Ledakowicz [34]

Table 2.8

The synthesis conversion rate at various reaction conditions of run 2.

P [bar]	$-r_{CO+H_2}/P_{H_2}$ [m/(min.bar]	X_{CO+H_2} [%]	P_{H_2} [bar]	H_2/CO [mol/mol]	P_{CO_2}/P_{CO}^2 [bar^{-1}]
9.0	28.1	52.1	2.9	0.78	0.16
9.0	25.9	80.2	2.0	1.43	2.55
9.0	21.7	73.7	2.2	0.99	0.87
9.0	16.0	27.8	2.4	0.42	0.03
4.5	14.5	34.4	1.6	0.71	0.16
3.0	10.0	41.7	2.3	46.3	0.45
1.5	4.6	11.7	1.1	3.3	0.44

In the first series, the H_2 pressure is increased by increasing the reactor pressure (other variables are kept constant). The water vapour pressure is low in this series which naturally means a low p_{CO_2}/p_{CO}^2 ratio. In the second series the pressure is approximately constant whereas the p_{CO_2}/p_{CO}^2 ratio is increased by co-feeding of CO_2. The results of the first series are presented in Table 2.9. This data clearly shows that the synthesis gas conversion rate is not first order in hydrogen. The nature of this activity increase is not fully understood but it may be considered as a decrease of inactive carbon on the catalyst surface caused by an increase in the hydrogen pressure. This explanation is supported by low pressure measurements which demonstrate that this catalyst loses activity when the H_2/CO ratio is lower than about 2 at reactor pressure of 1.5 bar. At even lower reactor pressure, namely 1 bar inclusive 0.4 bar Helium, an H_2/CO ratio of 8 is still not high enough to prevent deactivation (These experiments were carried out in the fixed-bed apparatus as described in Chapter 3.3.8). Thus, the lower the hydrogen pressure, the higher the H_2/CO ratio must be to prevent excessive carbon formation. In this connection it is worth noting that this catalyst does not lose activity when the H_2/CO is as low as 0.4 provided the reactor pressure is 9 bar or higher.

Table 2.9

Effect of the hydrogen pressure on the relative synthesis gas conversion rate (run 3).

Pressure [bar]	$-r_{CO+H_2}/P_{H_2}$ [ml/min bar]	X_{CO+H_2} [%]	P_{CO_2}/P_{CO}^2 [bar^{-1}]	P_{H_2} [bar]	Flow 1) [ml/min]	H_2/CO [mol/mol]
5	27.7	22.3	0.05	2.0	242	0.71
9	33.0	42.5	0.06	3.2	250	0.72
11	36.0	52.2	0.13	3.6	250	0.84
13	40.7	62.5	0.20	3.8	250	0.91

1) measured at 20°C and 1 bar

The results of the second series (high water vapour pressure and approximately constant H_2 pressure) are presented in Table 2.10. In this case the activity decrease with respect to first order H_2 dependency is obviously caused by water vapour as indicated by the correlation between the $-r_{CO+H_2}/P_{H_2}$ and the P_{CO_2}/P_{CO}^2 ratio. Note that the lowest P_{CO_2}/P_{CO}^2 ratio in Table 2.10 is higher than the maximum value in Table 2.9.

Table 2.10

Effect of the P_{CO_2}/P_{CO}^2 ratio on the relative synthesis gas conversion rate (run 3).

Pressure [bar]	$-r_{CO+H_2}/P_{H_2}$ [ml/min bar]	X_{CO+H_2} [%]	P_{CO_2}/P_{CO}^2 [bar^{-1}]	P_{H_2} [bar]	Flow 1) [ml/min]	F_{CO_2} [ml/min]	H_2/CO [-]
5	40.4	47.4	0.25	1.7	144	0	0.82
7	37.3	43.7	0.96	1.8	157	54	1.05
5	30.0	41.0	3.49	1.9	140	55	2.42
6	26.8	36.8	5.97	2.1	150	100	2.82

1) measured at 20°C and 1 bar

2.8.4 Conclusion

An increasing hydrogen pressure increases the synthesis gas conversion per hydrogen pressure unit. This effect dominates the inhibition by water vapour up to a moderate conversion level of CO. At a high conversion level the inhibition by water dominates as shown by the CO_2 addition experiments.

2.9 Olefin selectivity

2.9.1 Introduction

The production of low olefins from synthesis gas is an interesting potential of the Fischer-Tropsch synthesis. In that context much research has been carried out to develop selective catalysts which specifically produce olefins. Newly developed catalysts are often tested under differential conditions at atmospheric pressure. These reaction conditions obviously are unattractive for industrial application. Therefore, the catalyst performance (including the olefin selectivity) at a high conversion level and high pressure have to be known. In this section the influence of the reaction conditions on the olefin selectivity is investigated. The effects of the conversion level and water vapour is given special attention.

The main products of the Fischer-Tropsch synthesis, CO_2 and H_2O excluded, are olefins and paraffins. Paraffines can be considered as inert under Fischer-Tropsch conditions but olefins formed can undergo consecutive reactions. The experimentally determined olefin selectivity will thus depend on the primary olefin selectivity and the importance of secondary reactions involving olefins, such as hydrogenation, isomerization, cracking and insertion in growing chains. The importance of consecutive reactions depends on the reaction conditions and naturally on the catalyst.

Concerning the reaction conditions the space velocity often is the dominating factor. The magnitude of the effect of the space velocity on the olefin selectivity can be influenced by the temperature (Fe [5,41], Co [5]), the CO pressure (Co [5], FeMn [42]), the H_2 pressure (Fe [43]), the H_2/CO ratio [44], the alkali content (Fe [41,45]), the cystallite size (Mo [46]), the iron content of bimetallic catalysts (RuFe [47]) and the support (Ru [48]).

Apart from the space velocity it is possible that the water vapour and CO_2 pressure also affect the olefin selectivity. Unfortunately, the study of the effect of water and carbon dioxide on the olefin selectivity over potassium promoted iron catalysts is hindered by two problems:

1. The dominating effect of the CO conversion level on the olefin selectivity (as will be shown in section 2.9.4 below)
2. The high rate of the water-gas shift reaction, causing an interdependence of the water and carbon dioxide concentration. (as shown in section 2.6)

The dominating effect of the CO conversion level requires careful experimentation at a constant conversion. This fact had often been overlooked in literature.

Apart from the space velocity, the water vapour pressure also affects the olefin selectivity according to Dry [12] and Satterfield [8] et al. They report an increase of the olefin selectivity with increasing water vapour pressure. The first author also reports that increasing the CO_2 pressure at the entrance of an integral reactor leads to an increase of the C_2 olefin selectivity using an alkali promoted fused iron catalyst at 593 K. Since the conversion level in both reports was not kept constant, it is uncertain whether the olefin selectivity increase is caused by water and CO_2. This matter will be clarified with the help of new experimental data.

With regard to the catalyst and to iron catalysts in particular, it is clear from literature that promotors, specially potassium, stongly affect the rate of secondary hydrogenation of olefins and other consecutive reactions [12,46,49,50,51,52,53,54]. This rate decreases with higher potassium content on iron catalysts [41,45,53,54]. Up to approximately 1 wt% potassium does not affect significantly the synthesis activity of fused iron and precipitated iron catalysts [41,54,55]. Higher potassium contents than 1 wt% cause a decrease in activity (unless large amounts of Al_2O_3, TiO_2, or SiO_2 are present [54]) but do not result in a further reduction of secondary reactions [45]. The presence of potassium on iron does not affect the primary formation of olefins and paraffins [45].

2.9.2 Competition model for the olefin selectivity in a well-mixed slurry reactor

For a quantative description of the experimental results a simple model was developed in this study by which the olefin selectivity in a well-mixed reactor up to a CO conversion level of approximately 90% can be predicted. The model will be explained for the case of C_2.

In this model three types of reactions, the formation of olefins and paraffins from synthesis gas (primary reactions) and the hydrogenation of olefins into paraffins (secondary reaction) as shown in Figure 2.2.4 are considered.

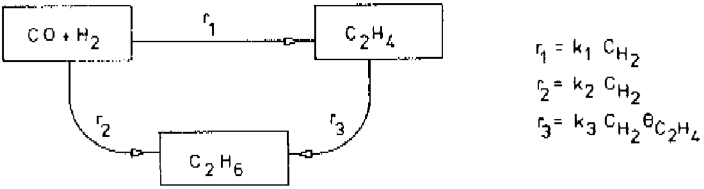

Fig. 2.24 Simplified model for the formation of olefins and paraffins from synthesis gas and the secondary hydrogenation of olefins. represented for C_2

For ethene + ethane the following mass balances can be written:

$$F_{out}\, C_{C_2H_4,G} = (r_1 - r_3)\, V_L \qquad (2.38)$$

$$F_{out}\, (C_{C_2H_4,G} + C_{C_2H_6,G}) = (r_1 + r_2)\, V_L \qquad (2.39)$$

Thus, the C_2 olefin selectivity $\dfrac{C_{C_2H_4,L}}{C_{C_2H_4,L} + C_{C_2H_6,L}}$

is as follows for a perfectly mixed liquid phase reactor

$$\frac{C_{C_2H_4,L}}{C_{C_2H_4,L} + C_{C_2H_6,L}} = \frac{r_1}{r_1 + r_2} - \frac{r_3}{r_1 + r_2} \qquad (2.40)$$

It was found that the conversion of synthesis gas and the production of hydrocarbons is approximately first order in H_2, up to a high synthesis gas conversion (about 60%) in agreement with literature [30,35]. Therefore, it is assumed that the reaction rates r_1 and r_2 are only dependent on the H_2 pressure. The order in hydrogen of the olefin hydrogenation is not measured but estimated on account of the following reports. Miller [56] reports that the hydrogenation of olefins over evaporated Fe metal films is first order in each reactant at low olefin concentrations and temperatures above 150°C. The hydrogenation of ethene is also reported to be first order in both reactants for a wide variety of forms of nickel above approximately 150°C. In our laboratory the same dependency, using Ni/Al_2O_3, for the hydrogenation of ethene in squalane at 250°C and 1 bar [57] was found. In the knowledge that it is questionable whether hydrogenation should be regarded as hydrogen addition directly to the adsorbed olefin [35] and that the mechanism is not fully understood, the following is assumed: secondary hydrogenation of initially formed olefins during Fischer-Tropsch synthesis is both first order in H_2 pressure and in the fraction of active sites occupied by the olefin (θ_{olefin}).Based on these assumptions, the following equation applies:

$$\frac{C_{C_2H_4,L}}{C_{C_2H_4,L} + C_{C_2H_6,L}} = \frac{k_1\ C_{H_2,L}}{(k_1+k_2)\ C_{H_2,L}} - \frac{k_3\ C_{H_2,L}\ \theta_{C_2H_4}}{(k_1+k_2)\ C_{H_2,L}} \qquad (2.41)$$

Replacing the concentration terms which are proportional via Henry's Law to partial pressure gives

$$\frac{p_{C_2H_4}/m_{C_2H_4}}{p_{C_2H_4}/m_{C_2H_4} + p_{C_2H_6}/m_{C_2H_6}} = \frac{k_1}{k_1 + k_2}$$

$$- \frac{k_3\ K_{C_2H_4}\ p_{C_2H_4}/m_{C_2H_4}}{(k_1 + k_2)(1 + K_{CO}p_{CO}/m_{CO} + K_{H_2}p_{H_2}/m_{H_2} + K_p\ p_p/m_p)} \qquad (2.42)$$

in which the ethene fraction on the catalyst surface is based on Langmuir adsorption.

Since CO is strongly bound on potassium promoted iron [33,49,52], it will dominate the adsorption of H_2 and of products at CO conversion levels below 90%. Assuming further, that the solubility of ethene and ethane are approximately equal, Eq.(2.42) can be simplified into

$$C_2 \text{ olefin selectivity} = \frac{p_{C_2H_4}}{p_{C_2H_4} + p_{C_2H_6}} = A - B\,\frac{p_{C_2H_4}}{p_{CO}} \qquad (2.43)$$

With $A = \dfrac{k_1}{k_1 + k_2}$ and $B = \dfrac{k_3\, K_{C_2H_4}\, m_{CO}}{(k_1+k_2) K_{CO}\, m_{C_2H_4}}$

Note that the olefin selectivity does not depend on the H_2 pressure in this model but on the olefin/CO partial pressure ratio alone.

Thus, the olefin selectivity in a well-mixed slurry reactor is determined by the competition between olefins and CO. With increasing CO conversion, the $p_{C_2H_4}/p_{CO}$ ratio increases, implying a higher probability of olefins to reach the catalyst surface and be hydrogenated.

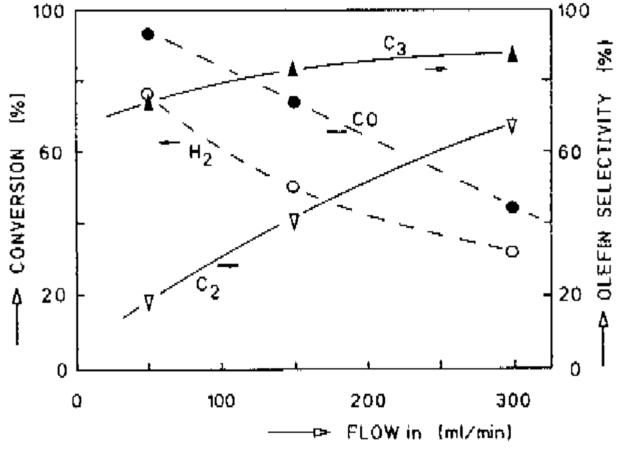

Fig. 2.25 Influence of the gas flow rate on the olefin selectivity and the conversion of CO and H_2. Reaction conditions: pressure = 9 bar; temperature = 250°C; H_2/CO inlet ratio = 1 (run 1)

2.9.3 Experimental

The measurements were carried out in the stirred autoclave reactor which is described in section 2.3. The reaction conditions are equal to those presented in Table 2.7 (section 2.8.2).

2.9.4 Results and discussion

A characteristic of a consecutive reaction is the flow dependency. Specially the C_2 olefin selectivity appeared to be strongly dependent on the gas flow as shown in Figure 2.25. This figure indicates that ethene formed during the Fischer-Tropsch synthesis can be subsequently hydrogenated into ethane. The decline of the C_3 olefin selectivity with decreasing gas flow is less pronounced than that of the C_2 olefin selectivity. This can be attributed to the lower reactivity of propene

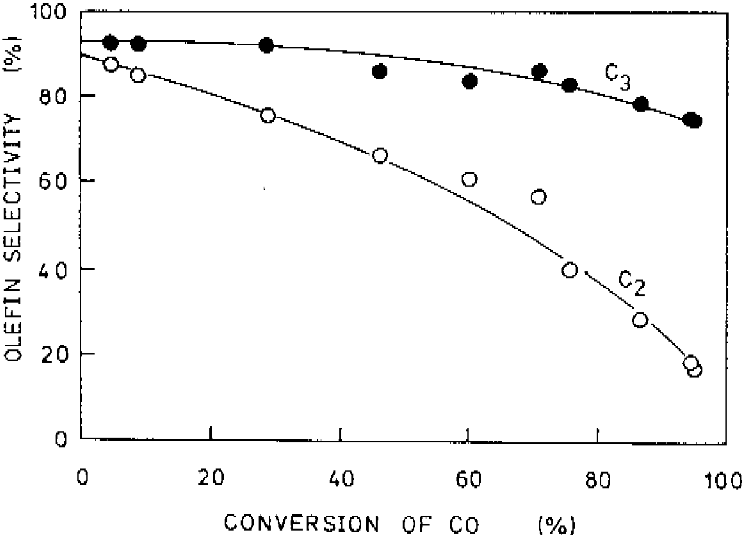

Fig. 2.26 The olefin selectivity as a function of the conversion of CO at 270°C (run 1)

due to a larger steric hindrance with respect to ethene [58]. In consequence of the change of the gas flow, both the CO and H_2 conversion change as well, as is shown in Figure 2.25. It can be seen in this figure that the increase of the olefin selectivity correlates with the decrease of the conversion level. The important role of the CO conversion is shown in Figure 2.26 wherein the decline of the olefin selectivity as a function of CO conversion is demonstrated. The decrease of the CO conversion was achieved by a combination of gas flow and reactor pressure variations.

The validity of the competition model, described in section 2.9.2, is tested by plotting the olefin selectivity versus the olefin/CO pressure ratio. The results for C_2 and C_3 are shown in Figure 2.27 and 2.28 respectively. Obviously, the model describes the experimental data quite

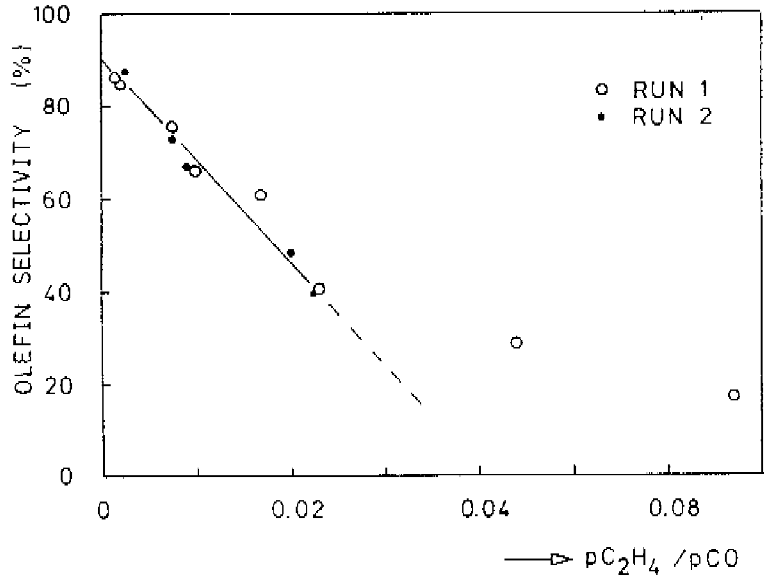

Fig. 2.27 The C_2 olefin selectivity as a function of the ethene/carbon monoxide pressure ratio at 250°C

satisfactory up to a CO conversion level of 90%. Above this level product concentrations becomes important. This means that it is not generally allowed to simplify Eq.(2.42) in section 2.9.2. This subject will again be dealt later on.

According to the competition model the hydrogen pressure does not affect the olefin selectivity. The results shown in Figure 2.29 and Table 2.11 confirm this independence of the H_2 pressure. Table 2.11 also demonstrates that the CO_2 pressure and the H_2/CO ratio do not correlate with the C_2 olefin selectivity. The results reported in Table 2.11 contradict those of Satterfield [43], who reported that the olefin selectivity over fused iron is entirely dependent on the H_2 pressure. Note that this exclusive H_2 dependency is unlikely since the strong dependency of the CO conversion in this report and by others [41, 53,59,60,61] cannot be explained by it.

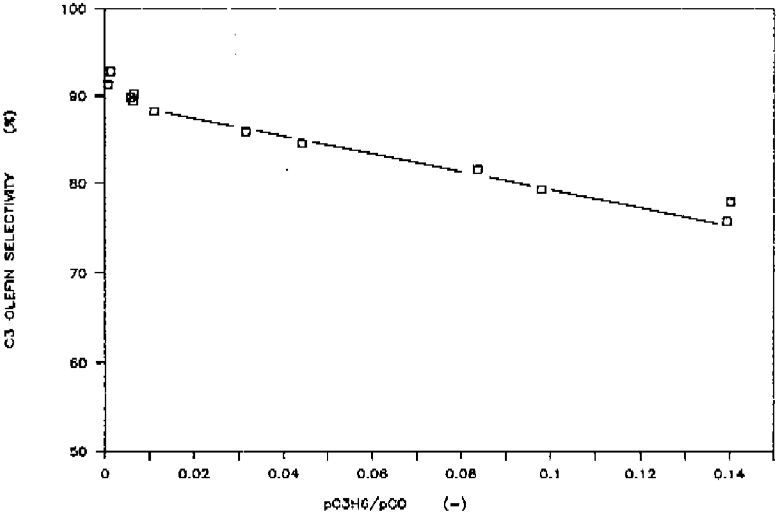

Fig. 2.28 The C_3 olefin selectivity as a function of the propene/carbon monoxide pressure ratio at 250°C (run 2)

Since it is improbable that the temperature would depend equally on the reaction rate constants in Eq.(2.43), the olefin selectivity will change by changing the temperature, whereas the olefin/CO pressure ratio is kept constant. This means that the slope in Figure 2.28 for example will be a function of temperature. When the temperature decreases to 230°C the C_3 olefin selectivity becomes practically independent of the C_3H_6/CO pressure ratio as shown in Figure 2.30. This indicates a relatively low secondary hydrogenation rate. On the other hand, increasing the temperature to 270°C result in an increase in the slope for both C_2 and C_3, as shown in Figure 2.31. Thus, when the C_2 olefin selectivity at 230, 250 and 270°C with a $p_{C_2H_4}/p_{CO}$ value of 0.02 are compared; the C_2 olefin selectivity then drops from 60% via 50% to 30%. The olefin hydrogenation rate thus strongly increases with increasing temperature.

Table 2.11
The C_2 olefin selectivity measured under various process conditions. T=250°C

CO_2 [bar]	H_2 [bar]	P [bar]	H_2/CO [mol/mol]	C_2 olefin sel. [%]
0.058	0.59	1.5	0.71	89
0.048	1.09	1.5	3.30	71
0.76	1.55	4.5	0.71	80
4.31	2.20	9.0	0.99	40
2.27	2.90	9.0	0.78	76
0.56	3.25	4.5	18	16

It is interesting to note that the olefin selectivity does not approach 100% at zero conversion (olefin/CO pressure ratio = 0). Hence, paraffins are not formed exclusively by secondary hydrogenation of olefins but can also be formed directly from CO and H_2. The initial olefin selectivity, $k_1/(k_1+k_2)$ in Eq.(2.43) is influenced by the temperature. The initial paraffin formation increases with decreasing temperature as shown for C_3 in Figure 2.32. Nevertheless, even at 200°C only 10% of the primary C_2 and C_3 hydrocarbons consist of paraffins.

Apart from the investigation of the influence of the temperature, the question whether the H_2/CO ratio affects the initial olefin selectivity has been investigated. The initial olefin selectivity did not appear to be dependent on the H_2/CO ratio over a large range of conditions, as shown in Table 2.12. This confirms the model assumptions in section 2.9.2 which involve that the olefin and paraffin production rate (r_1 and r_2 respectively) are only dependent on the H_2 pressure.

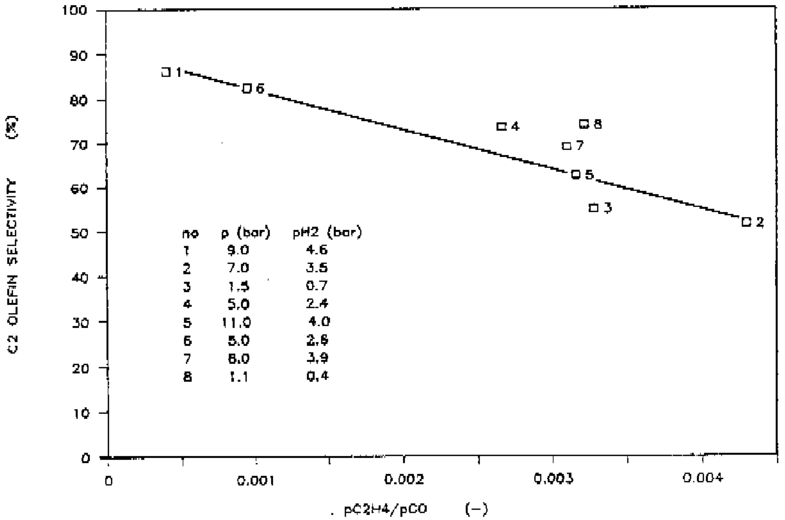

Fig. 2.29 The C_2 olefin selectivity as a function of the ethene/carbon monoxide pressure at 250°C (run 4). The reactor and hydrogen pressure is indicated in the figure

Table 2.12

The primary C_3 olefin selectivity as function of the H_2/CO ratio.

H_2/CO [mol/mol]	C_3 olefin selectivity [%]
0.67	93
2 [1]	95
4 [1]	92
23 [1]	92

[1] carried out in a differential fixed-bed reactor

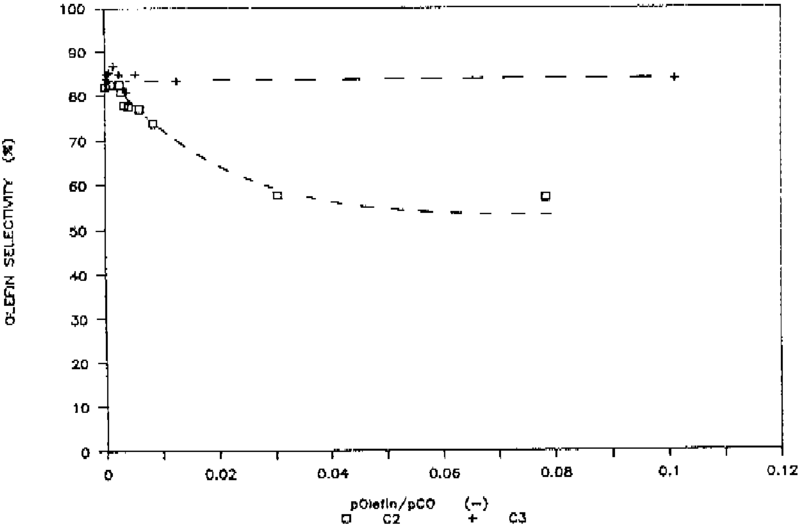

Fig. 2.30 The olefin selectivity as a function of the olefin/carbon monoxide pressure ratio at 230°C (run 1)

A conversion decrease is usually achieved by an increase of the gas flow or a decrease of either the H_2/CO ratio or the pressure. In the next experiment, however, the conversion decrease is caused by slowing down the stirrer speed. According to the competition model this method should result in a different value of the olefin selectivity with respect to the usual methods at an equal olefin/CO pressure ratio. Obviously, the olefin selectivity increases with decreasing stirrer speed due to the conversion decrease as shown in Table 2.13. However, this increase is significantly lower than with respect to measurements which are kinetically controlled as shown in Figure 2.33. This limited increase of the olefin selectivity is caused by the higher olefin/CO concentration ratio in the liquid phase as a result of the gas-liquid mass transfer limitation.

Table 2.13

Influence of the stirrer speed on the conversion of CO and the olefin selectivity. T=270°C; P= 9 bar

Experiment number	Stirrer speed $[min^{-1}]$	CO conversion [%]	Olefin selectivity C_2 [%]	C_2 [%]
1	1300	72	34	82
2	900	73	34	81
3	700	72	35	82
4	500	67	33	82
5	250	47	43	85
6	100	35	54	87

At a high CO conversion level the water vapour and CO_2 pressure may additionally affect the olefin selectivity. In a view of the dominating effect of the CO conversion (see Figure 2.26) the influence of H_2O and/or CO_2 on the olefin selectivity was investigated at a constant CO conversion level (H_2O and CO_2 cannot be distinguished in these experiments because H_2O is related to CO_2, see section 2.6). The water vapour and CO_2 pressure were increased by the addition of CO_2. The olefin

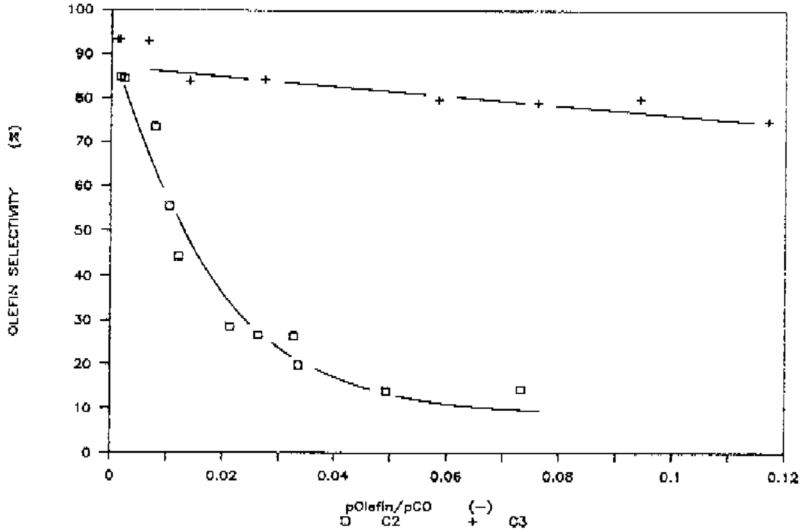

Fig. 2.31 The olefin selectivity as a function of the olefin/carbon monoxide pressure ratio at 270°C (run 1)

selectivity after addition of 0, 28 and 40% CO_2 is plotted in Figure 2.34. This figure shows that the C_2 olefin selectivity only slightly increases with increasing H_2O and CO_2 pressure (the H_2O/CO and CO_2/CO ratio is shown in Figure 2.22), but this increase of the selectivity can be solely attributed to H_2O and CO_2 because the olefin/CO pressure ratio was kept constant. This small selectivity increase implies that the influence of H_2O and CO_2 can be neglected under normal reaction conditions. Only in case of an almost complete conversion of CO the influence of H_2O and CO_2 will be significant. The latter is indeed shown by the remarkable increase of the C_2 olefin selectivity with increasing olefin/CO pressure ratio (and thus with increasing CO conversion), whereby the CO conversion level has passed 90% as shown in Figure 2.35!

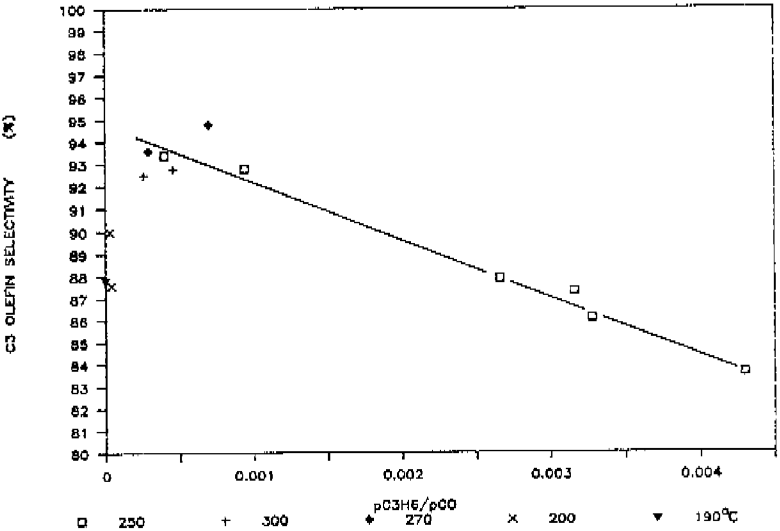

Fig. 2.32 Effect of the temperature on the C_3 olefin selectivity (run 4)

Under these extreme circumstances the water vapour pressure will reach high values due to the high H_2/CO ratio as shown by Eq.(2.44)

$$p_{H_2O} = \frac{p_{H_2}}{p_{CO}} \cdot p_{CO_2} K_S \tag{2.44}$$

When the water gas shift equilibrium is not reached the water vapour pressure will be even higher than predicted by Eq.(2.44). In this situation the competition model has to be adjusted. Since $pCO \ll pH_2O + pCO_2$ Eq.(2.42) may be written as:

$$C_2 \text{ olefin sel.} = A - \frac{k_3 K_{C_2H_4}}{(k_1+k_2) m_{C_2H_4}} \cdot \frac{p_{C_2H_4}}{1 + \frac{K_{H_2O}\, p_{H_2O}}{m_{H_2O}} + \frac{K_{CO_2}\, p_{CO_2}}{m_{CO_2}}} \qquad (2.45)$$

The CO_2 pressure does not significantly continue to change above the CO conversion level of 90%. For this reason it is more likely that the high H_2O vapour pressure and not CO_2 prevents the adsorption of olefins on the catalyst surface. This absorption of H_2O decreases both the rate of secondary hydrogenation of olefins and the formation of hydrocarbons as demonstrated by the decrease of the activity shown in Table 2.10.

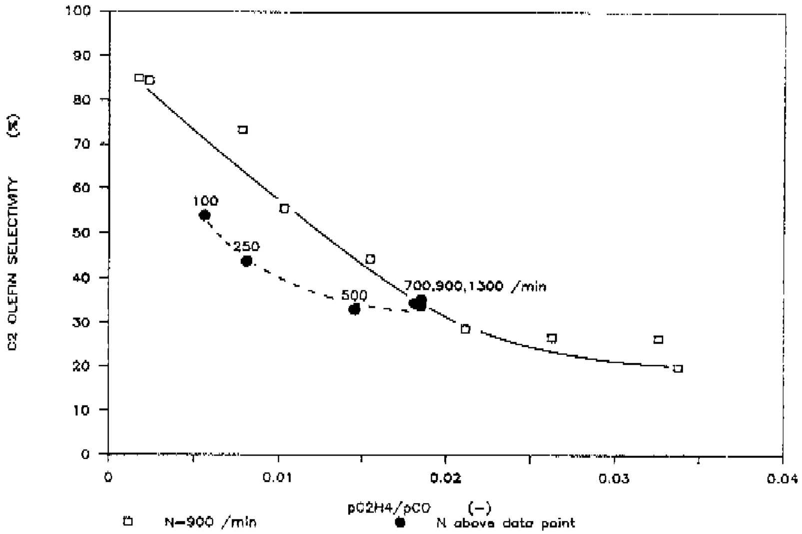

Fig. 2.33 Effect of the stirrer speed on the C_2 olefin selectivity at 270°C (run 1)