2.7 Product distribution

2.7.1 Introduction

This paragraph describes experiments in which the product distribution of C_1-C_7 and C_{10}^+ hydrocarbons were investigated over potassium promoted fused iron at various temperatures and pressures. The aim of this experimental work is to obtain a better understanding of the effect of the reaction conditions, especially the degree of CO conversion, on the hydrocarbon product selectivity. At a high degree of CO conversion the concentration of water and carbon dioxide may influence the product selectivity. The effect of a high CO_2 and H_2O pressure on the selectivity was investigated by co-feeding of CO_2.

This section is introduced with some remarks on the Schulz-Flory distribution followed by a review of deviations from this Schulz-Flory distribution.

The product distribution of a variety of Fischer-Tropsch catalysts can be considered as the result of a random chain growth process. It is generally accepted that on iron catalysts the chain growth of hydrocarbons proceeds via insertion of CH_x species [3,4]. The experimental product distribution indeed follows the so called Schulz-Flory distribution developed for polymerisation reactions. This Schulz-Flory distribution predicts a linear relationship between log M_n and n, where n is the number of C atoms in the chain and M_n is the mole fraction with chain length C_n:

$$\log M_n = n \log(\alpha) + \log((1-\alpha)/\alpha) \qquad (2.21)$$

with $\alpha = r_p/(r_p+r_t)$ where r_p and r_t are the rates of propagation and termination respectively. In the Schulz-Flory distribution it is a basic concept that the propagation and termination rates are independent of the chain length.

Deviations of the hydrocarbon product distribution from the ideal Schulz-Flory distribution can be categorized as follows: 1. Deviation of

C_1, 2. Deviation of C_2, 3. Larger value of α for C_{10}^+, 4. Non-Schulz-Flory distribution.

The deviation of C_1

The deviation of C_1 can be positive or negative. Higher methane fractions than predicted by the Schulz-Flory distribution are often reported for Co [5] and Ru [6] catalysts.The higher methane fraction is caused by extra mechanisms of methane formation [5]. The data of Kikuchi [6], demonstrate that the deviation of the methane fraction depends on the support; Al_2O_3 causes a much higher methane deviation than TiO_2. As a general trend, the fraction of methane decreases and the product distribution shifts towards higher molecular weights when the reactor pressure increases. However, the difference between the methane fraction observed and predicted did not significantly diminish with increasing pressure for Ru catalysts on Al_2O_3 and TiO_2 [6].

Selective suppression of the methane production rate, resulting in values lower than predicted by the Schulz-Flory distribution, can be achieved by the addition of poisons such as sulfur [7] to iron catalysts or by the use of carriers which cause strong metal-support interactions e.g. for ruthenium catalysts. The methane reduction for modified catalysts is mostly based on a suppressed chemisorption of hydrogen which often implies a lower overall activity.

Reaction conditions also can affect the methane selectivity, whereby the concentration of water is of particular importance. A high concentration of water, obtained by addition of water vapour, inhibits the methane production rate more strongly than the production rate of higher hydrocarbons. This causes methane formation to be out of line in the Schulz-Flory distribution [8]. The inhibiting effect of water depends on its concentration and was reversible up to 27 mole% [8], while water at higher concentrations or at exposure over a prolonged period caused a permanent loss of activity [9,10]. A reversible decrease of the methane selectivity over iron catalysts by the addition of water vapour is also reported by Tramm and Karn [9,10]. At a low degree of conversion (< 5%) the addition of only 0.6 vol% H_2O to synthesis gas ($H_2/CO = 9$) over fused iron leads to a decrease in methane selectivity due to a reduction of the methane production rate of 70% [11].The addition of CO_2 (5 vol%) to synthesis gas also resulted in a reversible decrease of the methane selectivity (8 %) [11]. According to Dry [12] the pressure of water did not influence the methane selectivity of fused iron at a high reaction temperature (325°C). On the other hand the CO_2 pressure at the entrance of the reactor appeared to play a major role in the control of the methane selectivity.

Deviation of C_2

Apart from the deviation in respect of methane, there are many reports of the observed C_2 fraction falling below the Schulz-Flory line. A high probability of ethene insertion may explain why the C_2 point of the Fischer-Tropsch products is often lower than that predicted by the Schulz-Flory distribution. According to Sachtler [13] the deviation of the fraction of C_2 hydrocarbons for rhodium catalysts is caused by a higher chain growth probability of C_2 intermediates on the catalyst surface. This is not necessarily true. Another explanation is that olefins readsorb on the surface and play a part in consecutive reactions (insertion, chain growth).

Larger value of α for C_{10}^+

There is increasing evidence from a variety of studies that the products from iron catalysts cannot be described with a single value of the chain growth probability, α. A larger α-value for C_{10}^+ products has been observed for fused iron catalysts [14,15,16,17,18], reduced Fe_2O_3 [19], FeMn [17], precipitated iron [16,17], nitrited iron [20] and silica supported iron [21]. Table 2.3 summarizes nearly all available data regarding the occurrence of two α-values for iron catalysts in slurry reactors.

The occurrence of two values of α is not caused by a particular type of reactor. Egiebor [21] reported two values of α over iron catalyst for both slurry and fixed-bed reactor.

Although it is clear that the product distribution of iron catalyst may show a break, it is unclear which compounds are responsible for the discontinuity of the Schulz-Flory distribution. Dictor [14] reported that the value of α is larger for both C_8^+ olefins and paraffins while according to Egieborn [21] the product distribution of olefins showed no break as opposed to paraffins. Satterfield [17] demonstrated that only the product distribution of oxygenates showed no discontinuity in the slope of C_{10}^+. Other authors reported only the sum of olefins and paraffins.

Table 2.3

Summary of values of chain growth probabilities for C_1–C_9 products and C_{10}^+ products over iron catalysts in the slurry phase, reported in literature

Ref.	Catalyst	Temp. [°C]	P [bar]	$(H_2/CO)_{feed}$ [mol/mol]	α_1 (-)	α_2 (-)
71	K/fused iron	248	6.0	2.0	0.63	>0.63
81	K/fused iron	263	7.9	0.55	0.68	0.93 1),0.68 2)
81	Fe/Mn	283	2.4	1.19	0.55	0.75
72	Fe_2O_3	250	8.0	3.0	0.53	0.66
72	K/Fe_2O_3	250	8.0	3.0	0.66	0.86
84	K/Fe/Ti/Zn	325	10.0	1.0	± 0.7 3)	?
88	K/Fe/Cu	250	9.9	1.4	0.68	0.86
24	K/Fe/Cu/Si	300	21.3	1.0	0.61	0.78
83	K/fused iron	260	20.4	1.0	0.70 3)	0.79 3)
78	K/fused iron	251	31.7	0.36	0.70	0.93
		277	31.4	0.78	0.78	0.78
		280	33.1	2.0	0.71	0.71
82	K/Fe/Cu (nitrided)	220	30	1.0	±0.88 3)	±0.99 3)
80	K/fused iron	232-263	5-15	0.5-1.8	?	0.90 4)
80	K/Fe/Cu	225-250	11-15	1.0-3.8	?	0.92 4)

1) for linear paraffins

2) for oxygenates

3) calculated from the data reported

4) determined from reactor holdup

An explanation for the break in the product distribution has not been established clearly. Schliebs [24] demonstrated that the addition of K_2CO_3 to iron catalysts caused a break of the Schulz-Flory line at C_{10} without changing the value of α for C_1–C_9. He proposed that the two branches observed with potassium promoted iron are due to synthesis over two groups of active sites: unpromoted and promoted regions. However, this interpretation may not be the only one because unpromoted iron [19] and iron-magnanese catalysts [17] also produce Schulz-Flory plots consisting of two branches. The observations of Bauer [15] (see Table 2.3) suggest that besides properties of the catalyst other effects may be important. The hypothesis of two distinct sites [17,24] may be an oversimplification. Stenger [25] has demonstrated that the distributed-site model and the two-site model [17,24] are equally capable of fitting the product distribution from potassium promoted iron. The distributed-site model which assumes that potassium is normally distributed is based on a more realistic description of the catalyst surface.

Non-Schulz-Flory distribution

The aim of many investigators was the development of catalysts of which the products would not follow a Schulz-Flory distribution. Until now these studies have not been very successful. Newly developed or modified catalysts invariably show distributions which are close to the Schulz-Flory distribution [15]. For example, the product distribution of Ru catalysts at high pressures (30 bar) showed a suppression of the C_2-C_8 fraction with respect to the Schulz-Flory distribution, but the C_9^+ fraction almost perfectly obeyed the Schulz-Flory distribution [26].

2.7.2 Experimental

The concentration of C_1-C_7 hydrocarbons, H_2, CO and CO_2 were analysed on-line. From these data the value of the chain growth probability was determined at various reaction conditions. The chain growth probability for C_{10}^+ hydrocarbons was determined by analysing the reactor holdup after 450 hours on stream with a high-temperature gas chromatography technique. The reactor holdup, 1000 times diluted with hexane, was separated by an empty fused-silica capillary column,applying an initial temperature of 70°C followed by heating to 320°C with a rate of 10°C per minute. The hydrocarbons were detected by a FID (350°C) because of its high sensitivity and identical responce factor for all hydrocarbons of interest.

Three batches with fused iron catalyst have been carried out. The catalyst concentration was 2.6, 9.1 and 13.0% respectively. The different catalyst concentrations were necessary to obtain a large range of the degree of CO conversion. The ranges of operating conditions were temperature: 230-270°C; pressure: 1.2-17.0 bar; H_2/CO inlet ratio: 0.67-3.0; gas flow: 100-300 ml (20°C, 1 bar)/min.

The reaction conditions of the batch from which the value of the chain growth probability for C_{10}^+ hydrocarbons was determined, were 230°C from 0 to 140 H.O.S., 250°C from 140 to 280 H.O.S., 270°C from 280 to 340 H.O.S. and 250°C from 340 to 450 H.O.S.; pressure and gas flow were kept constant at 9 bar and 200 ml (20°C, 1 bar)/min respectively. For each temperature three different values of the H_2/CO inlet ratio were applied: 0.5, 1.0 and 2.0 respectively.
The experimental set-up and catalyst reduction procedure is reported in section 2.3.

2.7.3 Results

The products of the Fischer-Tropsch synthesis over iron catalysts mainly consist of linear olefins and paraffins, methyl-branched olefins, aldehydes and alcohols.

At a low degree of conversion the distribution of hydrocarbons is perfectly described by a Schulz-Flory line. Figure 2.8 shows that all hydrocarbons up to C_7, C_1 and C_2 included, obey the Schulz-Flory distribution. However, at moderate conversion the C_2 point clearly lies below the Schulz-Flory line as shown in Figure 2.9. When the conversion of CO is very high, not only C_2 but also C_1 fall below the Schulz-Flory line! Figure 2.10 shows the distribution of hydrocarbons at such a high degree of conversion of CO. The deviation of the C_2 fraction appeares to be a function of the CO conversion level. Figure 2.11 demonstrates the decline of the C_2 fraction with respect to the sum of C_3 and C_4. The values of the chain growth probability were constant in these experiments. However, in contrast with the $p_{C_2}/(p_{C_3}+p_{C_4})$ ratio, the $p_{C_2}/p_{C_1-C_4}$ ratio did not change with increasing conversion of CO. This phenomenon can be explained by the decrease of both the C_1 and the C_2 fraction which apparently compensated each other.In our opinion the parameter $p_{C_2}/(p_{C_3}+p_{C_4})$ gives a better impression of the effect of the CO conversion on the C_2 fraction. Figure 2.12 shows that the same trend of the C_2 fraction as function of the CO conversion is also visible at lower conversions of CO.

In the literature it is reported that both CO_2 and H_2O influence the selectivity of the Fischer-Tropsch synthesis. We have studied the effect of the CO_2 and H_2O pressure on the product distribution by co-feeding of CO_2. The addition of CO_2 provided a high CO_2/CO pressure ratio as shown in Figure 2.22. However, due to the high CO_2 pressure, the conversion of water, produced by the Fischer-Tropsch reaction, was strongly reduced. The reduction of the conversion of H_2O is apparent from the decrease of the $r_{CO_2}/-r_{CO}$ ratio as shown in Figure 2.20. Thus, also the H_2O/CO pressure ratio increased due to the addition of CO_2.

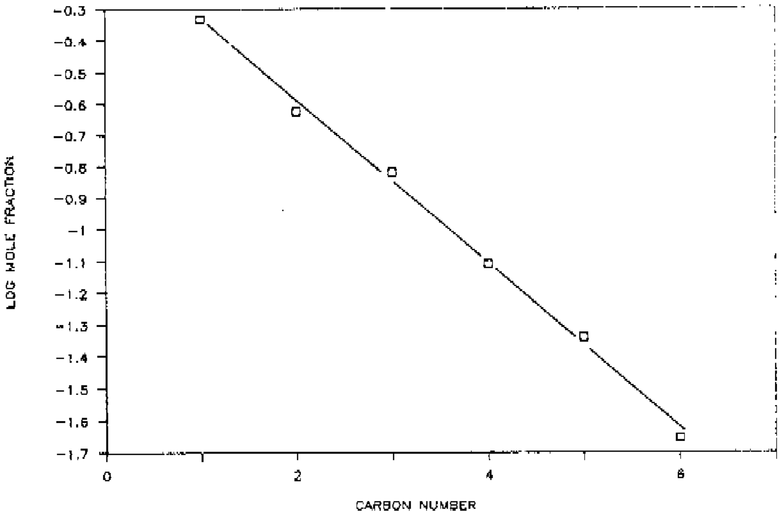

Fig. 2.8 Schulz-Flory distribution of hydrocarbons at a low conversion level. Reaction conditions: temperature = 250°C; pressure = 1.45 bar; H_2/CO outlet ratio = 1.15; conversion of CO = 10%; α = 0.55 (run 4)

Figure 2.13 demonstrated that even if the CO_2 concentration in the gas feed is as high as 40% the methane selectivity does not change. Although the CO_2/CO ratio corresponded with a CO conversion of 90% (without CO_2 co-feeding) the concentrations of CO_2 and/or H_2O relative to CO probably were not high enough to cause a selectivity change. It should be borne in mind that the maximum H_2O/CO pressure ratio was 0.15 in this study which is considerably lower than for example in the report of Satterfield [8]. He mentions a decrease of the methane selectivity of 24% with fused iron caused by the presence of 27 mole% H_2O in the gas feed. This addition of water lead to a H_2O/CO pressure ratio of about 4. The H_2O/H_2 pressure ratio does not appear to be a dominant factor.

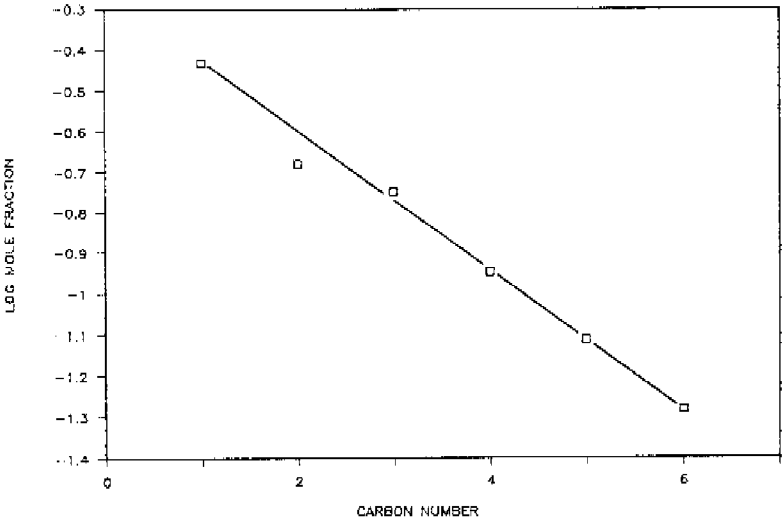

Fig. 2.9 Schulz-Flory distribution of hydrocarbons at a moderate conversion level. Reaction conditions: temperature = 250°C; pressure = 9 bar; H_2/CO outlet ratio = 0.82; conversion of CO= 47%; α = 0.66 (run 3)

The effect of the reaction conditions on the value of α for C_1-C_7 hydrocarbons is presented in Table 2.4. Obviously, the changes in α are relatively small over a wide range of reaction conditions. Increasing the pressure has only a negligible influence on the value of α. It is probable that the tendency of α to decrease due to increasing H_2 partial pressure and to increase due to increasing CO partial pressure results in a small effect of the total pressure.

Increasing the temperature causes a slight decrease in the value of α. Increasing of the H_2/CO ratio also reduces the value of α, as shown in Table 2.5. It is remarkable that the value of α remains relatively high, even at the extremely high H_2/CO ratio of 63!, that is attained when the conversion of CO is very high. The small influence of pressure, H_2/CO

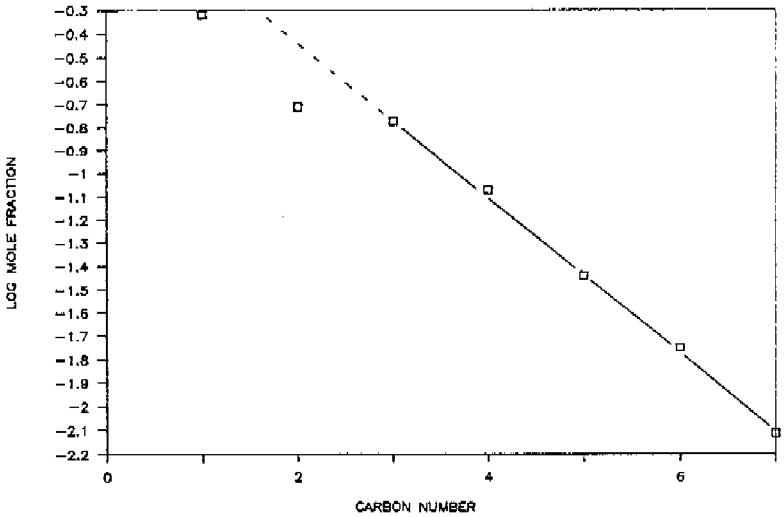

Fig. 2.10 Schulz-Flory distribution of hydrocarbons at a very high conversion level. Reaction conditions: temperature = 250°C; pressure = 9 bar; H_2/CO outlet ratio = 63; conversion of CO= 97%; α = 0.47 (run 2)

Table 2.4

Values of the chain growth parameter, α, at three different temperatures and pressures. H_2/CO inlet ratio was ± 0.67

Temp [°C]	Pressure [bar]	H_2/CO [mol/mol]	α [-]
230	1.2	0.69	0.62
230	9.0	0.68	0.64
230	17.0	0.66	0.64
250	1.2	0.74	0.60
250	9.0	0.80	0.61
250	17.0	0.94	0.61
270	1.2	0.68	0.55
270	9.0	0.89	0.62
270	17.0	1.19	0.59

Table 2.5

Variation of α with H_2/CO ratio at 250°C

Pressure [bar]	X_{CO} [%]	H_2/CO [mol/mol]	α [-]
9.0	27	0.41	0.66
9.0	69	0.81	0.61
9.0	57	0.82	0.62
9.0	52	0.82	0.61
9.0	58	0.91	0.62
9.0	75	0.93	0.58
1.5	18	3.5	0.49
9.0	97	63	0.47

ratio and temperature on the value of α of this fused iron catalyst promoted with potassium agree with results of Dictor [14]. The product distribution of *unpromoted* iron catalysts is more dependent on the reaction conditions [19]. Therefore, it may well be that the presence of potassium in this catalyst causes the reaction conditions to have a relatively small effect on the product distribution.

The (possible) existence of a second α-value for C_{10}^{+} products was also investigated. Reliable data in literature of the second α-value are scarce because it is difficult to measure the "second" value of α free of experimental errors. The main problem of the analysis of the value of α for the higher products from the gas outlet is due to the low production rate of the heavier products and the transient holdup in the reactor. Therefore, in this part of the study the reactor holdup has been analysed after a long exposure to synthesis gas. The disadvantage of this method

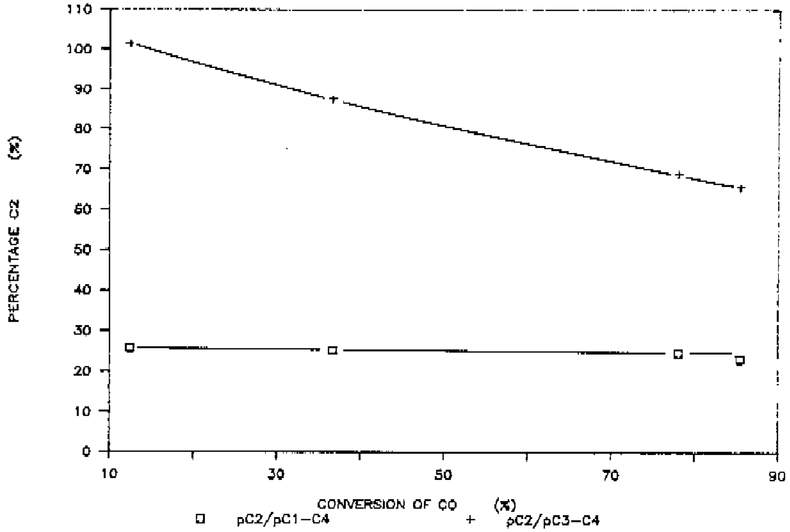

Fig. 2.11 The C_2 fraction as a function of the conversion of CO at a high conversion level range and 250°C

is the lack of knowledge of the influence of reaction conditions on the second value of α. Figure 2.14 shows the concentration of the n-paraffins as a function of carbon number. The variation of reaction conditions during the 450 hours on stream is mentioned in section 2.7.2. The shape of the curve for the C_{14}-C_{19} paraffins is caused by loss of these hydrocarbons from the liquid phase in the reactor due to their relatively high vapour pressure.The value of α for the heavier hydrocarbons, predominantly paraffins, is obviously larger than for C_1-C_7 hydrocarbons, namely 0.80 and 0.62 respectively. This result is also reported by other investigators as already summarized in Table 2.3.

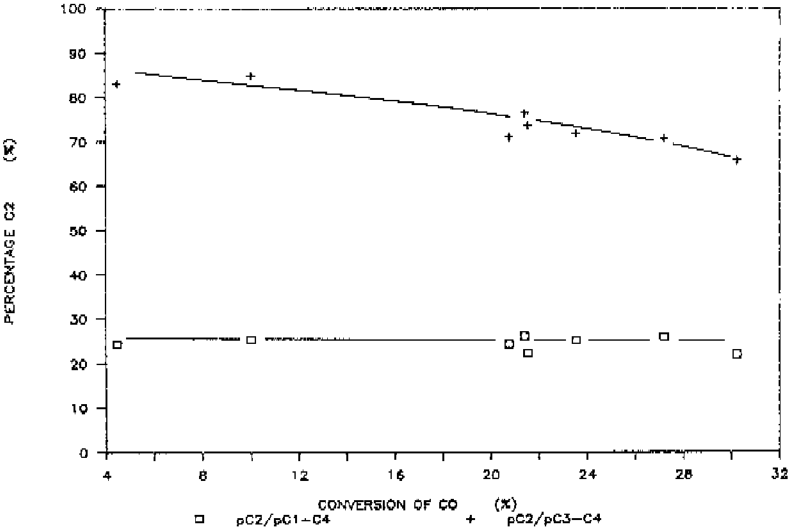

Fig. 2.12 C_2 fraction as a function of the conversion of CO at a low conversion level range and 250°C

2.7.4 Discussion

The degree of conversion of CO clearly dominates the product selectivity for fused iron. At low conversion no secondary reactions occur which cause the C_2 fraction to fall exactly on the Schulz-Flory line. This agrees with experiments with fused iron by Dictor [14].
The decline of the C_2/C_3 ratio with increasing CO conversion (α = constant) indicates that the C_2 reincorporation into products increases with decreasing CO pressure. As a result of this decreasing CO pressure the ethanol selectivity tends to decrease also (see Figure 2.15). This rules out the proposal that C_2 does fall on the Schulz-Flory line when the fraction ethanol is included in the C_2 fraction, as suggested by Satterfield [27]. The importance of C_2 incorporation agrees with other reports [5,8,28] but contradicts the conclusion that ethene incorporation plays no role for fused iron in a slurry reactor [29]. However, this

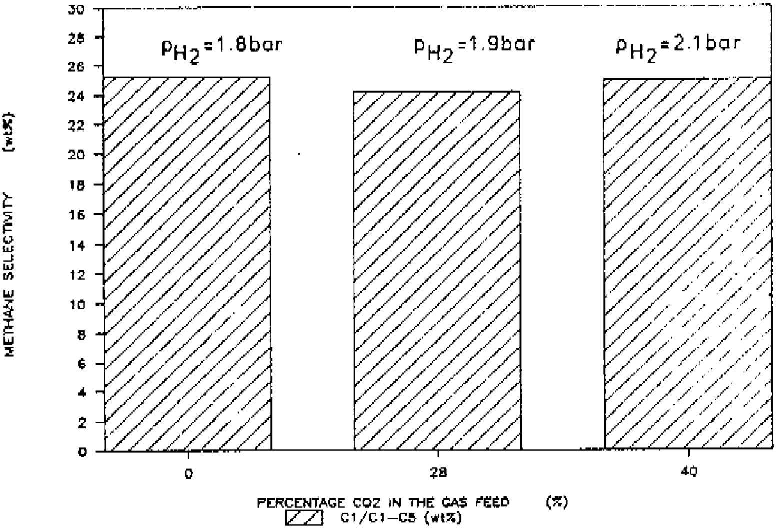

Fig. 2.13 Influence of the co-feeding of CO_2 on the methane selectivity at 250°C

conclusion is based on addition experiments of ethene at a too high degree of conversion of CO (>90%). This results in all rates of reactions to reduce, including consecutive reactions. The extent of incorporation of added ethene will be discussed in section 2.12.

It has been reported that water vapour inhibites the rate of the Fischer-Tropsch synthesis [8,9,10,12,30]. Therefore, it is likely that when there is a very high degree of conversion of CO the observed inhibition of both primary and secondary reactions is caused by the high pressure of

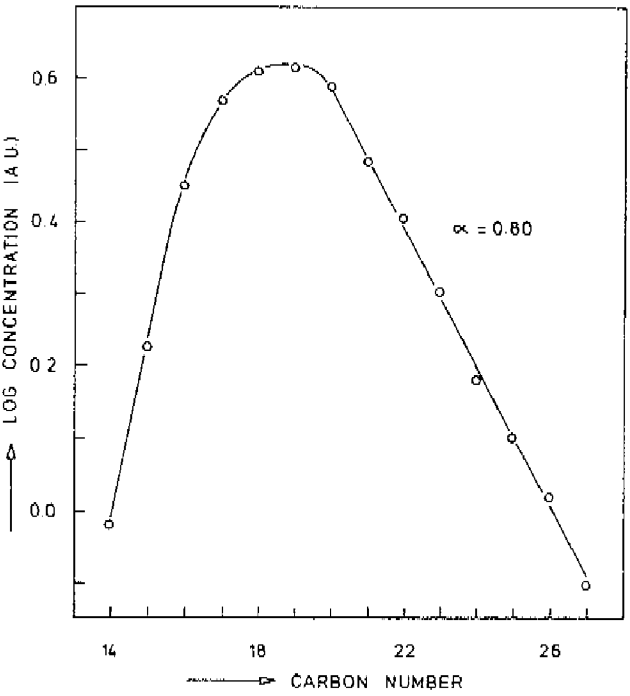

Fig. 2.14 Schulz-Flory distribution of C_{14}^+ paraffins accumulated in the liquid phase of the slurry reactor. The reaction conditions during the time on stream are reported in section 2.7.2

water vapour. Apparently, the production rate of methane is much more strongly dependent on the water vapour pressure than is the rate of production of the higher hydrocarbons.This specific suppression of the methane formation probably causes the observed deviation of the methane fraction from the Schulz-Flory line. It depends on the other reaction conditions whether the methane *selectivity* also decreases. When the H_2/CO ratio is very high because of a substantial degree of conversion of CO, the methane selectivity will not decrease, as a reduction of the value of the chain growth probability then compensates for the deviation of the methane fraction from the Schulz-Flory distribution.

The hydrocarbon distribution over fused iron cannot be described with a single value of the chain growth probability, α, at least not for a large range of carbon numbers. The value of α is larger for C_{20}^+ hydrocarbons than for C_1-C_7 hydrocarbons. This value of α is based on the

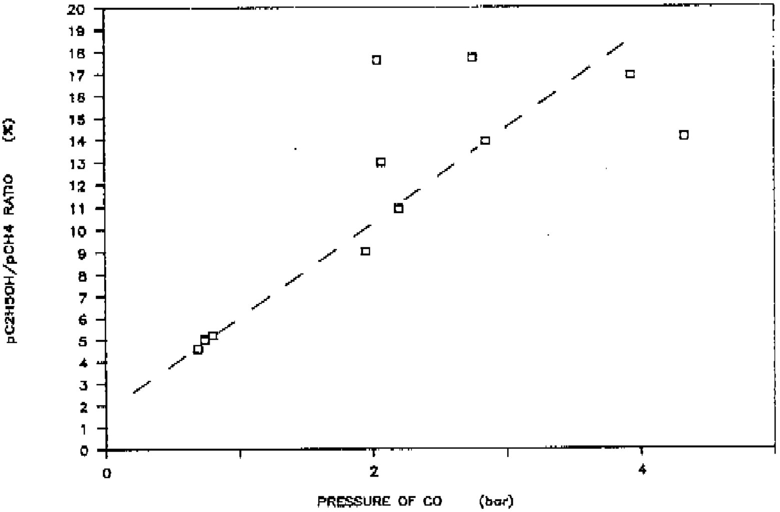

Fig. 2.15 Ethanol/methane pressure ratio as a function of the pressure of CO at 250°C

analysis of the liquid phase of the reactor after 700 hours on stream at various conditions. Thus it is not possible to exactly determine the carbon number for the point at which the break of the Schulz-Flory line occurs.

2.7.5 Conclusions

The C_1–C_7 hydrocarbons distribution for fused iron perfectly follows a Schulz-Flory distribution when the conversion of CO is low. At a higher degree of conversion of CO ethene incorporation occurs which causes a deviation of the C_2 fraction from the Schulz-Flory line. The incorporation of ethene increases with the CO conversion. When CO is nearly depleted the methane production rate is more strongly inhibited than the rate of production of higher hydrocarbons. This is probably due to the high water vapour pressure with respect to the CO pressure.

The product distribution of heavier hydrocarbons indicates that the value of the growth probability, α, of C_{20}^+ hydrocarbons is significantly greater than the value of α for C_1–C_7 hydrocarbons.

2.8 Kinetics of the conversion of synthesis gas

2.8.1 Introduction

Kinetic information is indispensible both for reactor design and for the selection of optimal process conditions. In this study special attention is given to the reaction kinetics in a slurry reactor at a low H_2/CO ratio and a high conversion level, as these are the conditions of industrial importance, specifically in a slurry reactor.

This section concerns the overall reaction rate, and hence the effect of the partial pressures of H_2, CO, CO_2 and H_2O on the conversion of CO and H_2. Secondary reactions are separately dealt with in section 2.9 - 2.12.

Preceding the experimental work a literature review will be given concerning kinetic models proposed for iron catalysts valid up to high conversion levels, and the effect of co-feeding of H_2O and CO_2 on the reaction rate.

In spite of the appropriateness of a slurry reactor for the measurement of the kinetics of the Fischer-Tropsch synthesis, most studies are carried out in the vapour phase. Except for the study of Hall et al.[31], all the kinetic data obtained in the slurry phase with iron catalysts is of recent date. The major kinetic studies concerning the Fischer-Tropsch synthesis over iron catalysts in a slurry reactor are summarized in Table 2.6.The rate determining step (RDS) in the kinetic models proposed can be considered as a hydrogenation of a surface intermediate which exhibits a first order dependency on the hydrogen concentration at low synthesis gas conversion. The zero order rate with respect to CO implies that CO probably occupies completely the available adsorption sites [32]. This theory is consistent with the findings of Dry [33] that no measurable amount of H_2 is adsorbed by alkali-free and K_2O promoted iron when CO was presorbed onto the iron catalyst. Two models reported in Table 2.6 will be handled in more detail, namely the model of Ledakowicz [34] and that of Huff and Satterfield [35]. Preceding these models the kinetic relation presented by Anderson [36] which is based on vapour phase research will be discussed.

Based on unpublished work at the US Bureau of Mines, Anderson [36] proposed that the conversion of CO and H_2 can be described as:

$$-r_{CO+H_2} = \frac{k\, p_{H_2}}{1 + a\, p_{H_2O}/p_{CO}} \tag{2.22}$$

Dry [30] reported that this equation was found to fit satisfactorily the kinetic data obtained in both fluidized and fixed-bed reactors for K_2O-promoted iron. Eq.(2.22) can be derived from the enol complex theory assuming the following reactions:

$$CO + * \rightleftharpoons CO* \tag{2.23}$$

$$CO_2 + * \rightleftharpoons CO_2* \tag{2.24}$$

$$H_2O + * \rightleftharpoons H_2O* \tag{2.25}$$

$$CO* + H_2 \xrightarrow{RDS} HCOH* \tag{2.26}$$

It is assumed that the hydrogenation of chemisorbed CO is the rate

Table 2.6.

Summary of kinetic studies for the Fischer-Tropsch synthesis with an iron catalyst suspended in a slurry reactor.

Catalyst	Temp. [°C]	P [bar]	$(H_2/CO)_{feed}$ [mol/mol]	Rate expression	Ref
K promoted fused iron	250-320	22-24	2.0	$k\ p$	31
K promoted fused iron	232-263	3-15	0.6-1.8	$k\ p_{H_2}/(1 + a\ p_{H_2O}/(p_{CO}\ p_{H_2}))$	35
Precipitated K promoted iron	220-260	10	0.7-0.8	$k\ p_{H_2}/(1 + a\ p_{CO_2}/p_{CO})$	34

determining step in the Fischer-Tropsch synthesis:

$$-r_{CO+H_2} = k\ p_{H_2}\ \theta_{CO} \tag{2.27}$$

The adsorption of CO can be described with a Langmuir equation. Neglecting the adsorption of CO_2 (Eq.(2.24)) and assuming that CO and H_2O saturate the catalyst surface leads to Eq.(2.22). This model can be conceived as a competition between product water and CO for available sites. At high conversion, the occupation with CO will reduce by the adsorption of H_2O.

When the adsorption of CO_2 is more important than the adsorption of H_2O and when thus CO_2 + CO saturate the surface, Eq.(2.27) then becomes:

$$-r_{CO+H_2} = \frac{k\ p_{H_2}}{1 + p_{CO_2}/p_{CO}} \tag{2.28}$$

According to Ledakowicz [34] this equation can be applied when the water concentration is low due to a high water-gas shift activity and a low

H_2/CO inlet ratio. Ledakowicz [37] pointed out that a model proposed earlier [34], which comprises both adsorption of CO_2 and H_2O:

$$-r_{CO+H_2} = \frac{k\ p_{H_2}}{1 + a\ p_{CO_2}/p_{CO} + b\ p_{H_2O}/p_{CO}} \qquad (2.29)$$

could not satisfactorily describe the experimental data obtained with different H_2/CO inlet ratios.

When rate inhibition by product water is predominant, the proposed model of Huff [35] turns out to be better than Eqs.(2.28) and (2.29):

$$-r_{CO+H_2} = \frac{k\ p_{H_2}}{1 + a\ p_{H_2O}/(p_{H_2}/p_{CO})} \qquad (2.30)$$

This model can be derived from the carbide [38] or the insertion [39] theory by making appropriate assumptions and simplifications. In case of the carbide theory it is postulated that the hydrogenation of adsorbed carbon is the rate determining step:

$$-r_{CO+H_2} = k\ p_{H_2}\ \theta_c \qquad (2.31)$$

The most important reactions in this model are:

$$CO + 2^* \rightleftharpoons C^* + O^* \qquad (2.32)$$

$$O^* + H_2 \rightleftharpoons H_2O + {}^* \qquad (2.33)$$

$$C^* + H_2 \xrightarrow{RDS} CH_2^* \qquad (2.34)$$

If the adsorbed carbon intermediate is assumed to be the most abundant species Eq.(2.31) turns to Eq.(2.30). In this model the rate of reduction by water vapour is explained by the decrease of the surface concentration of the carbon intermediate.

The short and long term effects of the addition of H_2O and CO_2 to synthesis gas over various iron catalysts will now be considered. The inhibition of the conversion of synthesis gas by the addition of water vapour is clearly shown in literature. Karn [9] has demonstrated that water is an inhibitor for *nitrided Fe*, but that the rate promptly regaines its previous value when the addition of water was stopped. The conversion of H_2+CO decreased monotonously from 80 to 38% when the concentration of the added water increased from 0 to 30 mole%. Due to the increased conversion of CO by the water-gas shift reaction the conversion of CO did not change.Satterfield [8] reports that also *alkali promoted fused iron* exhibits a completely reversible decrease of the catalyst activity when 12 or 27 mole% water is added to synthesis gas. The activity, however, did not recover after removal of the water vapour from synthesis gas that comprised 42 mole% water [8]. This irreversible reduction of the activity may be caused by a decreased surface area due to recrystallization of iron crystals. This also occurs during the reduction of ammonia catalysts by the water vapour formed from the iron oxide [12,37].

Brötz [40] reportes that besides water vapour, CO_2 also inhibits the Fischer-Tropsch synthesis. The addition of 35 mole % CO_2 to CO + H_2 resulted in a reduction of the activity of an iron catalyst from 40%. Tramm [10] reports that the activity was reduced by half when 52 mole% CO_2 (or 30% H_2O) was added to synthesis gas over iron. According to Dry [12] the presence of 5-28 mole % CO_2 in synthesis gas had no apparent effect on the activity. However, the addition of water vapour to the feed gas lowered the activity of fused iron. Based on addition of water vapour and carbon dioxide Karn [9] concluded that carbon dioxide has only a slight inhibiting effect on the activity of iron catalysts compared with water vapour. It has to be noted that possibly the CO_2 inhibition is not caused by CO_2 itself but by H_2O produced via the water-gas shift reaction from CO_2 added and H_2.

Thus, summarizing this introduction, in all kinetic models presented here a first order H_2 dependency is estimated and a hydrogen occupation which is independent of the CO pressure and that of other gases. The H_2O and CO_2 inhibition is explained by competition between these molecules and CO for the same active sites. Concerning the difference of the activity decrease between H_2O and CO_2 it can concluded that generally water seems to be a stronger inhibitor than CO_2. Furthermore, it is not certain that the conversion inhibition caused by CO_2 addition is caused exclusively by CO_2 itself.