1 INTRODUCTION

1.1. Alternatives to crude oil as chemical feedstock

The conversion of a mixture of carbon monoxide and hydrogen (synthesis gas) to aliphatic hydrocarbons, originated by Fischer and Tropsch [1], enables the chemical industry to replace crude oil as chemical feedstock by coal, natural gas or other carbon containing materials for the production of (synthetic) fuels, light olefins and other important chemicals. As this time coal seems to be the most promising carbon source to substitute oil in the future, since the recoverable resources proven and estimated are by far the largest of fossil fuels in the world [2]. In the past coal was already used for the production of synthetic transport fuels. In 1936 Ruhrchemie installed a Fischer-Tropsch plant with an annual capacity of 200.000 tons of hydrocarbons [3]. During the last year of World War II the installed capacity in Germany was enlarged to 600,000 tons/annual [3]. The discovery of large oil desposits in the Middle East in the mid-1950s terminated the use of coal for the production of fuels. Since that period the Fischer-Tropsch process is economically unattractive. The temporary rise of the crude oil price during the seventies caused a revival of interest in the Fischer-Tropsch route which led to a large amount of research at universities and industry. Because the oil price strongly decreased commercialization did not take place.

Political reasons and the availability of large resources of cheap coal resulted in the erection of a Fischer-Tropsch plant in Sasolburg, South Africa which started operation in 1955 [4]. This and much larger plants at Secunda, which started operation in the early nineteen-eightees, provide a large percentage of the fuels and chemicals in that country which are derived from crude oil elsewhere.

Energy strategy reasons and the availability of remote natural gas fields may lead to the utilization of natural gas as alternative feedstock for transport fuels [5]. According to a commercially available process of Shell (Shell Middle Destillate Process), synthesis gas with an H_2/CO ratio of about 2 can be converted into fuel gas (C_1 and C_2), LPG and liquid transport fuels. The synthesis gas is obtained by partial oxidation of natural gas. In this process a high selectivity for heavy paraffins and wax is obtained by the use of a Co catalyst promoted with Zr, Ti and/or Cr [6]. The wax fraction is hydroconverted over a noble metal catalyst into liquid fuels.

Instead of the Fischer-Tropsch route, synthesis gas can be converted into methanol as well, from which C_1 - C_{10} hydrocarbons can be produced via the Methanol-To-Gasoline process of Mobil using a ZSM-5 catalyst [7]. A commercial natural gas to gasoline plant using this technology is running in New Zealand since the end of 1985 [8].

1.2. The use of a slurry reactor for the Fischer-Tropsch synthesis

The early Fischer-Tropsch plants installed by Ruhrchemie made use of fixed-bed reactors. The technology of this type of reactor together with that of a high temperature circulating fluidised bed reactor, developed by M.W. Kellogg, were used by SASOL leading to the start of a plant in 1955. These reactors are the only types used commercially. The slurry phase system, developed by Kölbel and Ackermann, has only reached the pilot plant scale at Meerbeck in 1952-1953 [9]. Although the three phase bubble column operated succesfully, commercialization was not economically attractive due to the enormous supply of crude oil by which almost all activities dealing with synthesis gas were terminated. In the mid-1970s the research concerning the Fischer-Tropsch route revived leading to a renewal of interest in the slurry phase system. Despite several companies having built pilot plants with a slurry reactor, again commercialization did not occur because of the lower oil prices but also due to lack of experience in commercial scale operation resulting in the choice of a down flow fixed-bed reactor in case of the Shell Middle Distillate Process.

Nevertheless, the slurry reactor possesses a number of advantages [9]:

1. Uniform temperature in the reactor
2. High catalyst and reactor productivity
3. A catalyst efficiency of about 1
4. Good heat transfer
5. Simple construction and therefore low investment costs

Besides, the H_2/CO inlet ratio may be lower than 1, whereas fixed-bed and circulating fluidised bed reactors usually operate at a ratio of 2 or higher to prevent plugging and agglomeration of catalyst particles by the formation of wax. The formation of heavy hydrocarbons, however, does not affect the performance of slurry reactors as long as the liquid viscosity stays low at the reaction conditions. As will be pointed out in Chapter 2 an H_2/CO inlet ratio below 1 is only acceptable if the catalyst itself or a co-catalyst exhibits a high water-gas shift activity. As a consequence of the allowable low H_2/CO inlet ratio, the slurry reactor may use synthesis gas directly from the second generation coal gasifiers. These gasifiers, British Gas/Lurgi Pilot, Koppers/Totzek and Texaco Pilot, operate with a low steam usage by which the thermal efficiency increases to 0.46, 0.56 and 0.68 respectively instead of, for example 2.1 obtained with a conventional Lurgi gasifier [10]. Higher thermal efficiency means potentially lower-cost gasification which is important because the predominant costs of a complete Fischer-Tropsch plant is associated with the coal gasification [11]. A certain disadvantage of the bubble column reactor is that the residence time behaviour of the liquid phase may approach the behaviour in a stirred tank reactor while that of the gas phase may be deviate substantially from plug flow. This results in a lower synthesis gas conversion and lower selectivities of primary products which can undergo secondary reactions. On the other hand, mixing the liquid phase is essential for catalyst suspension, promotes the uniformity of the liquid phase for which reason the synthesis gas may contain such a high concentration of carbon monoxide.

The use of small catalyst particles in a slurry reactor may cause solid liquid separation problems. According to Farley and Ray [12] the best method investigated on pilot plant scale proved to be that of simple gravity separation. Kölbel [13], however, reported that centrifugal separation of the hot slurry is a suitable method. In case of iron catalyst particles Kuo [11] showed that the settling of catalyst particles can be accelerated by the use of magnets at 204°C. The settling time decreased from 3 to 1 hour due to the magnetic forces. It can be concluded that the separation of small catalyst particles on a large scale cannot be carried out with filter systems. Separations by settling at a high temperature seems to be a reliable method by which a sufficiently high separation rate is obtained.

1.3. Aim and outline of this investigation

The Fischer-Tropsch synthesis is a suitable way of converting coal-derived synthesis gas to hydrocarbons. These are of interest not only for the production of transport fuels but also as a feedstock for the chemical industry. In the latter case, the low olefins are the prefered compounds.

The slurry reactor, especially the bubble column reactor, seems the most promising for the production of low olefins with a high selectivity at a high conversion level.

This study is focussed on the production of low olefins in a slurry reactor, especially at high pressure, a high conversion level and a low H_2/CO inlet ratio. The work is particularly aimed at understanding the factors that determine the selectivity in industrially relevant conditions.

Two types of catalysts are included in this study. From previous research in this laboratory [14] $RuFe/SiO_2$ appeared to be a promising catalyst for making low olefins. However, this catalyst has only been investigated at a low conversion level. Therefore, the performance of $RuFe/SiO_2$ has been studied under industrial conditions in the slurry phase (Chapter 3). The performance of this catalyst has been compared with that of a potassium promoted fused iron catalyst which is similar to the type used commercially (Chapter 2).

The effect of the gas-liquid mass transfer on the overall reaction rate was separately determined in a three-phase bubble column using a rapid hydrogenation reaction under Fischer-Tropsch conditions (Chapter 4). This is justified as the Fischer-Tropsch synthesis over iron catalysts is approximately first order in hydrogen, provided the conversion level is not very high. Special attention has been paid to the influence of the type of the gas distributor, liquid height, concentration and diameter of solid particles. The effect of the reactor type on olefin selectivity has been investigated in a slurry bubble column with external recycle of the gaseous products together with unconverted synthesis gas (Chapter 5).

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2 CATALYTIC PERFORMANCE OF POTASSIUM PROMOTED FUSED IRON IN THE SLURRY PHASE

2.1. Introduction

Promoted iron catalysts have been applied industrially for the Fischer-Tropsch synthesis during many years. These catalysts appear to be stable when synthesis gas with a high H_2/CO ratio is converted in the gas phase. Industrial Fischer-Tropsch catalysts are not commercially available. However, they are closely related to the commercial ammonia catalysts. An ammonia catalyst was therefore selected for this study. As pointed out in the general introduction, the application of a slurry reactor offers a number of advantages including the important benefit of being able to use a low H_2/CO inlet ratio. Hence, special attention is given to the catalyst performance in the slurry reactor at a low H_2/CO ratio and a high conversion level as these are the conditions of industrial importance, especially in a slurry reactor.

Before presenting the catalytic performance of the catalyst in the slurry reactor, the problem of accumulation of hydrocarbons in the reactor will be discussed.

2.2 Materials and catalyst

All the gases (hydrogen, carbon monoxide, nitrogen, helium, argon, ethene and carbon dioxide) were obtained from cylinders supplied by Hoekloos or Air Products. The purity of carbon monoxide and the other gases exceeded 99.5 and 99.9% respectively. Before addition to the reactor, the gases were separately purified by a reduced copper catalyst (BASF R3-11) at 180°C and by a molecular sieve 5A (Union Carbide) at room temperature.

The catalyst was a commercial fused iron ammonia synthesis catalyst, supplied by Süd-Chemie and denoted as C73. On an unreduced weight basis, it contains approximately 1.7% K_2O, 2.7% Al_2O_3, 0.8% CaO, 0.3% MgO and <0.1% SiO_2. The promotors are unevenly distributed over the surface (measured by means of XPS analysis) and the concentration on various particles varies enormously (measured by means of AAS analysis).

The catalyst was reduced with hydrogen for 70 h at 450°C, atmospheric pressure and at a space velocity of at least 30 ml (20°C, 1 bar)/(g cat.min) in a fixed-bed reactor. After reduction the specific surface area was approximately 15 m^2/g (BET method, nitrogen adsorption).

2.3 Apparatus

A schematic drawing of the experimental apparatus is shown in Figure 2.1. The bold lines indicate the flow path of the main gas stream during continuous operation. The equipment is almost entirely made of stainless steel.

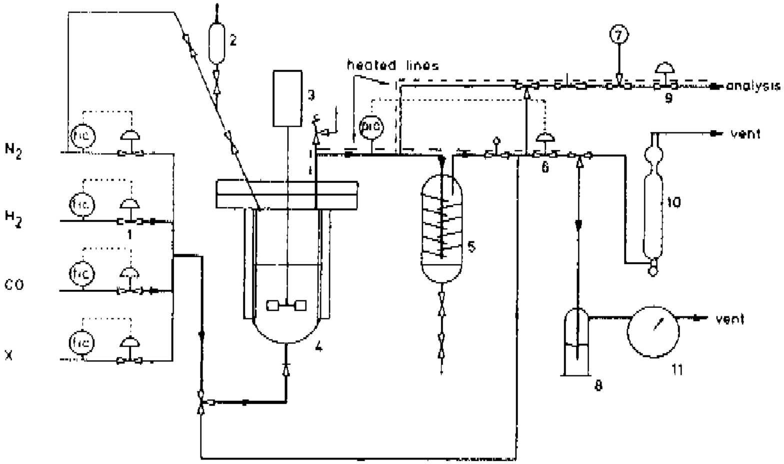

Fig. 2.1 Experimental set-up of the slurry reactor unit;(1) Mass flow controller; (2) Oil supply vessel; (3) Stirrer motor with magnetic transmission (4) Autoclave with electric heating; (5) Cold trap; (6) Pressure regulator valve; (7) Calibration mixture; (8) Washing-bottle; (9) Expansion valve; (10) Soap-film meter; (11) Wet-gas meter

Reactor. The synthesis was carried out in a 0.5-liter autoclave provided with a variable speed magnetic drive. The reactor contains four baffle bars (6 mm wide) spaced 90°C apart. The agitator is a 38 mm diameter turbine impeller. The impeller has 8 flat-bladed disks, each 156 mm^2 and is placed 35 mm above the vessel bottom. The autoclave is heated by resistance wire which is wrapped tightly around the reactor wall. The amount of heat is regulated by a PID temperature controller (Eurotherm 070) which controls the liquid temperature within ± 0.5°C, as measured by a type K thermocouple.

The exact temperature was measured by a second thermocouple connected with a flat-bed recorder (Kipp BD40). The two thermocouples were initially located in a thermowell filled with paraffin oil but the well became covered slowly with carbon. This caused the reliability of the temperature measurement to become unreliable. Therefore, the thermowell was removed and the thermocouples were placed directly in the liquid phase. Gas is sparged by a 0.5 mm bore tube placed in the bottom of the vessel. Studies in a reactor made of glass show that a stirrer speed of about 200 rpm is required to suspend 15 wt% of 45-90 µm unreduced iron particles (hexane, 20°C).

Gas flow. The flow of all gases (four different gases could be connected simultaneously to the reactor system) were regulated by mass flow controllers based on heat conductivity (Hi-Tec F 201). A calibration curve was constructed for each type of gas and controller before the start of a batch.The outlet gas flow rate was measured with a soap-film flowmeter or a wet-test meter. During a run the inlet gas flow could be checked via a bypass.

Product sampling. The composition of the reactor outlet gas flow was measured on-line via a heated sample line which was located ahead of the cold trap. A large amount of volatile products was condensed in this apparatus. The cold trap contained a large quantity of plates which appeared to be necessary for removing very fine liquid droplets in the gas flow. These liquid droplets can plug the orifice of the pressure regulator and this causes large variations of the reactor pressure. A run without catalyst particles at representative temperature and pressure (250°C, 9 bar) showed that no reaction occurred. This proves that the wall of the reactor is effectively inert and cracking of squalane is negligible.

Liquid carrier. Squalane (2,6,10,15,19,23-hexamethyloctacosane, $C_{30}H_{62}$) was applied as liquid phase. This relative expensive hydrocarbon has a melting point below room temperature which facilitates its handling. Squalane (Fluka AG, purity >95%) contains small amounts of squalene. The boiling point of squalane is 350°C at atmospheric pressure. Below 300°C squalane is thermally stable.

Operating procedure. Continuous experiments lasting more than 800 hours with one catalyst batch have been performed. Operating conditions were changed at intervals of 10 to 24 hours. The reactor system, including the on-line gas analysis, operated 24 h per day without interruption. Possible changes in catalytic activity or selectivity were monitored by periodically repeating a standard experiment.

Analysis. Hydrogen, carbon monoxide and carbon dioxide were separated over a molsieve 13X column ($T = 40°C$) in a HP5700A gas chromatograph with a TCD. Argon was used as carrier gas. Usually only the hydrogen signal was integrated. Carbon monoxide and carbon dioxide were separated over a porapak Q column ($T = 90°C$) in a HP5710A gas chromatograph with a TCD. For this analysis helium was used as carrier gas. C_1 to C_3 olefins, paraffins and alcohols were separated over a porapak QS column ($T = 95°C$) in a Pye 104 gas chromatograph equipped with a FID. C_1 to C_8 hydrocarbons were analysed with a Carlo Erba FID EL480 after separation over a n-octane/poracil C column. This column was attached in the oven of the HP5710A gas chromatograph ($T = 90°C$).

The signals of the detectors were connected alternately with a HP3392A integrator via a CB4052BM dual 4-channel analog multiplexer which was controlled by a mechanical time switch. A complete analysis could be carried out every 2 hours.

The chromatographs were regularly calibrated for C_1 to C_3 hydrocarbons, H_2, CO and CO_2. The response factors of C_4-C_8 hydrocarbons are based on the report of Dietz [1]. For a flame ionization detector these factors are nearly proportional to the number of carbon atoms in the product.

2.4 Accumulation of hydrocarbons in a stirred laboratory slurry reactor

2.4.1 Introduction

In a stirred slurry reactor the temperature control and uniformity is achieved by the good heat conductivity and homogeneity of the liquid phase. However, the presence of a relatively large liquid volume has its disadvantages when studying rapid changes of the catalytic performance. Hydrocarbons produced accumulate in the liquid phase. This accumulation causes delay in the appearance of the products in the gas phase. A further delay is caused by the gas holdup in and above the liquid phase. The time lag between the head of the reactor and the gas sample valve is negligible.

The reaction conditions affect the accumulation of the products both in the liquid and the gas phase. The accumulation in both phases will be larger at higher pressure because the solubility in the liquid phase and the concentration in the gas phase increases with increasing pressure. The gas flow also influences the accumulation within the reactor.

It is important to note that if the carbon number increases the solubility of the hydrocarbons also increases. This means that the time to attain the steady-state concentration increases with increasing carbon number. Hence, the apparent selectivity will change until the steady-state value of the largest hydrocarbon of interest has been reached.

In this section the length of the time required for hydrocarbons, formed by the Fischer-Tropsch reaction, to reach the steady-state is calculated and compared with the value determined experimentally. In addition, the effect of the reactor pressure on the accumulation within the reactor will be shown.

2.4.2 Theoretical and experimental results

Consider a well-stirred slurry reactor with a perfectly mixed gas, liquid and solid phase. It is assumed that the gas phase in and above the liquid is in equilibrium with the liquid phase. Synthesis gas is supplied to the reactor and gaseous products are removed overhead together with unconverted synthesis gas. The outlet pressure of component i, p_i, follows from a mass balance over the reactor:

$$\frac{p_i(t)\;F_{out}}{RT} = r_{p,i} - V_L\,\frac{d\,C_{L,i}(t)}{dt} - V_G\,\frac{d\,C_{G,i}(t)}{dt} \qquad (2.1)$$

Assuming that the concentration in the liquid phase is represented by the Henry's law, Eq.(2.1) can be written as

$$\frac{p_i(t)\;F_{out}}{RT} = r_{p,i} - \frac{V_L}{m_i\;RT}\cdot\frac{d\;p_i(t)}{dt} - \frac{V_G}{RT}\cdot\frac{d\;p_i(t)}{dt} \qquad (2.2)$$

Integration of Eq.(2.2.) and replacement of the actual gas flow F_{out} by the gas flow F^{*}_{out} measured at room temperature, T^*, and atmospheric pressure, p^*, results in

$$p_i\,(t) = p_i^{\infty} + (p_i^{0} - p_i^{\infty})\,\exp\,(-bt) \qquad (2.3)$$

with

$$b = \frac{F^{*}_{out}\;p^*\;T}{(V_G + V_L/m_i)\,p\;T^*} \qquad (2.4)$$

$$p_i^{\infty} = \frac{1}{b}\cdot\frac{r_{p,i}\;RT}{V_G + V_L/m_i} \qquad (2.5)$$

In these equations p_i^{0} and p_i^{∞} represent the pressure of i at t=0 and t=∞ respectively.From the inspection of Eq.(2.4) follows that the time constant b depends mainly on the gas flow, the pressure, the liquid and gas volume and the solubility. The gas volume is only important for C_1-C_4 hydrocarbons because the value of V_L/m for C_5^+ hydrocarbons is much higher than V_G. Reduction of the time constant can be achieved by increasing the gas flow or decreasing the pressure or liquid volume.

The length of time required to attain the steady-state value of gaseous hydrocarbons in a stirred 0.5-liter autoclave, as used in this study, is illustrated by the theoretical and experimental course of the pressure of various hydrocarbons as a function of time (see Figure 2.2). The course of the pressures is shown after a change of the inlet gas flow.

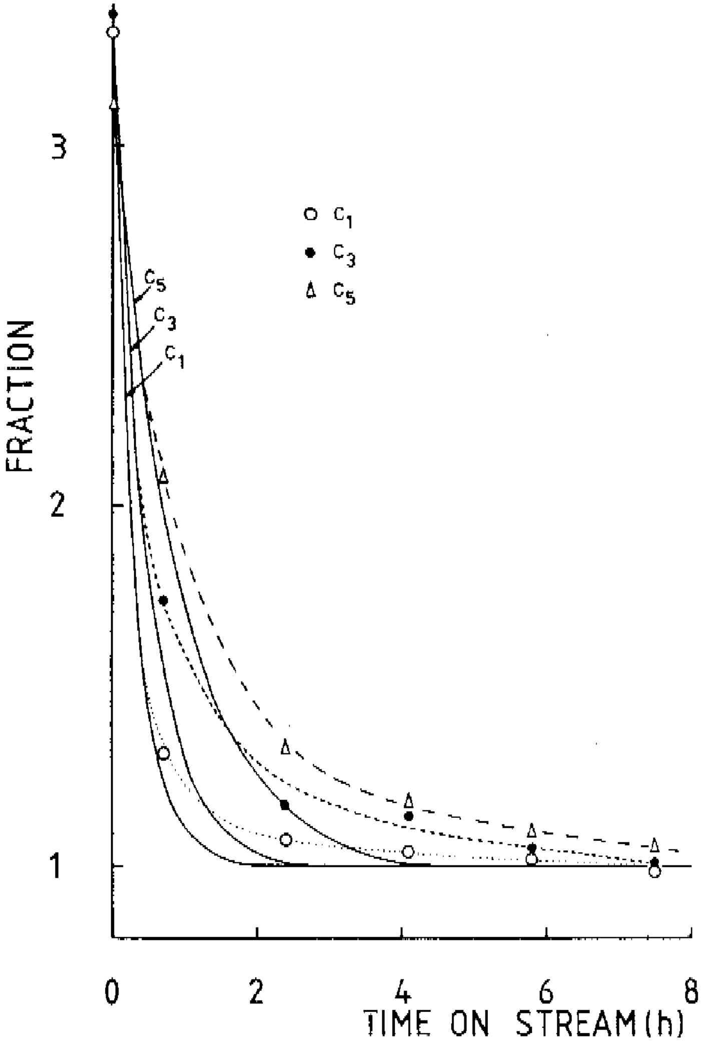

Fig. 2.2 Hydrocarbon pressure with respect to the steady-state value as a function of time on stream after an increase of the inlet gas flow. Reaction conditions: pressure = 17 bar temperature = 250 °C; F_{out} = 210 ml (20°C, 1 bar)/min. The data points are experimental values. The lines closed are calculated according to Eq.(2.3). Data used: V_L=250 ml; V_G=312 ml; m=2.48, 0.7 and 0.27 (m^3_L/m^3_G) for C_1, C_3 and C_5 respectively which are calculated according to Eq.(2.60)

This specific change of reaction conditions was chosen because in this manner the effect of the reaction conditions on the intrinsic catalyst activity is less important than in the case where the pressure or the temperature is changed. The theoretical lines in Figure 2.2 are calculated with help of Eq.(2.3) assuming that the production rate of hydrocarbons is constant. Figure 2.2 shows that the time observed experimentally to reach the steady-state is longer than the time predicted. After 4 hours the pressure of C_1, C_3 and C_5 (with respect to the steady state value) are 2, 5 and 7% higher than the steady state value, respectively. This value is reached after approximately 8 hours for the hydrocarbons shown in Figure 2.2. Taking into account the possibility that the catalyst activity increases slightly in the first hours after a change of the gas flow, the similarity between the time measured and calculated is satisfactory.

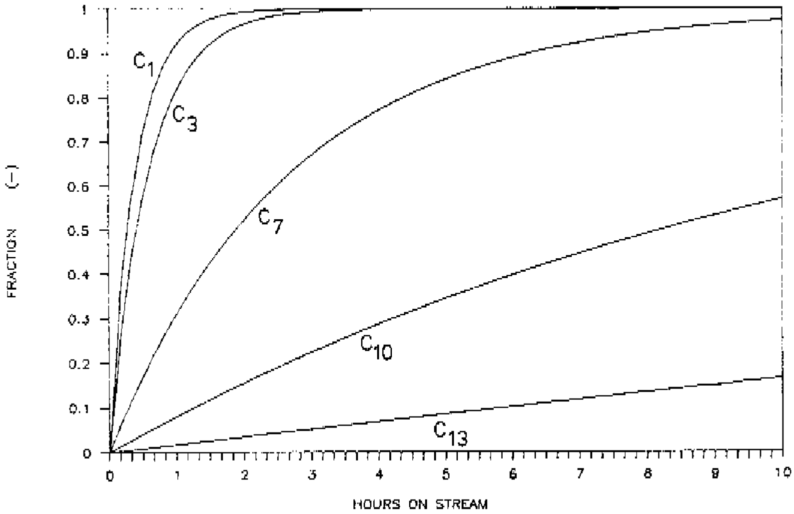

Fig. 2.3 Effect of the carbon number on the time required to reach the steady-state value in the gas outlet flow of the stirred autoclave. The lines are calculated according to Eq.(2.3) and the data given in Figure 2.2

The time required to attain the steady-state value increases with increasing carbon number due to the larger solubility of heavier hydrocarbons. Figure 2.3 illustrates the fraction of the steady-state pressure versus time. Obviously, the C_{10} and C_{13} fraction do not reach the steady-state value within 8 hours after changing the process parameters under the reaction conditions chosen.

As already mentioned, the time constant b in Eq.(2.4) depends on the reactor pressure. Figure 2.4 shows the effect of the reactor pressure on the course of the pressure of C_5 as a function of time. At low pressure the steady-state value of the products is reached rapidly. However, at a higher pressure more time has to elapse before the measured pressure is equal to the "intrinsic pressure". In this study, therefore, the reported performance of the catalyst properties are measured during at least 10 hours. Usually, the reaction conditions were varied after the reaction was monitored 24 h at a particular setting.

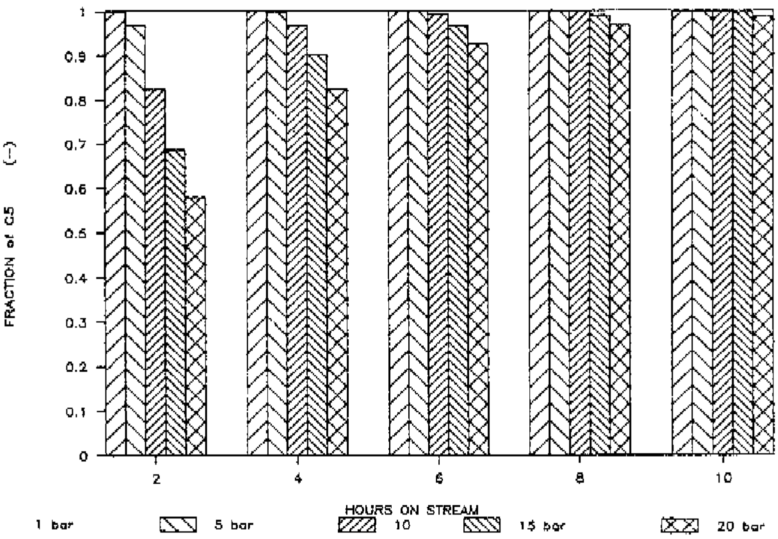

Fig. 2.4 Effect of the pressure on the time required to reach the steady-state value in the gas outlet flow of the stirred autoclave. The lines are calculated according to equation (2.3) and the data given in Figure 2.2

2.4.3 Conclusion

At a moderate pressure (10-15 bar) and a low gas flow rate (1 m^3 synthesis gas/m^3 squalane) a reliable analysis of the concentration of C_1-C_7 hydrocarbons, produced by the Fischer-Tropsch synthesis in a stirred 0.5-liter autoclave, is only possible when at least 8 hours are elapsed after setting the reaction conditions. Catalyst properties, which change much more rapidly and well within the above-mentioned 8-hour period, can only be measured accurately if the gas flow is increased or the total pressure is decreased.

2.5 The importance of the water-gas shift activity for the performance of Fischer-Tropsch catalysts

The H_2/CO outlet ratio in a well-mixed slurry reactor determines the H_2/CO concentration ratio in the liquid which in turn determines the H_2/CO ratio on the catalyst surface, provided mass transfer limitations are absent. The H_2/CO concentration ratio on the catalyst surface is of importance for the deposition of carbon which is the main cause of the deactivation of Fischer-Tropsch catalysts. The H_2/CO outlet ratio is influenced by the usage ratio [1] which in turn is affected by the water-gas shift activity of the catalyst. This section mainly deals with the relation between the water-gas shift activity of the catalyst and the H_2/CO outlet ratio. In addition, the stoichimetry and the conversion level will be discussed since they affect the H_2/CO outlet ratio as well.

The overall reaction for the production of hydrocarbons from CO and H_2 can be written as

$$CO + (1 + \tfrac{1}{2}x)H_2 \rightarrow CH_x + H_2O \qquad (2.6)$$

The product water can be converted to CO_2 by the water-gas shift reaction:

$$zCO + zH_2O \rightleftharpoons zCO_2 + zH_2 \qquad (2.7)$$

z being the fraction of the product water which is converted by the water-gas shift reaction.Combining of Eq.(2.6) and (2.7) results in the

---

[1] = net molar ratio in which CO and H_2 are consumed in the reaction

overall stoichiometry

$$(1 + z)CO + (1 + \tfrac{1}{2}x - z)H_2 \rightarrow CH_x + zCO_2 + (1 - z)H_2O \tag{2.8}$$

As will be pointed out below, the H_2/CO usage ratio, U, plays an important role in determining the required H_2/CO inlet ratio. The overall stoichiometry shows that the H_2/CO usage ratio depends on the H/C atomic ratio in the product (x) and on the fraction of water converted (z):

$$U = (1 + \tfrac{1}{2}x - z)/(1 + z) \tag{2.9}$$

The H_2/CO usage ratio for some typical products of the Fischer-Tropsch synthesis are presented in Table 2.1.

Table 2.1

The H_2/CO usage ratio (U) for some products of the Fischer-Tropsch synthesis when z = 0 and z = 1 (a low and high watergas shift activity respectively)

	U	
Product	z = 0	z = 1
CH_4	3	1
C_2H_6	2.5	0.75
$CH_{2.33}$	2.2	0.58
C_2H_4	2	0.5

Table 2.1 clearly demonstrates that a high water-gas shift activity is indispensable if the H_2/CO usage ratio has to be lower than the value 1. When the usage ratio is known, the effect of the conversion of CO and H_2 on the H_2/CO outlet ratio, E, can be calculated for a known value of the inlet ratio (I). The value of the outlet ratio follows simply from

$$E = I \frac{1-X_{H_2}}{1-X_{CO}} \qquad (2.10)$$

Both the conversion of H_2 and that of CO can be expressed as a function of conversion of CO + H_2 (X_{CO+H_2}):

$$X_{CO} = X_{CO+H_2} \frac{(1+I)}{(1+U)} \qquad (2.11)$$

$$X_{H_2} = X_{CO+H_2} \frac{U(1+I)}{I(1+U)} \qquad (2.12)$$

Substition of Eqs. (2.11) and (2.12) into (2.10) results in

$$E = \frac{I - X_{CO+H_2} \dfrac{U(1+I)}{(1+U)}}{1 - X_{CO+H_2} \dfrac{(1+I)}{(1+U)}} \qquad (2.13)$$

By substitution of Eq.(2.9) into (2.13) the H_2/CO outlet ratio can be calculated for each degree of conversion of CO + H_2 when the values of x are known:

$$E = \frac{I(2 + \frac{1}{2}x) - (1+I)(1 + \frac{1}{2}x - z)X_{CO+H_2}}{2 + \frac{1}{2}x - (1+I)(1+z)X_{CO+H_2}} \qquad (2.14)$$

The large effect of the water-gas shift activity on the usage ratio was already illustrated in Table 2.1. As a consequence the value of z strongly effects the outlet ratio as shown in Figure 2.5. Obviously, the H_2/CO outlet ratio decreases as a function of conversion of CO + H_2 if the value of z is lower than 0.6. When the H_2/CO inlet ratio has to be lower than 1.0, the value which was chosen in Figure 2.5, the value of z

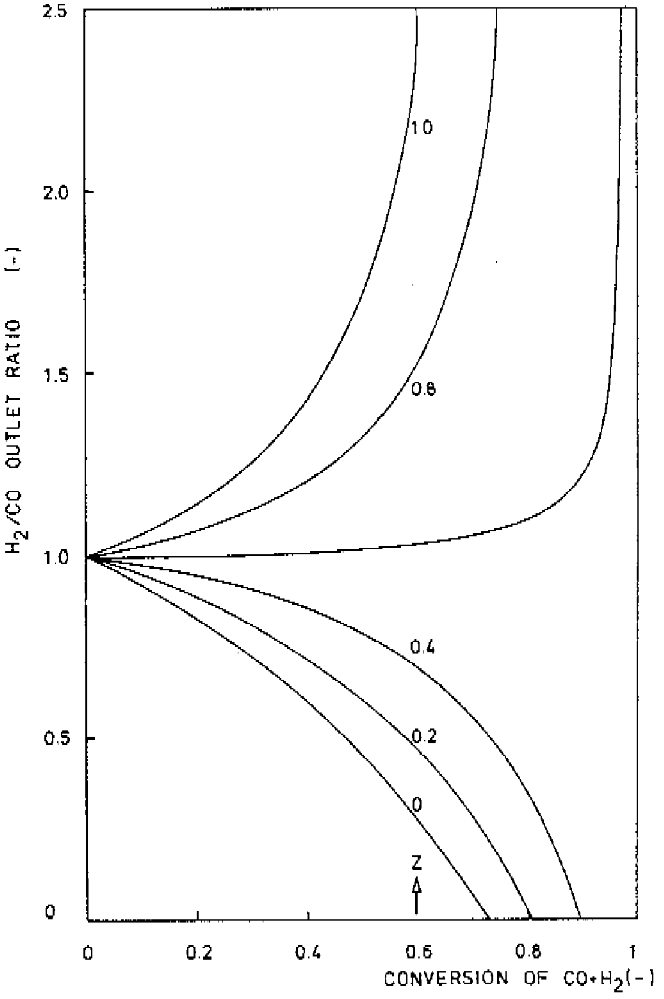

Fig. 2.5 The calculated H_2/CO outlet ratio as a function of the conversion of CO+H_2 for various values of z. The inlet ratio (I) is 1.0. The H/C atomic ratio in the product (x) is 2.33

has to be higher than 0.6 to avoid that the H_2/CO outlet ratio decreases with increasing conversion. Note that the value of x, assumed in Figure 2.5, is near the lowest which is possible for Fischer-Tropsch hydrocarbons (see Table 2.1). This means that, to convert synthesis gas with a low H_2/CO ratio, a high water-gas shift activity is absolutely essential.

2.6 The water-gas shift activity of potassium promoted fused iron

2.6.1 Introduction

It is generally accepted that the water-gas shift reaction is a consecutive reaction. Initially water is the principal by-product of the formation of hydrocarbons by the Fischer-Tropsch reaction. Depending on the rate of the water-gas shift reaction, the water formed by the Fischer-Tropsch synthesis will be converted into CO_2 or removed by the outlet gas stream. The water-gas shift reaction is an equilibrium reaction, see Eq.(2.7), of which the equilibrium lies on the CO_2 side for typical Fischer-Tropsch conditions. It can be seen from the equilibrium constant [2]

$$K_S = \frac{p_{CO_2}\, p_{H_2}}{p_{H_2O}\, p_{CO}} = 0.0132 \exp(4578/T) \qquad (2.15)$$

that only 1% of the water produced is not converted into CO_2 at 250°C and for H_2/CO ratio = 0.85. The question whether the equilibrium is actually reached in practice, in relation to the rate of the water-gas shift reaction, will be answered in this section.

2.6.2 Experimental

About 30 g of crushed (45-90 μm) fused iron (C73, Süd-Chemie) was reduced in a separate fixed-bed reactor with 0.9 l H_2 (20°C, 1 bar)/ min at 450°C, atmospheric pressure, for 70 hr. It was added into the stirred autoclave without exposure to air and then slurried with 200 g squalane. The stirrer speed (1000 min^{-1}) was high enough to avoid mass transfer limitations and to achieve perfect mixing of the gas and liquid phase.

Two batches of fused iron have been used the conditions for which are presented in Table 2.2.

Table 2.2
Experimental conditions

Conditions			
		Batch 1	Batch 2
Temperature	(°C)	250	230, 250, 270
Pressure	(bar)	1.5 - 9	1.5 - 9
$(H_2/CO)_{feed}$	(-)	0.7 - 3	0.67

2.6.3 Results and discussion

In principle, the water-gas shift activity can be determined directly on the basis of the amounts of water and carbon dioxide produced. However, the concentration of water in the outlet gas flow is difficult to measure accurately by means of gas chromatography or aluminium oxide sensors. Therefore, the water-gas shift activity is calculated and expressed by the value of z, which represents the fraction of product water converted to CO_2. The value of z can be calculated in different ways:

1. Calculation of the value z from the H_2/CO usage ratio and the H/C atomic ratio in the product according to Eq.(2.9) which can be rewritten into

$$z = \frac{1 - U + \frac{1}{4}x}{1+U} \qquad (2.16)$$

The H_2/CO usage ratio can be calculated from the measured conversion of H_2 and CO

$$U = I \frac{x_{H_2}}{x_{CO}} \qquad (2.17)$$

2. Calculation of z from the production of CO_2 and the conversion of CO. From the overall stoichiometry, Eq.(2.8), it follows that

$$z = \frac{r_{CO_2}}{-r_{CO} - r_{CO_2}} \tag{2.18}$$

Introducing the CO_2 partial pressure and the conversion of CO gives to rise to the following equation:

$$z = \frac{p_{CO}(1-X_{CO})}{p_{CO} X_{CO} - p_{CO_2}(1-X_{CO})} \tag{2.19}$$

This equation is prefered for the determination of the value of z because it is sufficient to know the CO_2 partial pressure and CO conversion. It makes it more accurate than Eq.(2.16). Rewriting of Eq.(2.19) shows that the CO conversion divided by $1-X_{CO}$ increases linearly with the increasing CO_2/CO pressure ratio:

$$\frac{X_{CO}}{1-X_{CO}} = \frac{z+1}{z} \cdot \frac{p_{CO_2}}{p_{CO}} \tag{2.20}$$

Together with data points, this relation is shown in Figure 2.6 for various values of z. Despite considerable scattering of the data points, the conclusion is justified that the value of z is close to 1 at 250°C. This high value indicates a high rate of the water-gas shift reaction. This means that the water-gas shift equilibrium will be attained at reaction conditions and that application of Eq.(2.15) is allowed for calculation of the water vapour pressure.

As a consequence of the high water-gas shift activity, the H_2/CO usage ratio is very low for the catalyst applied here. Therefore, synthesis gas with a low H_2/CO ratio, such as 0.67, can be converted up to a high degree of conversion. At such a high conversion level the outlet H_2/CO ratio is considerably larger than the inlet ratio as shown in Figure 2.7. The data points in Figure 2.7 can be fit with Eq.(2.13) assuming the H_2/CO usage ratio is 0.55.

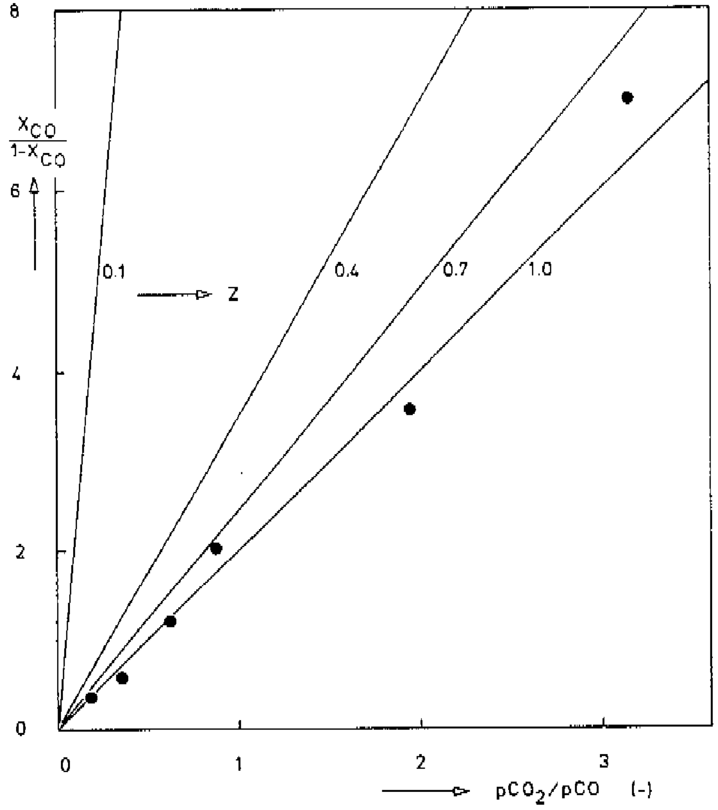

Fig. 2.6 Relation between the conversion of CO and the CO_2/CO pressure ratio. The lines represent the theoretical relation (see Eq.(2.16)) for various values of z indicated in the figure. The experimental data are obtained at 250°C (run 1)

2.6.4 Conclusion

The H_2/CO outlet ratio and the usage ratio are strongly dependent on the rate of the water-gas shift reaction. Due to the high water-gas shift activity of potassium promoted fused iron the H_2/CO usage ratio is low (approximately 0.6) and the partial pressure of water is very low even at a high degree of conversion. As a consequence of the high rate of the water-gas shift reaction over this catalyst, synthesis gas with a low H_2/CO ratio can be converted directly to hydrocarbons and carbon dioxide as the main side-product.

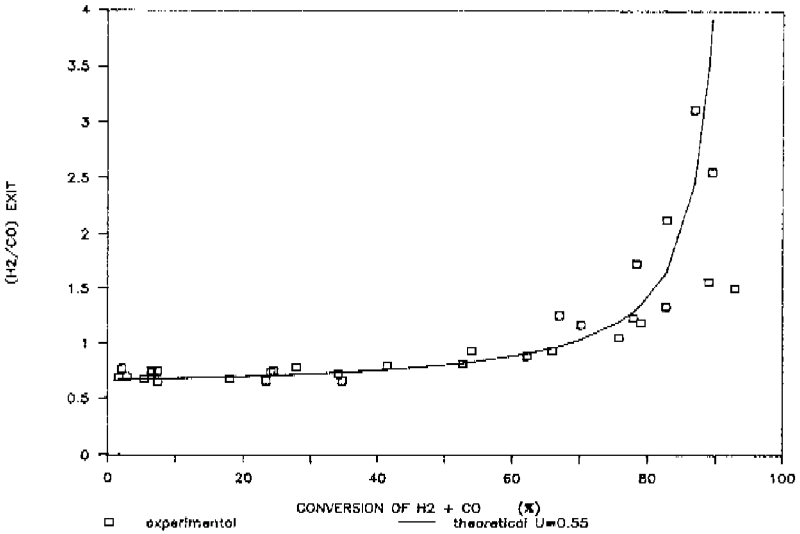

Fig. 2.7 The H_2/CO outlet ratio as a function of the conversion of CO+H_2. The reaction conditions are reported in Table 2.2 (run 2). The curve is calculated according to Eq.(2.13)