CHAPTER 1

Introduction

1.1. COAL CONVERSION

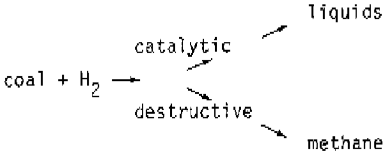
Since the so called energy crisis of 1973 interest in coal as a possible source of energy and as a raw material increased markedly. One reason for that increased interest is that the reserves of coal are estimated to be at least three times larger than the oil reserves /1/ and that they are geographically distributed less uneven than oil.

Coal chemistry dates back to about 1800 when the first research was carried out on the oxidation of coal. The systematic studies on the hydrogenation and extraction of coal started in the latter half of the last century /2,3,4/. All basic coal conversion processes aim at transforming coal into fuels that give less problems in utilization or that can be more easily transported. For these reasons high-sulphur coals are desulphurized, high ash coals are demineralized and coal is converted into liquid and gaseous products. A great amount of research work has been devoted to coal conversion and numerous processes have been developed during the years /5,6/. But in spite of all these efforts products from coal cannot yet compete with the products based on oil. However, as the prices of crude oils increase much faster than that of coal the break-even point for some products is expected to be rather near.

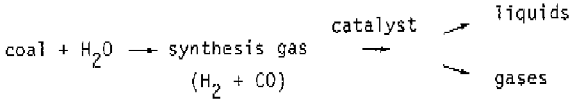
The processes for liquids and gases from coal can be divided into four groups /7,8/:

1) Pyrolysis,
   in which the volatile or complex organic compounds are separated and decomposed thermally;
2) Solvation (solvent extraction)
   By use of a hydrogen donor solvent (e.g. tetraline anthracene oil) coal is digested to yield a slurry which after filtration can further be hydrogenated to liquid fuels;

3) Direct hydrogenation with reactions



4) Indirect synthesis from a mixture of hydrogen and carbon monoxide



The chemistry of the direct and indirect hydrogenation of coal to hydrocarbons is characterized as follows:

direct hydrogenation:

$$\begin{array}{lcll} & & & \Delta H_{298}\ (\mathrm{kJ})\ /9/ \\ C + H_2O & \rightarrow & CO + H_2 & +\ 118.8 \\ CO + H_2O & \rightarrow & CO_2 + H_2 & -\ \ 41.2 \\ 2\ C + 2\ H_2 & \rightarrow & 2\ \text{-}CH_2\text{-} & -\ \ 55.4 \\ \hline 3\ C + 2\ H_2O & \rightarrow & CO_2 + 2\ \text{-}CH_2\text{-} & +\ \ 22.2 \end{array} \qquad (1.1)$$

indirect hydrogenation:

$$\begin{array}{lcll} & & & \Delta H_{298}\ (\mathrm{kJ}) \\ 3\ C + 3\ H_2O & \rightarrow & 3\ CO + 3\ H_2 & +\ 356.4 \\ CO + H_2O & \rightarrow & CO_2 + H_2 & -\ \ 41.2 \\ 2\ CO + 4\ H_2 & \rightarrow & 2\ \text{-}CH_2\text{-} + 2\ H_2O & -\ 293.1 \\ \hline 3\ C + 2\ H_2O & \rightarrow & CO_2 + 2\ \text{-}CH_2\text{-} & +\ \ 22.1 \end{array} \qquad (1.2)$$

In the first case much less heat is involved than in the latter case. The direct hydrogenation produces mainly branched and naphthenic hydrocarbons, which can be used very well as fuel; however, they are not attractive as cracking feedstocks. The product from the indirect hydrogenation consists mainly of straight chain hydrocarbons and olefins, which can be used as feedstocks for the chemical industry.

This thesis deals with the indirect conversion of coal to hydrocarbons, the so called Fischer-Tropsch synthesis. Therefore in the following sections a short survey of that process is given.

1.2. THE FISCHER-TROPSCH SYNTHESIS

The conversion of synthesis gas - a mixture of hydrogen and carbon monoxide from coal gasification - to hydrocarbons

$$2n\ H_2 + n\ CO \xrightarrow{\text{catalyst}} [CH_2]_n + n\ H_2O \qquad (1.3)$$

is called the Fischer-Tropsch synthesis after Frans Fischer and Hans Tropsch who discovered this process in 1925 /10/. Before that, in 1902, Sabatier managed to produce methane from synthesis gas using a nickel catalyst /10/.

At the end of the thirties the development had already advanced so far that nine plants had been erected in Germany. In all the processes cobalt catalysts were used at atmospheric or medium (0.6-1 MPa) pressures. About 50% of the output was a gasoline fraction. During the second world war various iron catalysts were tested. But after the war the low cost of oil made these plants economically unattractive and they were all closed. Some plants were built also in the U.S.A., France and Japan but at this moment the only commercial plants are in South Africa, where the economic situation is totally different from that in the rest of the world. The current output of gasoline is 1.7×10^5 ton per year and of petrochemicals 0.8×10^5 ton per year /5/, but because of enlargements the production of gasoline is expected to increase to 1.5×10^6 ton per year before 1982 /11-13/.

Several detailed reviews have been published on the developments of the Fischer-Tropsch catalysts, on the influence of process variables and on various processes applied and we refer to those for further general information /10,14-23/.

1.3. MECHANISMS PROPOSED FOR THE FISCHER-TROPSCH SYNTHESIS

The mechanisms that have been suggested for this reaction can all be divided into three steps: initiation, propagation (i.e. chain growth) and termination. The initiation step includes the adsorption of reactants and the formation of surface intermediates containing one carbon atom. The propagation step consists of the formation of surface intermediates with more than one carbon atom from the building blocks of one carbon atom. The termination step is the formation of hydrocarbons either via direct desorption or via hydrogenation and subsequent desorption of the intermediates.

The first mechanism, the so called carbide mechanism, has been proposed by Fischer /24/. According to that carbon monoxide dissociates and forms carbides, which are hydrogenated to CH_2-groups. The chain growth proceeds via polymerization of these CH_2-groups. Craxford and Rideal /25/ presented that mechanism in the following form:

$$\begin{aligned} &Co + CO \rightarrow Co\text{-}CO \\ &Co\text{-}CO + CO \rightarrow CoC + CO_2 \end{aligned} \qquad (1.4)$$

or

$$\begin{aligned} &Co\text{-}CO + H_2 \rightarrow CoC + H_2O \\ &CoC + H_2 \rightarrow Co\text{-}CH_2\text{-} \rightarrow \text{higher hydrocarbons} \end{aligned}$$

Many arguments were put forth against this mechanism /14,16/ and therefore it was neglected for several years.

In its place a mechanism proposed by Storch <u>et al</u>. /14/ has been widely used /23/. It was supported especially by Anderson /16/ and Kölbel /17/. Essential in that mechanism is the formation of an alcohol-type complex as an intermediate, the chain growth taking place via the dehydrocondensation of these complexes. The following reactions are suggested:

initiation:

$$CO(ads) + 2\ H(ads) \rightarrow CHOH(ads)$$

chain growth:

$$\mathrm{RCOH(ads)} + \mathrm{CHOH(ads)} \xrightarrow{+2H(ads)} \mathrm{RCH_2CHOH(ads)} + \mathrm{H_2O} \qquad (1.5)$$

termination:

$$\begin{tikzcd}
\mathrm{RCH_2COH(ads)} \arrow[r] \arrow[dr, "2H(ads)"'] & \mathrm{RCH_2CHO} & & \\
 & \mathrm{RCH_2CH_2OH} \arrow[r] & \text{olefins} \arrow[r, "+H(ads)"] & \text{paraffins}
\end{tikzcd}$$

Pichler has proposed a mechanism where the first intermediate is a carbonyl-type complex and the propagation proceeds via the insertion of carbon monoxide to the growing chain /19/. In a simplified form the mechanism can be described as follows /26/:

initiation:

the formation of a carbonyl $\mathrm{HM(CO)_x}$; M = metal

chain growth:

$$\mathrm{RM(CO)_x} + \mathrm{CO(ads)} \rightarrow \mathrm{RCOM(CO)_x} \xrightarrow{+2H_2} \mathrm{RCH_2M(CO)_x} \qquad (1.6)$$

termination:

$$\mathrm{RCH_2M(CO)_x} + \mathrm{H_2} \rightarrow \mathrm{RCH_3} + \mathrm{HM(CO)_x}$$

For several years the discussions considered mainly the latter two mechanisms, that of the alcohol complex and that of the carbonyl complex. Recent studies however have shown that the adsorption of carbon monoxide on transition metals is dissociative /27-29/. Also it has been demonstrated that surface carbon is an active intermediate in the methanation reaction /30-35/. Based on the results from experiments with nickel-copper alloys van Barneveld and Ponec /36/ proposed the following mechanism:

initiation:

$$CO(ads) \rightarrow C(ads) + O(ads)$$
$$C(ads) + x\,H(ads) \rightarrow CH_x(ads) \qquad (1.7)$$

chain growth:

$$CH_x(ads) + CO(ads) \rightarrow CH_xCO(ads)$$
$$CH_xCO(ads) + m\,H(ads) \rightarrow CH_xCH_{m-2}(ads) + H_2O$$

termination:

$$CH_xCH_{m-2} + y\,H \rightarrow \text{products}$$

The chain growth step of this mechanism is more based on speculations than on experimental evidence.

Shortly afterwards Biloen et al. /37/ presented experimental results on a nickel catalyst that indicate that the chain growth proceeds via CH_x entities:

$$C_mH_y + CH_x \rightarrow C_{m+1}H_{x+y} \qquad (1.8)$$
$$x = 0 \ldots 3, \text{ probably } x = 2 \text{ and } y = 2m + 1$$

Conclusions:

In the light of recent results it can be concluded that the initiation step of the Fischer-Tropsch synthesis proceeds via a dissociatively adsorbed carbon monoxide. The conclusion about the chain growth is less clear. But the chain growth via an intermediate without any oxygen e.g. via CH_x-groups is at least possible on a nickel catalyst.

1.4. THE PRESENT STATE OF THE ART

Problems of the Fischer-Tropsch synthesis

In spite of the large volume of research carried out on the Fischer-Tropsch synthesis several aspects of the process are still open for discussion:

i) The reason for the turnover frequencies of the Fischer-Tropsch synthesis to be much lower than found in most other heterogeneous catalytic processes.

ii) Is an increase of selectivity possible? The product distribution can viz. be directed to methane, higher hydrocarbons or oxygen containing compounds by varying reaction conditions, catalysts and processes, but in all cases a variety of products is formed.
iii) Practically always catalysts are deactivated during the operation by the formation of carbonaceous species. Can this be prevented?
iv) At this moment there is no generally accepted mechanism or a kinetic model. As the three previous points are all closely related to the network of reactions that constitute the reaction mechanism, a better understanding of the route by which the synthesis proceeds would undoubtedly help in solving the other problems.

Perspectives for the Fischer-Tropsch synthesis

Several calculations have shown that the only way to improve the economy of the Fischer-Tropsch synthesis is to improve the selectivity towards valuable products e.g. low olefins, naphtha fraction (C_5-C_{12} hydrocarbons) or unsaturated and saturated hydrocarbons in range C_{10}-C_{20} /38/. Light olefins could be used as raw materials for the chemical industry, the naphtha fraction as a cracking feedstock and the C_{10}-C_{20} fraction as a raw material for detergents. But it has also been shown that for the economic situation as of 1974, the selectivity for low olefins should be higher than 50% before the process would be economic /39/. On the conventional cobalt and iron catalysts this has never been achieved.

Several studies have been started, especially in Germany with the aim to develop catalysts for low olefin production. Several patents which claim a selective ethylene production have already been published twenty years ago /40-46/ but as far as we know no one has been able to reproduce these results. During the last years new patents have been published according to which catalysts based on iron or manganese are suitable for the low olefin production /47-50/. But the results published in the open literature are not convincing. In figure 1.1 the product distributions recalculated from the publications of Kitzelmann et al. /51/ and Kölbel et al. /52/ are shown as a function of the carbon number. In both cases the normal product distributions with a relatively low C_2-fraction are obtained and not the high olefin containing products as claimed in the patents.

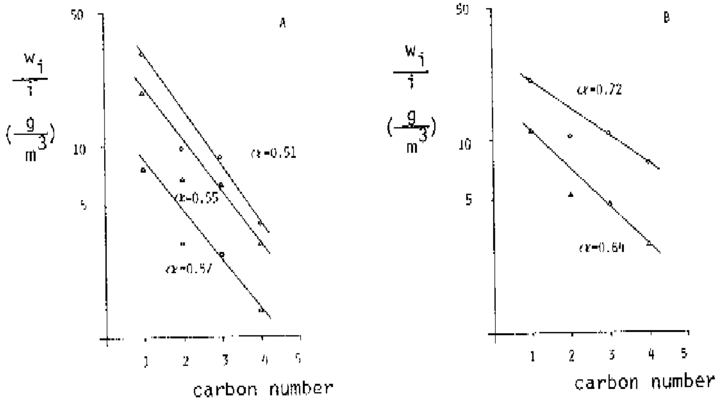


Figure 1.1. The weight of products as a function of the carbon number. A. Kitzelmann et al. /51/ B. Kölbel et al. /52/.

Gasoline production via the Fischer-Tropsch route is generally not able to compete economically with gasoline from oil /53/, although every year a great number of new patents for this process or for new catalysts for this process are published. A more promising route from synthesis gas to gasoline may be the process via methanol. This process, developed by Mobil Oil Corp., uses a shape selective zeolite ZSM-5 to convert methanol very selectively to C_5-C_{10} hydrocarbons with a high concentration of aromatics /54/. Recently some results have been published according to which gasoline production of the Fischer-Tropsch synthesis can be remarkably increased by combining the conventional iron catalysts with ZSM-5 zeolite /55-56/.

Next to conventional heterogeneous catalysts some homogeneous catalysts like iridium carbonyls have been reported also to convert synthesis gas to alkanes /57,58/.

Oxygen containing compounds are not used in the same quantities as gasoline or low olefins but on the other hand they can be rather valuable. Some alcohols, aldehydes and acids are formed as a by-product in the hydrocarbon synthesis, especially on iron catalysts. But attempts have also been made to direct the synthesis specifically to the formation of oxygen containing compounds. There are patents that claim the possibility of making polyhydric alcohols e.g. ethylene glycol directly from a mixture of hydrogen and carbon monoxide on rhodium carbonyl catalysts under the pressure of 300 MPa /59-62/.

Besides the improvement of the selectivity, also the mechanism of the Fischer-Tropsch synthesis has been the object of several studies. One of the aims is to explain why some metals are active in the process and some others are not. The adsorption of hydrogen is quite similar on several metals /63/ but differences have been found in the adsorption of carbon monoxide. Attempts have been made to correlate these differences with the catalytic activity in the Fischer-Tropsch synthesis. It has been noticed that metals which chemisorb carbon monoxide in the bridged form (like Ni) are better catalysts for hydrogenation to methane than metals (like Cu and Pt) which chemisorb carbon monoxide in linear form /20/. On the other hand Vannice /64/ has found a correlation between the methanation activity and the heat of adsorption of carbon monoxide. The heat of adsorption gives a relative measure of the bond-strength of the metal-carbon bond of the carbon monoxide surface species.

In the light of recent results the activity and also the selectivity depends on the ability of the catalyst to dissociate carbon monoxide /33,65/. The metals which do not dissociate carbon monoxide have a lower activity and form more oxygen containing products (Pd) than the metals which dissociate CO (Ni, Fe, Co, Ru).

Metals like molybdenum and tungsten which have been observed to dissociate carbon monoxide /66,67/ are found to be ineffective catalysts for the Fischer-Tropsch synthesis. This has been explained by too strong an adsorption of carbon monoxide on those metals /68/. But Kelley et al. /69/ have shown that the activity of tungsten in methanation is higher than that of nickel at low temperatures. These authors suggested that the low activity in earlier studies may be due to difficulties in preparing catalysts in a completely reduced and clean form.

1.5. THE AIM AND OUTLINE OF THIS THESIS

In spite of numerous studies of the Fischer-Tropsch synthesis several questions are still unanswered as illustrated in the previous sections. On the other hand the importance of coal chemistry in future became clear at the beginning of this decade. These were the main reasons for the research in this thesis.

The main aim has been to gain more insight in the mechanism and the kinetics of the synthesis, especially in the formation of various hydrocarbons, as well paraffins as olefins. This knowledge could be helpful in solving the selectivity problems which are very closely connected to the economy of the process.

For this study cobalt catalysts were chosen. Nickel catalysts are known to produce mainly methane and ruthenium catalysts saturated products. The product distribution of iron catalysts is very complex because except hydrocarbons also oxygen containing compounds are formed. Iron is also less resistant against carbon monoxide and water of which the former reacts with metal forming carbides and coke, and the latter can oxidize the metal. Thus cobalt catalysts were the most suitable for our purposes. Both supported and unsupported catalysts are used.

In chapter 2 various reactor systems used in this study are described. The definition of the turnover frequency, rate and selectivity are also given in that chapter.

Preparation of the two cobalt catalysts is presented in chapter 3. In the characterization of the catalysts reduction and adsorption experiments are used. The reduction of the unsupported catalyst by hydrogen and by carbon monoxide is analyzed by means of various kinetic models.

In chapter 4 attention is paid to the various aspects of the Fischer-Tropsch process. The influence of the concentration of the reactants, temperature and various catalyst treatments is investigated. Based on these results a qualitative reaction model is proposed and the differences between the supported and the unsupported catalysts are discussed.

Based on the conclusions of chapter 4 that the formation of carbonaceous species plays an important role during the synthesis, the carbonization of the catalysts is studied in the thermobalance and in the flow reactor. This as well as the formation of various carbon containing surface species is discussed in chapter 5.

Kinetic studies carried out with stabilized catalysts, are described in chapter 6. Kinetic models are proposed for all the three steps of the reaction: initiation, propagation and termination.

Finally in chapter 7 a mechanism for the Fischer-Tropsch synthesis based on the results obtained is given. The mechanism of the various steps is discussed in the light of the literature.

CHAPTER 2

Apparatus and Analysis

2.1. INTRODUCTION

When hydrogenation of carbon monoxide is investigated, several factors have to be taken into consideration.

i) The reaction is rather exothermic; the reaction enthalpy for methanation is 220 kJ mol^{-1} at 523 K and for the formation of the other hydrocarbons it is of the order of 140-185 kJ $(mol\ C)^{-1}$ /16/. In order to avoid overheating of the catalyst conversion must be kept low.

ii) Higher hydrocarbons may be formed during the operation. These can form a liquid layer on the catalyst surface which can hinder the diffusion of reactants and products to and from the surface.

iii) During the first few hours of an experiment deactivation of the catalyst occurs.

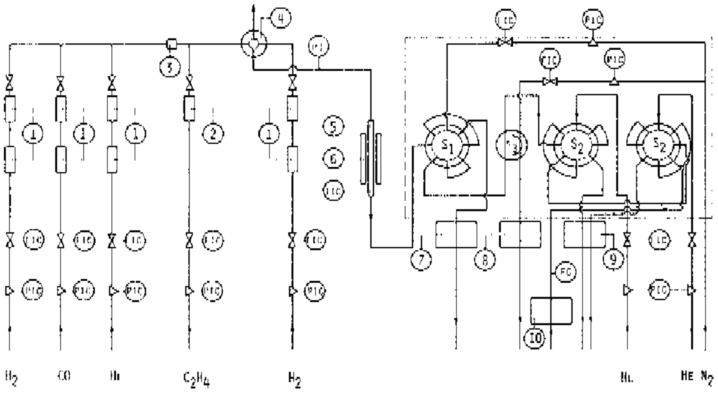
In order to maintain isothermal operation and to exclude mass transfer for interference we choose the reaction conditions in such a way that the CO conversion is below 3% and the rate of heat production remains below 0.1 W. During the kinetic experiments these are always fulfilled, and the partial pressures of the various hydrocarbons formed are always very much below the saturation pressure at the reaction conditions.

In order to cope with the deactivation the measurements are either carried out after a few hours when most of the deactivation has taken place already or with catalysts that only have a residual but constant activity.

2.2. THE REACTION SYSTEM

2.2.1. FLOW SCHEME AND REACTOR

The reactor system used for studying the reaction kinetics and the activity and selectivity of the catalysts is shown in figure 2.1.



1. COLUMNS FILLED WITH B.T.S. CATALYST AND MOLECULAR SIEVE
2. COLUMN FILLED WITH SILICAGEL
3. VAN DYKE MIXER
4. 4 - WAY VALVE
5. REACTOR TUBE
6. FURNACE
7. GLC 1 WITH F.I.D.
8. GLC 2 WITH F.I.D.
9. GLC 3 WITH KATHAROMETER
10. CO_2 MONITOR

S_1,S_2 8 - WAY BECKER GAS SAMPLING VALVES
S_3 4 - WAY DISC GAS SAMPLING VALVE

Figure 2.1. Reactor system

The gases, hydrogen (Hoekloos, purity > 99.9%) and carbon monoxide (Matheson, C.P., > 99.5%), and helium (Hoekloos, > 99.995%) are separately purified by passing them over a reduced copper catalyst (BASF R3-11 catalyst, B.T.S. catalyst) at 423 K and over a molecular sieve 5A (Union carbide) at room temperature. The reactor is made of glass with an inside diameter of 6 mm. The reactor is surrounded by an oven which is electrically heated. The temperature is regulated and controlled within 2 K by a Eurotherm thyristor controller and a chromel-alumel thermocouple.

From the product gas samples are taken either with 8-way valves or with a disc valve /70/ and analyzed by three gas chromatographs. Finally the product stream is led through a CO_2 monitor.

2.2.2. ANALYSIS

On the first gas chromatograph, a Pye series 104 FID gas chromatograph (GLC 1, figure 2.1) the analysis of hydrocarbons from C_4 to C_8 is achieved at 333 K with a squalane (5%) on chromosorb W-AW DMCS column of 2 m. In figure 2.2 a representative example of the separation with this column is given. On the second gas chromatograph - of the same type as the first one - C_1 to C_4 hydrocarbons are analyzed at 298 K with a combination of two columns: a 1.5 m phenylisocyanate on Poracil-C column and a 0.5 m n-octane on Poracil-C column. All columns are made of stainless steel, with an internal diameter of 2 mm. Figure 2.3 shows a typical chromatogram.

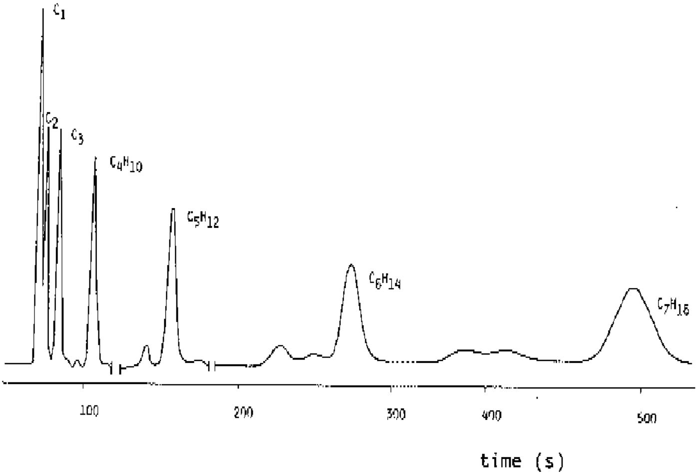


Figure 2.2. Chromatogram of product separation with a squalane column.

Nitrogen is used as carrier gas in both gas chromatographs. The quantitative determination of the concentrations of hydrocarbons is done by comparing the peak area of the compound with that of the propylene formed. This peak is calibrated by the peak area of propylene in the gas mixture of a precisely known composition. The calibration factors are calculated according to Kaiser /71/.

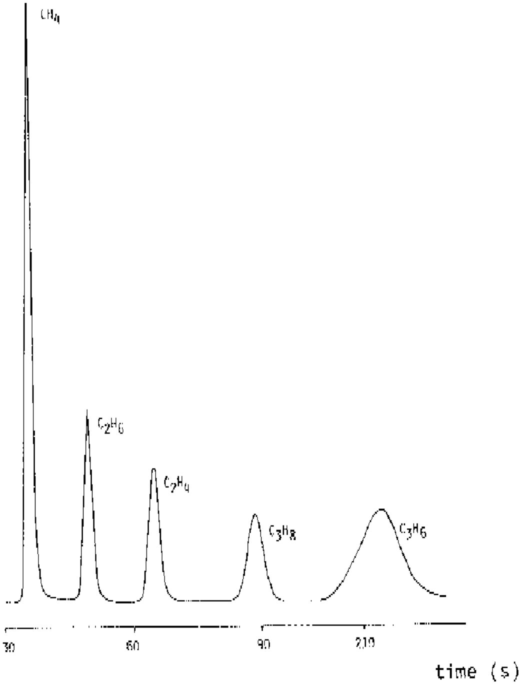


Figure 2.3. Chromatogram of product separation with a phenylisocyanate and a n-octane column.

Two parallel columns are used in the third gas chromatograph equipped with a katharometer detector. The samples are injected alternatingly to each column. One of the columns is a 2 m molecular sieve 5A column and is used to separate hydrogen and carbon monoxide. This column is activated by heating under the carrier gas at 520 K for 60 ks. The other column is a 3 m Porapak Q column made of glass, with an internal diameter of 2 mm and is used to separate carbon dioxide and water. Both columns are operated at 333 K, and helium is used as carrier gas.

The quantitative analyses of all gases are obtained by calibrating the analyzing system with gas mixtures of well known concentrations. Formation of carbon dioxide is often too small to be determined quantitatively by a katharometer. Therefore a CO_2 monitor (Unor CO_2

monitor, Maihak) is added after the gas chromatographs. This apparatus detects carbon dioxide by means of infra-red absorption. The detection limit is about 1 ppm.

2.2.3. CHARACTERIZATION OF THE FLOW REACTOR

If a flow reactor can be considered as an ideal plug flow reactor operating under isothermal conditions several simplifications can be made in the kinetic equations. According to Anderson /72/ axial diffusion can be neglected if the ratio of the catalyst bed length to the particle diameter exceeds 30-100 and the ratio of the catalyst bed diameter to the particle diameter exceeds 6-10. In our experiments these conditions are generally satisfied. According to the methods described by Satterfield and Sherwood /73/, Hougen /74/ and Yoshida et al. /75/ we find that the difference between the concentration in bulk gas phase (c_g) and on catalyst surface (c_s) is much smaller than the bulk gas phase concentration: $(c_g-c_s)/c_s$ is about 10^{-2}. The temperature difference between the gas phase and the catalyst surface is less than 0.1 K. These estimated values mean that no film diffusion or heat transfer limitations are expected. An extra support for this conclusion is found in section 6.4 where the apparent activation energies are calculated. The overall activation energy is of the order of 100 kJ mol^{-1}. Reactions with a film diffusion limitation usually have activation energies lower than 10 kJ mol^{-1}. The influence of pore diffusion i.e. the diffusion inside the catalyst particles is estimated by calculating the effectiveness factor η, for which we find $\eta \sim 0.99$ /73/.

2.3. THE THERMOBALANCE

The reduction experiments (chapter 3) and the carbonizations of the catalysts (chapter 5) are performed in a thermobalance, Dupont 950 thermogravimetric analyzer, with a Dupont 990 thermal analyzer regulation unit. The sensitivity of the system is about 2 μg absolute.

A schematic diagram of the balance with its flow system is shown in figure 2.4. The sample chamber is a Pyrex glass tube, 21 mm i.d., which is heated by an electric furnace. A glass envelope encloses the

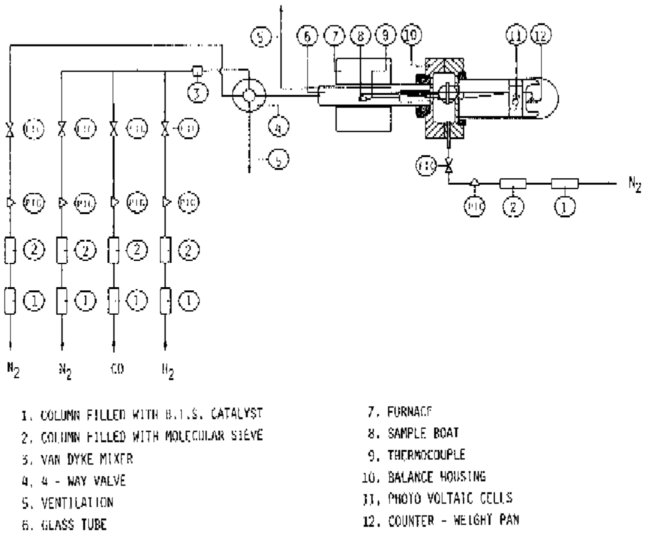


Figure 2.4. Thermobalance.

control end of the balance. This part is continuously purged with nitrogen (0.4 cm^3 s^{-1}). The temperature is regulated within 0.2 K and measured with a thermocouple (chromel-alumel), placed just above the sample boat. The sample boat is made of quartz glass and is suspended from the arm of the balance.

Carbon monoxide and nitrogen used as an inert diluent are purified separately by passing them over a reduced copper catalyst and a molecular sieve 5A as described in section 2.2.1. Hydrogen for the reduction experiments is dried by a liquid nitrogen cold trap. After mixing of the reactants the gas stream is admitted to the balance via a 4-way valve.

2.4. THE ADSORPTION APPARATUS

The hydrogen adsorption measurements are performed in an apparatus made of Pyrex glass and consisting of four parts: vacuum pumps, gas bulbs for storing the gases to be adsorbed, a system for measuring adsorbed amounts and a sample holder (see figure 2.5). Two vacuum

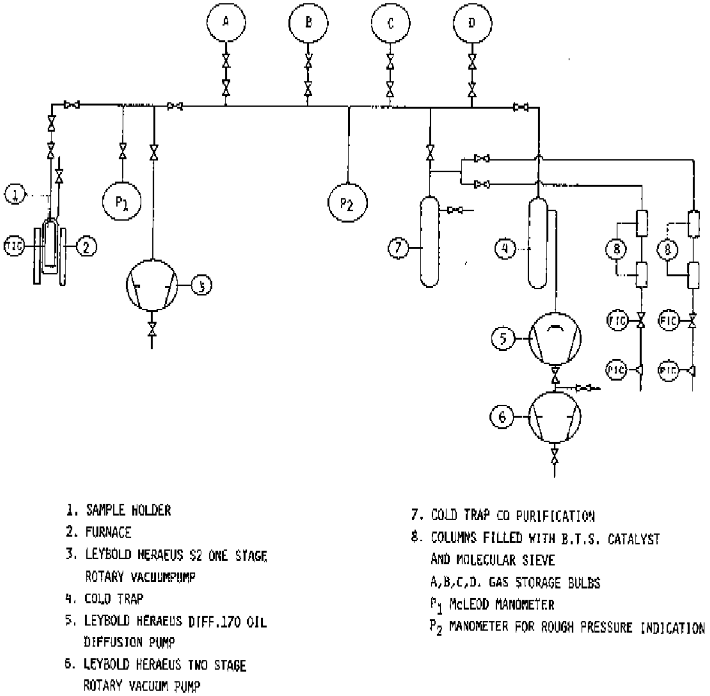


Figure 2.5. Adsorption apparatus.

pumps are used in series: a two-stage rotary pump and an oil diffusion pump (both Leybold-Heraeus) with which a pressure of 0.1 mPa is reached. The pressure in the system is measured by a McLeod manometer (P1). The maximum pressure which can be measured is 2.6 kPa.

A quantity of catalyst, about 2 g, is in the sample holder which can be heated by an electric oven. The temperature is measured by a chromel-alumel thermocouple which is placed in a canal in the middle of the sample holder.

2.5. DEFINITIONS

2.5.1. RATES

We use the following symbols for various rates:

C_i the rate of formation of hydrocarbons with i carbon atoms; mol $(\text{g cat s})^{-1}$

C_i^- the rate of formation of paraffins with i carbon atoms; mol $(\text{g cat s})^{-1}$

$C_i^=$ the rate of formation of olefins with i carbon atoms; mol $(\text{g cat s})^{-1}$

For the overall rate of hydrocarbon formation, r_T, we use two expressions:

1) $$r_{T,1} = \sum_i C_i = C_T \text{ mol } (\text{g cat s})^{-1} \qquad (2.1)$$

i.e. the rate is proportional to the number of molecules formed per unit of time.

2) $$r_{T,2} = \sum_i i\, C_i = \Delta\text{CO mol } (\text{g cat s})^{-1} \qquad (2.2)$$

i.e. the rate is proportional to the number of carbon monoxide molecules converted to hydrocarbons per unit of time.

Equation (2.1) is preferred if the rate determining step occurs only once per molecule e.g. only in the initiation step for each molecule formed. Equation (2.2) is preferred if the rate determining step occurs for each carbon atom included in the hydrocarbons produced. The overall rate can be used as a measure of the initiation activity as will be shown in chapter 4.

In comparing the activities of the supported and the unsupported catalyst the turnover frequencies (TOF) are used, i.e. the overall rate is calculated per active site on the catalyst. The amount of adsorbed hydrogen atoms at room temperature is taken as a measure for the number of active sites.

2.5.2. PRODUCT DISTRIBUTION AND SELECTIVITIES

The Fischer-Tropsch synthesis can be approximated by the following simplified scheme:

$$\begin{tikzcd}
CO + H_2 \arrow[r] & {[C_1^*]} \arrow[r, "r_{p,1}"] \arrow[d, "r_{t,1}"] & {[C_2^*]} \arrow[r, "r_{p,2}"] \arrow[d, "r_{t,2}"] & {[C_3^*]} \arrow[r, "r_{p,3}"] \arrow[d, "r_{t,3}"] & {} \\
 & C_1 & C_2 & C_3 &
\end{tikzcd} \tag{2.3}$$

The product distribution is often described by a Flory-Schulz distribution /76/, for which it is assumed that the probability of chain growth (α) and the probability of termination ($1-\alpha$) are the same for every growing step; i.e.

$$\alpha = \frac{r_{p,i}}{r_{p,i} + r_{t,i}} \tag{2.4}$$

$r_{p,i}$ = the rate of the chain growth of the surface complex with i carbon atoms

$r_{t,i}$ = the rate of the termination of the surface complex with i carbon atoms.

The weight of products containing i carbon atoms can then be expressed by the form

$$w_i = i w_o \, (1-\alpha)^2 \, \alpha^{i-1} \tag{2.5}$$

which can be transformed into

$$\log \frac{w_i}{i} = \log \left(w_o \frac{(1-\alpha)^2}{\alpha} \right) + i \log \alpha \tag{2.6}$$

where w_o is the weight of molecules formed.

The Flory-Schulz distribution in which the weight fraction m_i is given as a function of the number of carbon atoms is /76/

$$m_i = (\ln \alpha)^2 \, i \alpha^i \tag{2.7}$$

which, of course, is independent of the weight of molecules. Equation

(2.7) is often used to describe the product distribution of polymerization. Both equation (2.6) and (2.7) give the same linear relation between the logarithm of the weight fraction and the carbon number. We present our results according to equation (2.6): the logarithm of the weight of the products containing i carbon atoms divided by the number of carbon atoms (i) as a function of the number of carbon atoms. The lines obtained are called "Flory-lines". The probability of the chain growth is calculated from the slope of the line. The product distribution is sometimes also calculated according to equation (2.7) and the probability, α, is then calculated both from the slope and from the ordinate intercept.

For a more detailed characterization of the reaction product the following quantities are used:

i) The selectivity of olefins is defined as

$$C_i^{=}/C_i^{-}$$

i.e. the ratio of the rate of olefin formation to the rate of paraffin formation in a product fraction with i carbon atoms per molecule. This ratio is calculated for the C_2- and C_3-fractions. For these two fractions accurate analysis is possible, because only one olefin and one paraffin are formed.

ii) It is noticed that the formation of the C_2-fraction usually does not obey the Flory distribution. Therefore the ratio

$$C_2/C_3$$

i.e. the ratio of the rate of formation of the total C_2-fraction to the rate of formation of the C_3-fraction is calculated as well.

iii) The selectivity of methane, ϕ_1, is defined as follows:

$$\phi_1 = \frac{C_1}{\sum_i C_i}$$

i.e. the ratio of the rate of the methane formation to the overall hydrocarbon formation rate.