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The effect of diffusion on the gasification rate of wood-derived char particles

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Award date:
2003

Link to publication
The Effect of Diffusion on the Gasification Rate of Wood-Derived Char Particles

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June 5, 2003
Gasification is a technology that can be used to convert biological materials into combustible gases. In recent years, gasification of biomass has aroused new interest because it is one of the energy sources that can be employed to meet the criteria of the Kyoto protocol. In contrast to small scale applications, large scale applications in the industry require detailed knowledge about gasification process.

In the present study, a contribution is given to the research of biomass gasification. The aim is to investigate the effect of diffusion on the gasification rate of wood-derived char. In the investigation, a threefold strategy is applied:

1. Investigation of the material properties of the char, in particular porosity and pore size.

2. Development of a simple numerical model which takes into account diffusion of reactant gas into, and product gas out of a single char particle.

3. Measurements of the gasification of char, to observe whether the predictions of the numerical model are visible in the experimental results.

This work starts with the development the gasification model. For the reaction source term in the model, Langmuir-Hinselwood kinetics are applied. The Maxwell-Stefan law is used to describe diffusion. The dusty gas model was applied to calculate the diffusion coefficients for a large range of Knudsen numbers.

The modelling work indicates that the interplay of reaction and diffusion results in the existence of two gasification regimes. In the reaction controlled regime, the characteristic time of reaction is larger than that of diffusion. In the diffusion controlled regime, the opposite situation occurs. The magnitude of Second Damköhler Number, a dimensionless parameter related to the model equations, is found to be indicative for the regime type.

The model shows that the two gasification regimes can be discerned in an experiment. If in the experiment, the reaction rate is kept constant by choosing fixed partial pressures of carbon dioxide and carbon monoxide, the diffusion velocity can be altered by changing the partial pressure of nitrogen. A change of the diffusion velocity has a minor impact on the apparent gasification rate in the reaction controlled regime, whereas it has a large impact in the diffusion controlled regime.

For the investigation of the material properties, chars were prepared in an oven. The chars were made from the commercially available wood powder ‘Lignocel’. The desired pyrolysis temperatures were determined by means
of a TGA measurement. On the basis of the results, four series of chars were prepared in the temperature range from 700 K to 1000 K.

The porosity of the char was investigated by means of analyzing SEM pictures and by gas adsorption measurements. From the SEM pictures, it was concluded that the nerve structure of hard wood was no longer present in lignocel, due to grinding in the production process of the wood powder. Therefore, the natural structure of the wood cannot give rise to porosity. From CO₂ adsorption measurements it was concluded that the char is microporous. Micropores have a size smaller than 2 nm, which means that access to these pores of reactant gas is difficult. Therefore, it is expected that diffusion does not play a role in the gasification of the prepared char.

Some preliminary gasification experiments with the prepared series of char have been performed in a grid reactor. The apparent gasification was determined by using an infrared absorption technique, by which the time-resolved concentration of CO could be measured. The results of the measurements show the existence of two gasification regimes. The activation energy, obtained by a fit of the Arrhenius equation, indicates that at low temperature gasification is reaction controlled. The cause of the existence of a different regime at high temperatures is not clear yet. It is expected to be found in diffusion effects in the direct environment of the char, or in diffusion in the inter-particle space of the pile of char on the grid.
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Chapter 1

Introduction

1.1 Biomass, an Environment Friendly Energy Source

Gasification is a technology that can be used to convert biological materials (wood, peat, crops) into combustible gases. Like fossil fuels, these gases can be used by the industry as a source of energy. However, as opposed to biomass gases, the use of fossil fuels can bring damage to our environment. This damage is related to the problem of global warming, which arises due to increasing levels of carbon dioxide (and other so-called greenhouse gases) in our atmosphere due to combustion of large amounts of fossil fuels. The rising concentration of $CO_2$ disturbs the heat balance of the earth. While the same amount of radiative heat from the sun passes through the atmosphere to earth, less can be radiated back into space due to the absorption of radiation by increasing amount of $CO_2$ in the atmosphere. The increase of the average temperature of the earth can cause climate changes with severe consequences: disturbed biotopes, floods due to melting of ice on the poles and growth of deserts.

The first step made to tackle the problem of global warming was the establishment of the UN panel IPCC (Intergovernmental Panel on Climate Change) in 1988. In this committee, nations from all over the world discuss the measures necessary to get a grip on the exhaust of greenhouse gases. Shortly after the founding of the IPCC, the UN started a series of conferences on environment and development, of which the most important was held in Kyoto, Japan in 1997. During this conference, the Kyoto protocol was adopted. The protocol commits participating parties to individually, legal binding targets to limit or reduce their greenhouse gases exhaust. The target of the protocol is a total reduction of 5% with respect to the greenhouse gases exhaust in 1990. This reduction should be achieved in the period 2010-2012.

The individual countries have the responsibility to realize their target reduction percentages. For example, the Netherlands have to meet a reduc-
tion percentage of 6%. The Dutch government has taken up this task by measures among which are energy savings, subsidies to stimulate the production of green energy and convenants with energy suppliers. The target for the Netherlands is achievable, but more effort has to be made. [1].

On a national level, the government has has to start partnerships with companies to ensure that they bring products to the market that enable individuals to use green energy, as well as to increase the share of green energy in the total energy consumption of companies. Important partners in the latter type of partnerships are the electricity suppliers, because electricity has a large share in the national Dutch energy consumption. Furthermore, only technical adjustments to a limited number of plants are necessary.

In 2001 2.8% of the electricity produced in the Netherlands was 'green' electricity. Approximately one third of the green electricity was produced by using biomass [2]. The use of biomass is based on the fact that it doesn't affect the net carbon concentration in the atmosphere. Biomass consists of (parts of) plants. During their growth, the plants absorb carbon-dioxide from the atmosphere. When the biomass is combusted, the carbon-dioxide is released again. The net CO₂ production is then zero. In case fossil fuels are used, carbon that has since long been out of the carbon cycle will be brought into the environment. This will disturb the equilibrium of the carbon cycle, resulting in a growing concentration of CO₂ in the atmosphere.

Although the use of biomass is quite successful, the urgency of large scale application has created a need for more knowledge to overcome barriers to its use. The main limitation is the availability of proper materials. As now is generally the case in the Netherlands, the biomass is co-combusted with coals in an electricity plant. The biomass thus has to be rather clean, because otherwise the product gases would contaminate the atmosphere. However, if the biomass is converted into combustible gases first, this condition has not to be fulfilled. The combustible gases can be cleaned before they are added to the furnace in which coals are combusted. This greatly increases the availability of suitable biomass, because now e.g. waste wood can be used.

The reason that the supply gas coming from a gasifier can be cleaned more efficiently than exhaust gases of the coal furnace, lies in the the lower volumetric flow rates of the supply gas. This means that the concentration of pollutants in the supply gas are much higher. A second advantage of gasification is that the fly-ash, a by-product of an electricity plant, doesn't suffer from quality deterioration by contamination with the ashes of the wood.[3]

Thus, gasification offers the possibility to the government to boost the share of green energy in the total energy consumption. At the same time it gives the industry, in particular the electricity plants, the opportunity to integrate the demands of society in a suitable way into their existing production processes.
1.2 Principle of Biomass Gasification

To successfully apply biomass gasification as a source of energy, the process of gasification has to be mastered. The heart of a gasification plant is the gasification reactor. An example of such a reactor is the countercurrent gasifier (figure 1.1). In this gasifier, the feedstock enters at the top, while air comes in at the bottom. The product gases leave the reactor at the top side. Because feedstock and gases move in an opposite direction through the gasifier, it is said to be of the counter-current type.

The reactor is kept at an elevated temperature, typically 1000 K. When the biomass enters the reactor, it heats up. Moist, present in the biomass, evaporates. The environment in the reactor becomes humid.

After drying, the biomass is pyrolyzed. During pyrolysis, it is heated in a nearly oxygen-free environment. The feedstock consists mainly of organic compounds. Apart from some functional groups, the organic compounds in turn consist mainly of carbon and hydrogen atoms. When these organic compounds are heated in the oxygen free environment, hydrogen-rich gases and tars originate from the particle. Consequently, a carbon-rich material, the char, is left. Both drying and pyrolysis take place in the upper part of the reactor.

Then, the char enters the gasification zone. Here, the carbon in the char reacts with the carbon dioxide present in the reactor to form the main product gas, carbon monoxide:

\[
C + CO_2 \rightarrow 2CO
\]  

In addition other gases are formed in due to the presence of water vapor.
The water reacts with the carbon to form small concentrations of a number of organic gasses, among which is $H_2$.

In the oxidation zone, part of the char is combusted. The combustion generates the heat necessary for gasification, as this is an endothermic process. During combustion, $CO_2$ is formed,

$$2C + O_2 \rightarrow 2CO_2, \quad (1.2)$$

which is necessary for the gasification process in the previous zone.

Not all gases leaving the reactor are combustible. The inlet of air means that apart from oxygen and small amounts of other gasses, nitrogen enters the reactor. This gas is chemically inert, i.e. it does not participate in any reaction. The high concentration of incombustible nitrogen lowers the heat of combustion of the outlet gas. In the literature, this is indicated by the term 'low Joule gas'. This property of the gas has to be taken into account for application of the gasifier.

The counter-current gasifier is only one of the multiple types of gasifiers that exist [4]. One of the alternative types is the co-current gasifier (figure 1.2). In this reactor, both the feedstock and the gases move downwards. Each reactor type has its own advantages. Among the criteria which should be taken into account when choosing for a certain type, are the outlet temperature of the gas, the flexibility in the type and size of the feedstock and the complexity of the design. One of the most important criteria is the tar content of the product gas. The tars are vapors, which means that when the outlet gas cools down they will condense. A sticky, condensed tar layer on parts of for example an engine combusting the product gas, can cause damage or breakdown.

To choose a suitable type of reactor, to adjust the design of the reactor for specific needs and to enable continuous control of operation requires detailed
knowledge of gasification. Especially tar formation and optimization of the efficiency of the reactor are very important.

1.3 Scientific Background

The need for more knowledge about gasification asks for answers on scientific questions of a different nature. First, there are phenomena related to the chemistry. An example of the complex chemistry is pyrolysis, during which a great number of reactions occur at the same time. Also, the gasification of the char involves several reaction mechanisms. Reactions can be enhanced by the presence of minerals in the char, which act as a catalyst. The type of chemical reactions that occur determine the composition of the outlet gas and the amount of tar formation.

The chemical reactions are affected by the temperature and the concentrations of the species in the gasification environment. As some types of feedstock, for example wood, has a porous structure, the reaction involves diffusion of reactant and product gas in and out of the particle. In general, the biomass particles do not heat up instantaneously, which means that the transport of heat in the particle is another important process. Both heat transport and diffusion are examples of problems related to the second important field, namely physical transport phenomena.

The temperature and concentrations of species are not homogenous in the reactor space, but are local quantities. Therefore physical transport phenomena do not only play a role on the scale of single particles, but also on the scale of the entire reactor. This explains the strong dependence of temperature and tar contents of reactor characteristics, as mentioned in the previous section.

The complexity of gasification does not mean that the process is too difficult to apply without vast knowledge. In fact, the first applications of gasification already took place in the beginning of the nineteenth century. The first gasification company started in London in 1812 and produced gas for lighting by dry distillation of coal. (Dry distillation is gasification by heating of the feedstock in an oxygen-free atmosphere, i.e. only pyrolysis). The technique of gasification of coal applied here is relevant to to biomass gasification, because both show great similarities. During the second world war, small gasifiers for wood and peat were constructed for car and lorry traction due to the shortage of liquid hydrocarbons in continental Europe. The small-scale applications of gasification in the past resulted in some empirical knowledge about reactor design.

After the second world war, oil and natural gas took over the previously dominant position of coal, thus reducing the importance of gas production. Gasification started to be considered as a technology suitable for small scale application in developing countries. Biomass was no longer considered as
an energy source for the industry. The energy crisis in 1973 [4, 5] and the Kyoto protocol radically changed this.

Groeneveld [4] pointed out in 1983 that there is the lack of knowledge about gasification. He noted that that basically only some empirical design rules were available. Such rules pertain to for example the design of devices to introduce air into the reactor and the geometry and dimensions of the reactor close to the air inlet.

The findings of Groeneveld were generally recognized by colleague scientists. This is illustrated by one of the conclusions originating from the 1st European Workshop on Thermochemical Processing of Biomass in 1983 [5], which states that although some mathematical models for small (up to 50 kg/h) reactors have been made, most units are still designed empirically.

An extensive review of the progress in the gasification of biomass issued in 2001 mentions only the availability of some very simple models made by Göbel [6] and Struis [7]. The gasifier at the Amercentrale electricity plant (Geertruidenberg, the Netherlands), which is said to be one of the largest in the world, is has been designed on the basis of a simple thermodynamic model. Thermodynamics is in fact not the suitable approach to describe the non-equilibrium processes in the reactor. It can be concluded that the need for modelling in both science and technology is still existent.

The research of Groeneveld gave a start to overcome the need for more modelling experience. His model for a gasifier based on the gasification of a single wood particle, having a size in the range of 2.5 — 25mm. The wood particle is porous, with pore diameters in the order of 50μm. By including both diffusion and local volumetric reactions, he obtained results for pyrolysis and gasification for the particle. Then, he incorporated the single particle model into the model for entire reactors, the largest of which had a height of 1.2m and a diameter of 0.7m. He concluded that his model could explain profiles of char conversion, temperature and gas composition. Simplified models, based on a shrinking core or a homogeneous reaction in the particles could not predict this.

The work of Groeneveld has to be proceeded to make gasification more suitable for sophisticated applications. More modelling work is required for a better fundamental understanding of the reaction mechanism in a gasifier.

1.4 Scope of the Present Work and Outline

The work presented here is part of a research program that meets the need for a better understanding of gasification. The focus of this work lies in the gasification step. As the steps in the overall gasification have mutual influence (for example, the water vapor resulting from drying influences the species produced in pyrolysis), investigation of this step is simplified by separating in physically of the other steps, i.e. drying, pyrolysis and
combustion. This is performed by preparing char from wood particles in a separate oven, under well specified conditions.

The kinetics of gasification is the main interest here. To observe pure kinetics, the char particles should have a uniform temperature at the surface where the reaction occurs. In addition, mass transport towards and outwards of the surface should play no limiting role for the reaction rate. In this case true kinetic parameters, only dependent on the temperature of the wood, can be measured. To exclude the effect of heat transport, the char particles considered are very small (in the order of micrometers).

To simplify further, the gasification environment is chosen to exist only of the chemically inert nitrogen and carbon dioxide. No water vapor is present. Together with the product gas, carbon monoxide, the gasification environment thus consists only of three gases.

The main goal of the experiments is to determine under what circumstances (char properties, temperature, pressure) diffusion of product gas into and reactant gas out of a char particle affects the reaction rate. The effect of diffusion on the gasification rate is investigated by a threefold strategy:

- Investigating the material properties of the char, in particular its porosity and pore size. A high porosity and large pore size indicate the presence of a large internal surface that can easily be reached by the reactant gases.

- Construction of a simple numerical model for the gasification reaction. The model takes into account diffusion of reactant gas into, and product gas out of a single char particle.

- Measurements of the gasification of char, to observe whether effects predicted by the numerical model are visible in the experimental results.

This report will start with the discussion of the simple numerical model for the gasification (chapter 1). The results of the model for a variation of parameters (pressure, temperature, porosity and pore size) will help to interpret the gasification experiments (chapter 2). The first part of the experiments mainly consists of preparation and characterization of the char (chapter 3). The characterization is performed by TGA-measurements and gas adsorption measurements. Then, the setup and the scheme for gasification experiments in a grid reactor are discussed (chapter 4). This will be followed by the results of the grid reactor experiments (chapter 5). Finally, the conclusions and recommendations are listed (chapter 6).
Chapter 2

A Simple Gasification Model

2.1 Introduction

In this chapter, the theory of a simple gasification model is discussed. With the aid of the model, the gasification of porous char particles can be understood. The gasification process is governed by two phenomena. First, there is the gasification reaction on the internal surface of the particle. Secondly, there is diffusion of reactant and product gases in and out of the particles. The interaction of these phenomena plays an important role in gasification experiments discussed later in this report. Therefore, the model is helpful to interpret these results.

2.2 Chemistry: Langmuir-Hinselwood Kinetics

The chemistry in the model consists of the gasification reaction. During gasification, solid carbon in the char reacts with carbon dioxide in the environment to form carbon monoxide,

$$CO_2(g) + C(s) \rightarrow 2CO(g).$$  \hfill (2.1)

Experimental work in the past [8] shows that an increased level of CO in the gasification environment can inhibit this reaction. The inhibition effect can be described with an empirically obtained formula for the surface reaction rate,

$$R_s = \frac{k_1 p_1}{1 + k_2 p_2 + k_3 p_1},$$ \hfill (2.2)

in which the $k$'s are fit parameters and $p_1$ and $p_2$ are the partial pressures of $CO_2$ and $CO$, respectively. An increase of $p_2$ results in a decrease of $R_s$.

For $T = 1500 K$, values from the literature [8] can be used to calculate the $k$'s. Substituting these values and dividing by $p_1$ results in

$$R_s = \frac{3 \cdot 10^{-7}}{p_1 + 5.0 \cdot 10^{-5} p_2 + 2.87 \cdot 10^{-5}}.$$ \hfill (2.3)
Here, the pressure is in \( \text{Pa} \) and the surface reaction rate in \( \text{mol} \cdot \text{m}^{-2} \text{s}^{-1} \). Using this expression, the limiting behavior of \( R_s \) can be investigated. In case \( p_1 = 1 \cdot 10^5 \text{Pa} \) and \( p_2 << p_1 \), the first two terms in the denominator of equation 2.3 can be neglected with respect to the third term. The reaction rate becomes independent of the partial pressures of carbon dioxide and monoxide. In case \( p_1 = 1 \cdot 10^5 \text{Pa} \) and \( p_2 >> p_1 \), the first and the last term in the denominator can be neglected with respect to the first term. Now, the rate is proportional to \( \frac{k_1}{p_2} \).

The first case reflects that an excess of carbon dioxide is present. A further increase of \( p_1 \) does not result in a higher reaction rate. The second case illustrates the inhibition effect. An increase of \( p_2 \) results in a decrease of the reaction rate.

The behavior of the gasification rate suggests that reaction 2.1 has to be replaced by a more sophisticated reaction mechanism. A possible candidate is the Langmuir-Hinselwood mechanism, expressed by

\[
\begin{align*}
C(\cdot) + \text{CO}_2 & \underset{i_1}{\overset{i_2}{\rightleftharpoons}} \text{C(O)} + \text{CO}, \\
\text{C(O)} & \rightleftharpoons \text{CO}.
\end{align*}
\]

Here, the \( i \)'s and \( j \)'s are the rate constants of the reactions. \( C(\cdot) \) represents an active site, related to a carbon atom \( C \) on the surface of the char. Active sites are locations at which there is an increased probability for the reaction to take place.

The Langmuir-Hinselwood kinetics indicate that the following process takes place during reaction. First, a carbon dioxide molecule impinges on the active site and dissociates (reaction 2.4). One of the oxygen atoms of the molecule is adsorbed at the surface and forms a chemical bond with a solid carbon atom at the active site. This is termed a 'complex'. The other oxygen atom returns with the carbon atom as a carbon monoxide molecule to the gas phase. There are two possibilities for the complex to continue. The reverse of reaction \( \text{LH1} \) can take place. In this case a carbon monoxide molecule reacts with an adsorbed oxygen atom to form a gaseous \( \text{CO}_2 \) molecule, leaving behind an empty active site. Instead, the oxygen atom at the active site can also leave the surface together with a solid carbon atom to form a gaseous \( \text{CO} \) molecule (reaction 2.5). The latter reaction is the actual gasification step.

The Langmuir-Hinselwood kinetics explain the inhibition effect of carbon monoxide by a change in the equilibrium of reactions 2.4. A higher concentration of carbon monoxide near the surface will cause an increased rate in the backward reaction. The surface density of complexes, or occupied active sites decreases. This decrease leads to less production of carbon monoxide by reaction 2.5.

From the reaction mechanism it can be deduced that the number of active sites per unit surface area is an important factor for the gasification.
Figure 2.1: Sketch of the surface of a char particle. The carbon monoxide molecule (white particle) at location 1 interacts with three neighboring carbon atoms (gray particle) in the surface. The particle at location 2 interacts only with two carbon atoms.

rate. Therefore, it is worthwhile to discuss in some more detail the nature of these sites.

The active sites are places with an increased surface potential. This potential is caused by the interaction of the gas molecules, in this case CO, with molecules in the surface of the solid, the char. The potential is stronger where an impinging gas molecule interacts with more molecules of a solid 2.1. This can be caused by irregularities (dislocations) at the surface of the solid. If the molecule impinges at such an irregularity, it interacts with more molecules on the surface then in case of a regular surface. The strong interaction with the surface potential can cause breaking of the chemical bonds, which is exactly what happens when a carbon dioxide molecule dissociates in the kinetics considered here. The number of dislocations in the surface depends on the crystallinity of the char and the presence of impurities. A second factor is the presence of other species in the surface. These may have a much stronger interaction with the gas molecules, which means an increase in potential.

To obtain a rate expression from the Langmuir-Hinselwood Mechanism, we consider the configuration depicted in figure 2.2. Here, a small volume $V$ which includes part of the surface $A$ of a char particle is shown. We indicate the density of active sites on the surface as $N_1 \text{ (m}^{-2} \text{)}$. With $\theta$, we will indicate the fraction of sites on which an oxygen atom is absorbed. The concentrations of $CO_2$ and $CO$ in the volume are termed $c_1$ and $c_2$, respectively. It is assumed that these concentrations are uniform in the volume, i.e. the dimension of the box perpendicular to the wall is small enough for diffusion effects to be neglected. From the environment, $CO_2$ can
flow into the volume, in the negative direction with respect to the normal $\vec{n}$. CO can flow out of the box, in the opposite direction. The fluxes of the two species are indicated with $\phi_1$ and $\phi_2$.

Keeping in mind the configuration of figure 2.2, the change in time of the concentration of carbon monoxide in the volume can be expressed as

$$V \frac{d\text{CO}_2}{dt} = i_1c_1(1-\theta)N_tA - j_1c_2\theta N_tA + i_2\theta N_tA - \phi_2A.$$  

Here, the terms $A$, $B$ and $C$ are related to reactions 2.4 and 2.5. Term $A$ is originating from the forward reaction $i_1$. It states that due to this reaction, the concentration of carbon monoxide in the volume increases in time. The increase is proportional to the rate constant, the concentration of $CO_2$, the fraction of free active sites $(1-\theta)$, the number of active sites and the surface area considered. Term $B$ and $C$ are originating from the backward reaction $j_1$ and reaction $i_2$. Term $D$ represents the change in the concentration of CO due to a flux of $CO_2$ from the exterior into or out of the considered volume.

Equations similar to equation 2.6 can be written down for the concentration of carbon dioxide and for the number of occupied active sites. The latter equation reads

$$AN_t \frac{d\theta}{dt} = +i_1c_1(1-\theta)N_tA - j_1c_2\theta N_tA - i_2\theta N_tA.$$  

The steady state assumption that was made for the present model is now
used to express the rate of CO-production by the char. In a steady state, the derivatives with respect to the time in equations 2.6 and 2.7 are zero. This means that equation 2.7 can be solved for the equilibrium value of $\theta$:

$$\theta_e = \frac{i_1 c_1}{i_1 c_1 + j_1 c_2 + i_2}$$

(2.8)

From equation 2.6, an expression for $\phi_2$ can be obtained,

$$\phi_2 = i_1 c_1 (1 - \theta_e) N_t - j_1 c_2 \theta_e N_t + i_2 \theta_e N_t.$$ 

(2.9)

Substituting $\theta_e$ yields

$$\phi_2 = 2i_2 \frac{n_i S i_1 c_1}{i_1 c_1 + j_1 c_2 + i_2}$$

(2.10)

Keeping in mind that $p_i = c_i RT$, this can be written as

$$\phi_2 = 2i_2 \frac{i_1^2 P_1}{i_1^2 P_1 + j_1^2 P_2 + i_2},$$

(2.11)

where $i_1' = \frac{i_1}{RT}$. A similar relation holds for $j_1'$. In terms of molar fractions $x_i = \frac{p_i}{p}$, this relation becomes

$$\phi_2 = 2i_2 \frac{i_1' x_1}{i_1' x_1 + j_1' x_2 + \frac{i_2}{p}}.$$ 

(2.12)

In a steady state, $\phi_2$ is the production rate of carbon monoxide per unit surface area. Moreover, under steady state conditions, this is equal to $2\phi_1$, the consumption rate of carbon dioxide. The surface reaction rate is defined as $\frac{1}{2} \phi_1$. Leaving out the primes (but keeping in mind the difference in units of the rate constants), it becomes.

$$R_s = i_2 \frac{i_1 x_1}{i_1 x_1 + j_1 x_2 + \frac{i_2}{p}},$$

(2.13)

where the factor $\frac{1}{2}$ results from the stoichiometric constant of the over-all reaction.

The fraction of active sites is determined by the equilibrium of the three reactions. To investigate how the position of the equilibrium depends on the rate constants and the partial pressures, the magnitude of the terms in the denominator of equation 2.13 is important. The rate constants of this equation are given by the Arhenius expression. For $i_1$, this expression is

$$i_1 = i_{10} e^{-\frac{E_a}{RT}},$$

(2.14)

where $i_{10}$ is the frequency factor and $E_a$ the activation energy. For $j_1$ and $i_2$ similar relations hold. Values for the frequency factors and activation energies are given in appendix B.
Figure 2.3: The ratios $\frac{i_1}{i_2 p_1}$ and $\frac{j_1}{j_2 p_2}$ as a function of temperature

The data for the rate constants enables closer investigation of formula 2.13. Choosing the partial pressures $p_1$ and $p_2$ equal to $1 \cdot 10^5 \text{Pa}$, figure 2.2 can be made. In the low temperature limit, reaction $j_1$ is the fastest. The rate becomes

$$R_g \sim i_2 \frac{i_1 x_1}{j_1 x_2}.$$  \hspace{1cm} (2.15)

Because $j_1 x_2 >> i_1 x_1$, the reaction rate is rather small in this limit.

In the high temperature limit, reaction $i_2$ determines the rate. The rate expression becomes

$$R_g \sim i_2 x_1.$$  \hspace{1cm} (2.16)

which is much larger than in the low temperature limit.

In between these two limiting cases, there are more complex equilibrium positions, dependent of temperature and pressure.

The Langmuir-Hinselwood mechanism is not the only mechanism that fits to the empirical expression. Another possible reaction mechanism is [9]

$$C(\cdot) + CO_2 \rightarrow C(O) + CO,$$  \hspace{1cm} (2.17)

$$C(O) \rightarrow CO,$$  \hspace{1cm} (2.18)

$$C(\cdot) + CO \leftrightarrow C(CO).$$  \hspace{1cm} (2.19)

The inhibition of gasification by CO is here caused by the last reaction. The carbon monoxide in the gas phase and the adsorbed carbon monoxide form an equilibrium. The adsorbed carbon monoxide reduces the amount of free active sites, thus reducing the reaction rate.
Up to now there is no agreement on which of these reaction mechanisms is occurring in practice. As literature data was available for the Langmuir Hinselwood kinetics and this reaction mechanism fits well to the experimental data [8], it was chosen for the present modelling work.

2.3 The Diffusion Coefficient

In the gasification model, the Stefan-Maxwell equations, equations in the form

$$\nabla x_i = \sum_{j \neq i} \frac{x_i \bar{N}_j - x_j \bar{N}_i}{cD_{ij}},$$

are used to calculate the fluxes $\bar{N}_i$ and molar fractions $x_i$ of the species $i$ in a mixture a porous medium. To be able to employ the Stefan-Maxwell formula, the diffusion coefficients $D_{ij}$ have to be known. This section deals with the calculation of these coefficients for a porous medium.

Diffusion occurs because a system is not in equilibrium. This can be due to for example a concentration gradient. Due to the gradient, there is a net force on the diffusing molecules. On the other hand, there is a balancing force due to friction in the system. Friction is related to the transport of momentum from one species to other species in the gas mixture or to the wall. The way in which the species transport momentum determines the type of diffusion:

- **Knudsen Diffusion**
  Due to a low molar density and very narrow channels in a porous medium, the main momentum loss of molecules in a mixture is directly to the wall.

- **Bulk Diffusion**
  At high concentrations and wide pores, molecules of one component in the mixture lose their momentum mainly to other components in the mixture.

- **Viscous flow**
  The molecules of one species lose momentum to the wall via a sequence of molecule-molecule collisions, terminating in a molecule wall collision. Here, we have indirect momentum loss to the wall.

In our case, we assume that no pressure gradients exist in the medium, which makes it possible to neglect viscous flow. In contrast, the other two diffusion types need to be taken into account. We will use the Knudsen number to estimate which of these mechanisms is dominant:

$$Kn = \frac{\lambda_{ij}}{d_p}.$$
Here, $\lambda$ is the mean free path of the molecules of species $i$ with respect to molecules of species $j$ and $d_p$ is the diameter of a pore. An expression for the mean free path is given by [10]:

$$
\lambda_{ij} = \frac{2}{\pi(d_i + d_j)^2 n_j} \sqrt{\frac{M_i M_j}{M_i + M_j}}
$$

Here, $n_j$ is the molecular density ($m^{-3}$) of species $j$, $d_j$ the molecular diameter and $M_j$ the molecular mass.

The Knudsen number can be used to distinguish the following three cases:

- **$Kn \gg 1$**
  The mean free path is much larger than the diameter of the pore. Molecules will collide much more often with the wall than with other molecules. Knudsen diffusion is the main diffusion mechanism.

- **$Kn \sim O(1)$**
  The mean free path is of the order of the pore size. The momentum transfer of one species to the other and to the wall are of the same magnitude. Both Knudsen diffusion and bulk diffusion play an important role.

- **$Kn \ll 1$**
  The mean free path is much smaller than the diameter of the pore. Molecules will collide much more often with other molecules than with the wall. Knudsen diffusion is the main diffusion mechanism.

For the first and the third case a mathematical description is available. In case of Knudsen diffusion the diffusion law is given by

$$
\dot{N}_i = -cD_i^e \nabla x_i.
$$

Here, $D_i^e$ is the effective Knudsen diffusion coefficient. Effective coefficients are used to include the effect of the medium. They are related to the ordinary diffusion coefficients by

$$
D_i^e = \frac{\epsilon}{\tau} D_i.
$$

Here, $\epsilon$ is the porosity of the medium. It represents the decrease of the volume available for the flow due to the presence of the medium. This results in a decrease of fluxes compared to the situation in which a medium

---

1In this law, the sum of the fluxes is in general not zero. This is caused by the fact that gases in the pore do not interact. This means that diffusion of two gases in a narrow pore can be regarded as two times a Knudsen flow. Each of the gases has its own diffusion coefficient that determines the magnitude of its flux. As these diffusion coefficients are in general not equal, the sum of the fluxes does not cancel.
is absent. $\tau$ is the tortuosity, which is a measure for the average orientation of the pores. In this way it can be taken into account that diffusion through a medium having a random orientation of the pores is more difficult than in case it has parallel, straight pores.

For a cylindrical pore of radius $r_p$ the Knudsen diffusion coefficient is given by [11]

$$D_i = \frac{2}{3} v_{th,i} r_p.$$  \hspace{1cm} (2.25)

The quantity $v_{th,i}$ is the average thermal velocity of the gas species $i$:

$$v_{th,i} = \sqrt{\frac{8RT}{\pi M_i}}$$  \hspace{1cm} (2.26)

Here, $R$ is the universal gas constant, $T$ the gas temperature and $M_i$ the molar mass of the species $i$.

In the third case, bulk diffusion, the diffusion law is the Stefan-Maxwell equation (eqn. 2.20). The binary diffusion coefficients $D_{ij}$ can be expressed as [12]

$$D_{ij} = \frac{1}{3} v_{th,i} \lambda_{ij}$$  \hspace{1cm} (2.27)

An equation which is commonly used to calculate binary diffusion coefficients is the Fuller expression, [13]

$$D_{ij} = C_F \frac{T_i^2}{p(V_{F,i}^{1/3} + V_{F,j}^{1/3})} \sqrt{\frac{M_i + M_j}{M_i M_j}},$$  \hspace{1cm} (2.28)

in which $C_F = 3,16 \cdot 10^{-8}$. Here, $V_{F,i}$ (in moles/m$^3$) is the diffusion volume of species $i$, $p$ (in Pa) the total pressure and $T$ (in K) the temperature. In case of a porous medium, also the bulk diffusion coefficients have to be effective coefficients. In the Stefan-Maxwell equations, instead of $D_{ij}$ we write

$$D^e_{ij} = \frac{\epsilon}{\tau} D_{ij}.$$  \hspace{1cm} (2.29)

In the second case, corresponding to $Kn \sim O(1)$ no simple and rigorous mathematical description is available. For this case, the two diffusion mechanisms can be combined by using the dusty gas model. This model is based on the analogy between a porous structure and a gas containing dust particles. The dust particles are assumed to be homogeneously spread through the gas. Furthermore, they are limited in number and have a very big mass which prevents them from moving in the gas mixture. By increasing the concentration of dust particles, the momentum exchange between the gas and the dust increases. In reality, this corresponds to an increase in the momentum exchange between the gas and the porous structure due to narrower pores. In other words, Knudsen diffusion becomes more important.
with respect to bulk diffusion. If we decrease the concentration of dust, the reverse occurs. Thus, by changing the dust concentration, we can describe the intermediate case between Knudsen diffusion and bulk diffusion.

To obtain a useful formula from this model, we employ the Stefan-Maxwell equation for the dusty gas. Then we will try to include the effect of the dust into the diffusion coefficient. For the calculation of the new diffusion coefficient \( \Gamma_{12} \) we will assume that we have only two gas species (1 and 2) in our gas. The dust is the third species (3). We now can write the Stefan-Maxwell equations for the two gas species,

\[
\nabla x_1 = \frac{x_1 \tilde{N}_2 - x_2 \tilde{N}_1}{cD_{12}^*} + \frac{x_1 \tilde{N}_{\text{dust}} - x_{\text{dust}} \tilde{N}_1}{cD_{13}^*},
\]

\[
\nabla x_2 = \frac{x_2 \tilde{N}_1 - x_1 \tilde{N}_2}{cD_{21}^*} + \frac{x_2 \tilde{N}_{\text{dust}} - x_{\text{dust}} \tilde{N}_2}{cD_{23}^*}.
\]

The fact that the dust particles are assumed not to move results in \( \tilde{N}_{\text{dust}} = 0 \). The diffusion coefficients related to the dust now become

\[
D_{i,dust}^* = \frac{D_{ij}^*}{x_{\text{dust}}}.
\]

Substituting this in the equations 2.30 and 2.31 results in

\[
\nabla x_1 = \frac{x_1 \tilde{N}_2 - x_2 \tilde{N}_1}{cD_{12}^*} - \frac{\tilde{N}_1}{cD_{1,dust}^*},
\]

\[
\nabla x_2 = \frac{x_2 \tilde{N}_1 - x_1 \tilde{N}_2}{cD_{21}^*} - \frac{\tilde{N}_2}{cD_{2,dust}^*}.
\]

A second assumption is that the dust particles have a very low molar fraction: \( x_{\text{dust}} \sim 0 \). Then, the molar fractions of the gas species are related by

\[
x_1 + x_2 \approx 1,
\]

and the gradients of the molar fractions by

\[
\nabla x_1 + \nabla x_2 = 0.
\]

If we add equations 2.33 and 2.34 we obtain

\[
\frac{\tilde{N}_1}{\tilde{N}_2} = - \frac{D_{1,dust}^*}{D_{2,dust}^*}.
\]

Now the right-hand side of equation 2.33 can be cast in a similar form as the right-hand side of equation 2.20, defining new diffusion coefficients \( \Delta_{12} \) which include both bulk diffusion and the effect of the dust:

\[
\frac{x_1 \tilde{N}_2 - x_2 \tilde{N}_1}{c\Delta_{12}} \equiv \frac{x_1 \tilde{N}_2 - x_2 \tilde{N}_1}{cD_{12}^*} - \frac{\tilde{N}_1}{cD_{1,dust}^*}.
\]
Dividing both sides by \((x_1 \tilde{N}_2 - x_2 \tilde{N}_1)/c\) yields:

\[
\frac{1}{\Delta_{12}} = \frac{1}{x_1 \tilde{N}_2 - x_2 \tilde{N}_1} \left\{ \frac{x_1 \tilde{N}_2 - x_2 \tilde{N}_1}{D_{12}^{*}} - \frac{\tilde{N}_1}{D_{1,dust}^{*}} \right\}. \tag{2.39}
\]

Rewriting gives:

\[
\frac{1}{\Delta_{ij}} = \frac{1}{x_1 - x_2 \frac{\tilde{N}_1}{\tilde{N}_2}} \left\{ \frac{x_1 - x_2 \frac{\tilde{N}_1}{\tilde{N}_2}}{D_{12}^{*}} - \frac{\tilde{N}_1}{D_{1,dust}^{*}} \right\}. \tag{2.40}
\]

Substituting equation 2.37 and rearranging results in:

\[
\frac{1}{\Delta_{12}} = \frac{1}{D_{12}^{*}} + \frac{1}{D_{1,dust}^{*} D_{2,dust}^{*}} \left( \frac{x_1}{D_{1,dust}^{*}} + \frac{x_2}{D_{2,dust}^{*}} \right). \tag{2.41}
\]

Now, if we let the dust molar fraction \(x_{dust}\) increase, the diffusion coefficients \(D_{1,dust}\) will decrease. The consequence of the decrease of \(D_{1,dust}\) is that the the second term in the right-hand side of equation 2.41 becomes dominant, resulting in

\[
\Delta_{ij} = x_2 D_{1,dust}^{*} + x_1 D_{2,dust}^{*}. \tag{2.42}
\]

The diffusion coefficient in this case should be equal to the Knudsen diffusion coefficient. If we choose

\[
D_{1,dust}^{*} = D_{1}^{*}, \tag{2.43}
\]

\[
D_{2,dust}^{*} = D_{2}^{*}, \tag{2.44}
\]

the coefficient \(\Delta_{ij}\) becomes a function of the effective Knudsen coefficient and the molar fractions.

If the dust molar fraction goes to zero, the coefficients \(D_{i,dust}\) become large. In equation 2.41 the second term of the left-hand side becomes very small. The equation reduces to

\[
\Delta_{ij} = D_{ij}^{*}. \tag{2.45}
\]

In this case, only bulk diffusion takes place. The coefficient \(\Delta_{ij}\) should be equal to the effective bulk diffusion coefficient,

\[
D_{ij}^{*} = D_{ij}^{*}. \tag{2.46}
\]

Summarizing the result:

- Diffusion law for a porous medium:

\[
\nabla x_i = \sum_{j \neq i} \left( \frac{x_i \tilde{N}_j - x_j \tilde{N}_i}{cD_{ij}} \right) \tag{2.47}
\]

\[
\text{for } i = 1, 2
\]
• Diffusion coefficient:

\[ \frac{1}{\Delta_{12}} = \frac{1}{D_{12}^t} + \frac{1}{D_{12}^t D_{22}^r \left( \frac{\partial}{\partial r} + \frac{\partial}{\partial x} \right)} \quad (2.48) \]

The derivation of equations 2.47 and 2.48 is done for a special case, i.e. a binary mixture. If three or more species are present in the mixture, equation 2.47 remains the same, and equation 2.48 becomes

\[ \frac{1}{\Delta_{ij}} = \frac{1}{D_{ij}^e} + \frac{1}{D_{ij}^e D_{jk}^r \sum_k \left( \frac{\partial}{\partial r} \right)} \quad (2.49) \]

The more general case is discussed in Ref. [11]

2.4 Model Equations for the Binary Case

With the knowledge of the reaction mechanism and the diffusion process, a simple model has been build which includes both phenomena. In the model, a cylindrical char fibre is considered. The porous structure of the fibre and its chemical composition are assumed to homogeneous over the fibre volume. Furthermore, the fibre is assumed to have a length much larger that its radius, \( r_p \). This means that all fluxes \( N_i \) and molar fractions \( x_i \) are only a function of the radius. The temperature of the particle is assumed to be uniform, as well as the pressure. The latter assumption entails that the Stefan-Maxwell equation in the form of 2.20 can be used.

First, a situation is considered in which only \( CO_2 \) and \( CO \) are present, i.e. binary diffusion. The purpose of modelling is then to find solutions for the fluxes \( N_1, N_2 \) and the molar fractions \( x_1, x_2 \). As the molar fractions are related by \( x_1 + x_2 = 1 \), the number of unknowns reduces to three. Thus, three equations are needed. The first two equations are obtained by writing down the mass balance for the two species,

\[ \nabla \cdot N_1 = -R_v, \quad (2.50) \]
\[ \nabla \cdot N_2 = 2R_v. \quad (2.51) \]

Here \( R_v \) is the volumetric reaction rate \((mol \cdot m^{-3} \cdot s^{-1})\), which is obtained by multiplying the surface reaction rate with \( S \), the internal surface per unit volume \((m^2 \cdot m^{-3})\),

\[ R_v = R_s \cdot S \quad (2.52) \]

The third equation of our model is given by the Stefan-Maxwell equation for one of the species

\[ \nabla x_2 = \frac{1}{c \Delta_{12}} (x_2 N_1 - x_1 N_2). \quad (2.53) \]
Substituting the total molar flux, \( \vec{N}_t = \vec{N}_1 + \vec{N}_2 \), into the Stefan-Maxwell equation and rearranging yields:

\[
\vec{N}_1 = c\Delta_{12} \nabla x_2 + x_1 \vec{N}.
\] (2.54)

Using this result, the mass balance for CO becomes

\[
c\Delta_{12} \nabla^2 x_2 + \nabla x_1 \cdot \vec{N} + x_1 (\nabla \cdot \vec{N}) = -R_v.
\] (2.55)

Adding equations 2.50 and 2.51 results in

\[
\nabla \cdot \vec{N} = R_v.
\] (2.56)

Substituting this in equation 2.55, together with \( x_1 = 1 - x_2 \) and equation 2.50, yields after rearranging:

\[
c\Delta_{12} \nabla^2 x_2 - \nabla x_2 \cdot \vec{N} = -(2 - x_2)R_v.
\] (2.57)

Equations 2.56 and 2.57 are to be solved for \( \vec{N} \) and \( x_2 \).

By introducing non-dimensionless parameters,

\[
r' = \frac{r}{r_f},
\] (2.58)

\[
\vec{N}_1' = \frac{\vec{N}_1}{R_{vo} r_f},
\] (2.59)

\[
Da = \frac{R_v r_f}{c\Delta_{12}},
\] (2.60)

\[
R_v' = \frac{R_v}{R_{vo}}
\] (2.61)

the equations can be written in a non-dimensionless form. Here, \( R_{vo} \) is the volumetric reaction rate at the surface of the particle,

\[
R_{vo} = R_v(x_{2a}, p, T),
\] (2.62)

with \( x_{2a} \) is the ambient molar fraction of CO. The second Damköhler Number \( Da \) is a dimensionless group which reflects the ratio of the characteristic time of diffusion, \( \tau_d = r_f^2 \Delta_{12} \), over the characteristic time of reaction, \( \tau_r = \frac{r}{R_{vo}} \).

\[
Da \sim \frac{\tau_d}{\tau_r}
\] (2.63)

In terms of the non-dimensionless parameters, equations 2.56 and 2.57 become

\[
\nabla \cdot \vec{N}_1' = R_v',
\] (2.64)

\[
\frac{1}{Da} \nabla^2 x_2 - \nabla x_2 \cdot \vec{N}_1' = -(2 - x_2)R_v'.
\] (2.65)
For the cylindrical geometry, these equations become:

\[ \frac{1}{r'} \frac{d}{dr} (r' N'_1) = R'_v, \]  
\[ \frac{1}{Da} \frac{1}{r'} \frac{d}{dr} (r' \frac{dx_2}{dr'}) - \frac{dx_2}{dr} N'_1 = -(2 - x_2)R'_v. \]  

### 2.5 Analytical Solution for $Da << 1$

Equations 2.56 and 2.57 cannot be solved analytically. However, an approximate solution can be obtained for $x_2 << 1$. This requires a linearization of the dimensionless reaction term, which can be expressed as

\[ R'(x_1, x_2) = \frac{x_1}{K_1 x_1 + K_2 x_2 + K_3}. \]  

The $K$'s are constants, given by

\[ K_1 = \frac{i_1}{\xi}, \]  
\[ K_2 = \frac{j_1}{\xi}, \]  
\[ K_3 = \frac{i_2}{\xi p}, \]

where

\[ \xi = \frac{x_{1a}}{i_1 x_{1a} + j_1 x_{2a} + \frac{i_2}{p}}. \]

Using $x_1 = 1 - x_2$ and dividing by $K_1 + K_3$ yields

\[ R'(x_2) = \frac{1 - x_2}{K_1 + K_3} \frac{1}{K_2 - K_1 x_1 + 1}. \]

Assuming that

\[ \frac{K_2 - K_3}{K_1 + K_3} x_2 << 1, \]

the rate can be expressed as

\[ R'(x_1) = \frac{1}{K_1 + K_3} \left( \frac{K_1 + K_2}{K_1 + K_3} x_2 \right) + O(x_2^2). \]

Substituting this expression in equations 2.67 and 2.67 and collecting terms up to $O(x_2)$ yields

\[ \frac{1}{r'} \frac{d}{dr} (r' N'_1) = \frac{1}{K_1 + K_3} \left( \frac{K_1 + K_2}{K_1 + K_3} x_2 \right), \]  
\[ \frac{1}{Da} \frac{1}{r'} \frac{d}{dr} (r' \frac{dx_2}{dr'}) - \frac{dx_2}{dr} N'_1 = \frac{1}{K_1 + K_3} \left( 2 - \frac{3K_1 + K_2 + K_3}{K_1 + K_3} x_2 \right). \]
For the case $Da << 1$, a regular perturbation procedure can be applied to this equation. In this case, the molar flux can be expressed by $N' = N'_{i0} + N_{11}Da + O(Da^2)$ and the molar fraction by $x_2 = x_21Da + x_22Da^2 + O(Da^3)$. Substituting this in equations 2.76 and 2.77 and separating the terms of different order of $Da$, we obtain:

$$O(1): \quad \frac{1}{r'} \frac{d}{dr'} (r'N'_{i0}) = \frac{1}{K_1 + K_3},$$
$$O(1): \quad -\frac{1}{r'} \frac{d}{dr'} (r'\frac{dx_2}{dr'}) = \frac{2}{K_1 + K_3},$$
$$O(Da): \quad \frac{1}{r'} \frac{d}{dr'} (r'N'_{i0}) = -\frac{(K_1 + K_3)^2}{K_1 + K_3} x_{21},$$
$$O(Da): \quad \frac{dx_2}{dr'} N'_{i0} - \frac{1}{r'} \frac{d}{dr'} \left(r'\frac{dx_2}{dr'}\right) = -\frac{3K_1 + K_2 + K_3}{(K_1 + K_3)}.$$

Together with the boundary conditions,

$$\frac{dx_2}{dr'} = 0, x_{2a} = 0,$$

this results in the solution

$$x_2 = \frac{1}{2(K_1 + K_3)} \left( (1 - r'^2)Da + \left( \frac{7K_1 + 2K_2 + K_3}{(K_1 + K_3)^2} - 3K_1 + K_2 + K_3 \right)r'^2 + \frac{1}{K_1 + K_3} \right) Da^2,$$

$$N_i = \frac{1}{2(K_1 + K_3)} \left( r' + \frac{K_1 + K_2}{4(K_1 + K_3)^2} (r'^3 + 2r')Da \right).$$

If the Damköhler approaches zero, the reaction becomes infinitely slow compared to the diffusion. This has the consequence that the molar fraction of carbon dioxide in the particle becomes equal to its ambient molar fraction: $x_2 = 0$. The flux becomes a linear function of position, as at each radial position the same amount of carbon monoxide is produced per unit time.

In case $Da$ is larger (although the linearization and perturbation conditions are still valid) the effect of diffusion becomes visible (figure 2.4). The concentration of carbon dioxide becomes slightly higher than zero at $r' = 0$, and decreases towards the surface of the particle. Because the magnitude of the variation of $x_2$ over the particle radius is very small, no effect on the flux becomes visible. Under these conditions, it remains a linear function of position.

### 2.6 Numerical Model for the Ternary Case

The analytical solution is only valid for the reaction controlled case. Furthermore, it holds only for the presence of two gases, $CO$ and $CO_2$. The dependence of the diffusion coefficient on the mixture composition was also not taken into account. As the Knudsen diffusion coefficient can vary as...
Figure 2.4: Analytical solution for the binary case. The molar fraction (left) of carbon dioxide and the total molar flux (right).

much as 30% due to the difference in molar mass of carbon monoxide on one hand and carbon dioxide and nitrogen on the other hand, it is worthwhile to include this in the model. Therefore, a numerical code was developed for the case of ternary diffusion, which includes the dependence of the diffusion coefficient with mixture composition.

The equations of the ternary case contain in principle three variables, consisting of the fluxes and molar fractions for each of the gases. As the solution is time-independent, the flux of Nitrogen, $N_3$, will be zero, because nitrogen does not take part in the reaction. As in the binary case, the fluxes of carbon monoxide and dioxide are related by their stoichiometric numbers in the over-all gasification reaction, i.e. $N_1 = -2N_2$. This means that the solution can be found in terms of $N_2$. Because the molar fractions should add up to one, the other to variables in the problem are $x_1$ and $x_2$.

Now, three independent equations should be found for the three variables. The Stefan-Maxwell equations form two of these:

$$\frac{dx_1}{dr'} = Da \left\{ \frac{1}{\Delta_{12}} (x_1 + 2x_2) + \frac{2}{\Delta_{13}} (1 - x_1 - x_2) \right\} N_2, \quad (2.82)$$

$$\frac{dx_2}{dr'} = Da \left\{ \frac{1}{-\Delta_{12}} (x_1 + 2x_2) + \frac{2}{\Delta_{13}} (1 - x_1 - x_2) \right\} N_2. \quad (2.83)$$

Here, the Damkohler number is defined as

$$Da = \frac{R_{0}r_{p}^{2}}{c\Delta_{12}}, \quad (2.85)$$

in which, following equation 2.49,

$$\Delta_{12} = \Delta_{12}(x_{1a}, x_{2a}). \quad (2.86)$$

The coefficients $\Delta_{ij}$ in the Stefan-Maxwell equations are the diffusion coef-
ficients, made dimensionless with the coefficient $\Delta_{12}(x_{1a}, x_{2a})$. 

$$
\Delta'_{ij}(x_1, x_2) = \frac{\Delta_{ij}(x_1, x_2)}{\Delta_{12}(x_{1a}, x_{2a})} 
$$

(2.87)

The third equation in our model is the mass balance for carbon monoxide,

$$
\frac{1}{r'} \frac{d}{dr'} (r' N'_2) = 2R'.
$$

(2.88)

2.7 Conclusions

In this chapter, a model was developed for the gasification of a char particle. The model includes the Langmuir-Hinselwood kinetics for the chemistry and the Stefan-Maxwell law for the diffusion of reactant and product gases. The model can cope with Knudsen-diffusion and bulk diffusion. In the non-dimensionless form of the model, the Damköhler number appears. The magnitude of this number indicates which phenomenon is dominant; reaction or diffusion. The model can be solved numerically. The numerical code was tested by comparing it to an analytical solution of the equations for the binary case with an approximated reaction term. The solution of the model consists of the molar fractions and fluxes of each of the species as a function of radius.
Chapter 3

Results of the Gasification Model

In the previous chapter, a simple gasification model was developed. In this chapter, solutions of the model for various parameters are presented. First, the binary case is discussed, followed by a discussion of the ternary case.

3.1 The Binary Case

3.1.1 The Damköhler Number

Before considering the results of the model, it is wise to obtain an impression of the Damköhler number as a function of temperature, pressure and pore size. From its values, it can be derived at which conditions the reaction or diffusion is dominant.

The Damköhler number increases with temperature (figure 3.1(a)). For temperatures of $1000K$, it is of the order one. With an increase of the pore size, it decreases. The decrease of $Da$ when increasing the pore size from $10\text{nm}$ to $100\text{nm}$ is larger than when the pore size increases from $100\text{nm}$ to $1\mu\text{m}$.

The rapid increase with temperature is caused by the exponential dependence of the reaction rate on the temperature. The temperature dependence of the particle concentration and the diffusion coefficient can be neglected with respect to this dependence. At $1000\text{K}$, the Damköhler number is of the order one because the reaction rate and diffusion rates are of the same order of magnitude. The decrease with increasing pore size is caused by a higher diffusion rate due to less friction with the pore walls. At low pore size, this effect is strong, because Knudsen diffusion is the main diffusion mechanism. At larger pore sizes, the effect becomes less, because bulk diffusion becomes dominant, which is independent of pore size. At low Knudsen numbers, the pore size has no effect at all.
The Damköhler number decreases with pressure (figure 3.1(b)). With a change in pressure of a factor $10^4$, $Da$ changes with only a factor 100 for a pore size of 10nm. For larger pore sizes, this factor becomes even less. At low pressure, $Da$ is strongly dependent on the pore size, whereas at high pressure, it becomes independent of pore size.

The decrease of $Da$ with pressure is caused by the decrease of the concentration of carbon dioxide. In the Knudsen regime, this change does not lead to a change in the diffusion coefficient, as the Knudsen diffusion coefficient is independent of pressure. This means that the diffusion velocity of individual $CO_2$ molecules remains constant. However, due to their lower density their flux decreases, which causes the reaction rate to drop. The reaction rate becomes slower with respect to diffusion, which results in a lower Damköhler number.

At high pressure, a change from Knudsen diffusion to bulk diffusion occurs. Collisions between molecules become dominant with respect to collisions with the pore walls due to a higher concentration of gas molecules. The bulk diffusion coefficient is independent of the pore size. Apart from the pore size, all other conditions for the three curves (figure 3.1(a)) are equal. This means that in the high pressure limit the Damköhler number has the same value for all of them.

The independence of the Damköhler number on the pressure in the high pressure limit is due to the pressure dependence of both the $CO_2$ concentration and the diffusion coefficient. The concentration is proportional to the pressure, while the diffusion coefficient is inversely proportional to the pressure. In the definition of $Da$ they are multiplied, which yields that $Da$ is independent of pressure.

Physically, the pressure independence of $Da$ means that the growth of the fluxes due to an increase of the particle concentration is prohibited because of the increase of the friction in the gas. The increase of the friction is a result of the decrease of the mean free path length due to the growth of the number of collisions between different gas species.

### 3.1.2 Molar fractions and Fluxes as Functions of Radius

Now the behavior of the Damköhler number has become clear, its effect on the radial profiles of the molar fractions and the fluxes as functions of the radial coordinate can be discussed. The molar fraction of carbon monoxide (figure 3.2(a)) increases with increasing $Da$. At $Da \sim O(10^2)$, the center of the particle gets saturated with carbon monoxide. For high values of $Da$, only in a small boundary layer, just below the surface, the molar fraction of carbon dioxide is significant. The flux of carbon monoxide (3.2(b)) decreases everywhere in the particle with increasing $Da$. Also here, the boundary layer character can be observed.

The increase of the concentration of carbon monoxide is caused by the
interplay between reaction and diffusion. Because transport of $CO_2$ into the center of the particle and transport of $CO$ from the center to the environment becomes slower with respect to the reaction, $CO$ piles up in the particle. When the reaction rate becomes very high with respect to the diffusion rate, $CO_2$ can only diffuse over a very small distance near the surface before it takes part in the reaction. This explains the formation of the boundary layer. Because the reaction rate is only significant at locations where sufficient carbon dioxide is present, the flux $N'_2$ will only augment in the boundary layer.

3.1.3 The Apparent Surface Reaction Rate

The molar flux at the surface of the particle, $N'_2$, can be regarded as the dimensionless apparent surface reaction rate. A graph of the dimensionless...
Figure 3.3: The dimensionless molar flux versus $Da$ (c) and dimensional molar flux versus the temperature (d). The temperature is varied, while other parameters are kept constant: $p_{1a} = 1 \cdot 10^5 Pa, T = 1000 K, r_f = 10 \mu, r_p = 10 nm.$

apparent rate (figure 3.3(a)) shows that it decreases as a function of the Damköhler number. For low $Da$, it is close to one, whereas at high $Da$ it approaches zero. The dimensional apparent rate (3.3(b)) shows a continuous increase, although the slope of the curve decreases with temperature.

The dimensionless apparent rate is close to one at $Da << 1$ because diffusion plays no significant role. For high $Da$, de diffusion becomes dominant. The reaction effectively only takes place in the boundary layer just below the surface. Therefore, the rate diminishes. The dimensional apparent rate keeps rising due to the exponential dependence of the reaction of the temperature. Though, the rising speed in at high temperature is smaller than at low temperature, because of the limitation caused by diffusion.

3.2 The Inhibition Effect

The reaction rate is dependent of the concentration of both $CO_2$ and $CO$. Elevated ambient concentrations of carbon monoxide inhibit the reaction, as was discussed in chapter 2. The change of the reaction rate has consequences for the radial profiles of molar fractions and fluxes. The molar fraction of carbon dioxide rises everywhere in the particle when $x_{2a}$ rises (figure 3.4(a)). The variation of the molar fraction over the particle radius becomes less. At $x_{2a} = 0$ it is 0.1, whereas at $x_{2a} = 0$ it becomes of $O(10^{-2})$. The dimensionless flux increases rapidly when $x_{2a}$ goes from 0 to 0.2. When $x_{2a}$ is increased further, the flux approaches unity.

The behavior of the flux suggests that a change in the balance of reaction and diffusion takes place. Because at the conditions at which figures 3.4(a) and 3.4(b) are made are at $Da \sim O(1)$, a change in the reaction rate can easily lead to a regime change. The reaction rate decreases rapidly with
growing $x_{2a}$. This causes a change from the diffusion controlled regime to the reaction controlled regime. The profile of the flux at $x_{2a} = 0$ is a typical profile of the diffusion controlled regime, because of its curvature and small magnitude. The profiles at elevated levels of $x_{2a}$ approach a straight line from the origin to $N_2 = 1$ at the surface. These are typical profiles for the reaction controlled regime.

The behavior of the profile of the molar fractions of carbon monoxide can be explained correspondingly to that of the fluxes. At $x_{2a} = 0$, the profile of $x_2$ is curved, typical for the diffusion controlled regime. At elevated ambient levels of $CO$ it becomes flat, typical for the reaction controlled regime.

Figures 3.4(c) and 3.4(d)) show the apparent surface reaction rate for a variation of the molar fraction of carbon dioxide. The dimensionless apparent rate drops rapidly for $Da << 1$, whereas it decreases more slowly for $Da >> 1$. The logarithmic plot of the dimensional apparent rate shows a similar behavior.

The rapid initial decrease of the dimensionless apparent rate is caused by the balance between reaction and diffusion. A small Damköhler number corresponds to a high concentration of carbon monoxide, i.e. a low reaction rate. The decrease of the dimensionless apparent rate for $Da < 1$ is thus directly related to a change of the reaction rate. For $Da > 1$ the apparent rate is determined by diffusion. This corresponds to a slower decrease.

The existence of a diffusion controlled regime and the reaction controlled regime also explain the behavior of the dimensional reaction rate. At low ambient molar fractions of carbon monoxide, the diffusion controlled regime is visible. Here, the reaction rate is high, but it is limited by diffusion. The slope of the curve is determined by the balance between reaction and diffusion. At high ambient molar fractions of carbon dioxide, the reaction rate decreases. The regime is reaction controlled and the slope of the curve is determined by the reaction only.

3.3 The Ternary Case

3.3.1 Partial Pressures and Fluxes as Functions of Radial Position

In the ternary case, three gases are present in the mixture, i.e. carbon dioxide, carbon monoxide and nitrogen. In this section, the effect of the presence of nitrogen is investigated. An overview of the partial pressures of the components and the flux of $CO$ for different mixture compositions is given in figure 3.5. The mixture composition is varied by keeping the partial pressure of carbon dioxide constant, while changing the partial pressure of nitrogen. In this way, the reaction term is kept constant, while the diffusion
Figure 3.4: The inhibition of the reaction rate by CO. The molar fraction (a) and flux (b) of CO as a function of the radial coordinate, and the apparent surface reaction rate, both dimensional (c) and dimensionless (d). Here, $p = 1 \cdot 10^5 Pa$, $T = 1000 K$, $r_f = 10 \mu m$, $r_p = 10 nm$. 
The way in the mixture composition is varied makes it more appropriate to represent the results in terms of partial pressures. Therefore, instead of using $x_{1a}, x_{2a}, \tilde{x}_{2a}$, here the 'relative partial pressures' $\tilde{\mathcal{P}}_{1a}, \tilde{\mathcal{P}}_{2a}$, and $\tilde{\mathcal{P}}_{3a}$ are used. Note that the partial pressures of CO and CO$_2$ are relative to the ambient partial pressure of carbon dioxide, whereas the partial pressure of N$_2$ is given relative to its own ambient partial pressure. The ambient partial pressure of nitrogen is again given relative to $P_{1a}$, i.e. $\tilde{\mathcal{P}}_{1a}$.

In the reaction controlled regime ($Da \sim O(10^{-6})$), the partial pressures of CO and CO$_2$ vary only little as a function of mixture composition. When $\tilde{\mathcal{P}}_{3a}$ is increased from zero to 6, the relative partial pressure of carbon dioxide becomes slightly lower ($\sim 10^{-6}$) and the relative partial pressure of carbon monoxide slightly higher than their ambient partial pressures. The partial pressure of nitrogen varies only with $10^{-7}$. The fluxes remain a linear function of the radius when the relative partial pressure of nitrogen is increased. The flux slightly decreases from 1 to 0.9.

In contrast with the reaction controlled regime, the partial pressures of the different species show greater dependence of $\tilde{\mathcal{P}}_{3a}$ in the diffusion controlled regime. The relative partial pressure of carbon dioxide in the center of the particle is approximately 0.15 when no nitrogen is present. At a relative ambient nitrogen partial pressure of 6.0 becomes smaller than 0.05. The relative partial pressure of carbon in the center of the particle grows from 0.8 to 1.4, thus becoming larger than the ambient partial pressure of carbon dioxide. The relative partial pressure of nitrogen in the center of the particle decreases when $\tilde{\mathcal{P}}_{3a}$. A relatively larger amount becomes located near the surface of the particle. The flux of carbon dioxide decreases from 0.25 to 0.15. For all changes of the relative partial pressures and fluxes, it can be observed that when $\tilde{\mathcal{P}}_{3a}$ is varied from 0 to 1, they are larger then for an increase of $\tilde{\mathcal{P}}_{3a}$ from 2 to 3 and higher.

The minimal dependency of the considered quantities of the relative ambient partial pressure of nitrogen in the reaction controlled regime can be explained by the small role diffusion plays in this regime. The reaction is so slow, that the concentrations of species hardly change. Carbon dioxide is transported so fast compared to the reaction, that its concentration barely changes towards the center of the particle. The addition of extra nitrogen, which makes the diffusion more difficult, has only a limited effect on its partial pressure. Similarly, no piling up of carbon monoxide in the center of the particle occurs, even at higher relative partial pressures of nitrogen. The nitrogen itself is almost homogenously spread through the particle. Outgoing carbon dioxide molecules cannot drag the nitrogen molecules towards the

---

1 The opposite, varying the reaction rate while keeping the diffusion constant is not possible. One could suggest to achieve this by varying the temperature. However, for both Knudsen diffusion and bulk diffusion this implies also a change of the diffusion coefficient.
surface because the reaction is too slow. The nearly constant concentration of nitrogen throughout the particle makes that the effect of increased friction with the other species is the same for all radii. As the partial pressures of the other species are also nearly independent of radius, the reaction rate will also be constant for different radii. This explains the linear behavior of the flux with increasing partial pressure of nitrogen.

In the diffusion controlled regime, diffusion is the dominant phenomenon. As the diffusion speed limits the apparent reaction rate, the increase of friction for the species involved in the reaction becomes significant. The transport of carbon dioxide towards the center of the particle becomes more difficult, which explains the decrease of its partial pressure there. The rise of the partial pressure of CO in the center of the particle is caused by more difficult transport to the surface. The fact that the partial pressure of carbon monoxide becomes higher in the center of the particle than the ambient partial pressure of carbon monoxide is explained by the difference in the total flux of the species. In equilibrium, the stoichiometric constants of the overall gasification reaction demand the magnitude of the flux of CO to be twice the magnitude of the flux of CO₂. This requires a concentration gradient of CO that is larger than the concentration gradient of CO₂. This effect is enhanced by the magnitudes of the diffusion coefficients $D_{13}$ and $D_{23}$. As $D_{13} > D_{12}$, the carbon monoxide molecules experience more friction of the nitrogen than the carbon dioxide molecules. (This is a result of the mass of the involved species, as discussed previously.)
3.3.2 The Apparent Surface Reaction Rate

The behavior of the apparent gasification rate as a function of mixture composition (figure 3.3.2) can be understood with the explanation given above. At high temperature \( T = 1300 \), the rate is low and decreases with decreasing nitrogen pressure. Clearly, this is the diffusion controlled regime. At low temperature, i.e. in the diffusion controlled regime, the apparent rate is high \((\sim 1)\) and is almost independent of the ambient partial pressure of nitrogen.

3.4 Bulk Diffusion versus Knudsen Diffusion

The apparent surface reaction rate as a function of mixture composition for different pore radii in the diffusion limited regime (figure 3.7(a)) shows a decrease of the the rate with decreasing pore size. At low pore size the rate is constant when \( p_{3a} \) is varied. For pore radii of 100nm and 1\( \mu \)m, the apparent rate decreases with an increase of \( p_{3a} \).

The increase of the rate with pore size is caused by the decrease of friction of \( CO \) and \( CO_2 \) with the pore wall. At pore sizes of 100nm, bulk diffusion starts to play a role. This explains the influence of mixture composition for larger pore size.

Enlarging the curve for \( r_p = 10nm \) (figure 3.7(b)), a peculiarity becomes visible. The apparent reaction rate initially increases when nitrogen is added. This is caused by the change from binary diffusion to ternary diffusion. Unlike the case of binary diffusion, in ternary diffusion the partial pressures of carbon dioxide and carbon monoxide are independent parameters. The partial pressure of carbon monoxide can grow, while the partial pressure of carbon dioxide stays approximately equal. The higher concentration of carbon dioxide in the particle results in a larger concentration gradient over the particle radius, which in turn causes a higher rate of diffusion of \( CO \). Consequently, the apparent rate rises.

The reason that the effect does not occur in case of bulk diffusion lies not in the increase of the partial pressure of \( CO \), as this effect can also be observed in figure 3.5. It is caused by the difference of the diffusion mechanism. In case of bulk diffusion, the increase of the concentration gradient is counterbalanced by a decrease of the diffusion coefficient, i.e increased friction with nitrogen molecules.

3.5 Predictions of Experimental Results

To investigate whether diffusion plays a role in the gasification of wood particles, predictions of the model have to be compared with experiments. The main question here is how a time-independent model can predict the time dependent behavior of the experiment.
Figure 3.5: The non-dimensional partial pressures and flux of carbon monoxide as a function of the radius of the char particle. The left pictures are in the reaction controlled regime, the right pictures in the diffusion controlled regime.
Figure 3.6: Apparent reaction rate as a function of partial pressure of nitrogen for different gasification temperatures. Pictures made at $p_{1a} = 1 \cdot 10^5 Pa, r_f = 10\mu m, r_p = 1\mu m$

Figure 3.7: The apparent reaction rate versus the partial pressure of nitrogen. Conditions are $p_{1a} = 1 \cdot 10^5 Pa, T = 1000K, r_f = 10\mu m$. 

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Under the present circumstances, one has to be satisfied a qualitative prediction. The apparent surface reaction rate as defined in this chapter can be seen as a measure for the speed of gasification. In case of bulk diffusion, this will result in a lower apparent rate when nitrogen is present. In an experiment the rate can be measured. Although the pore size will change with time, an increase of the partial pressure of nitrogen will certainly result in a decrease of the reaction rate in the diffusion controlled regime. Even in case of Knudsen diffusion, this will occur, because during the reaction the pore size increases and the regime shifts during the gasification reaction from Knudsen- to bulk diffusion.
Chapter 4

Material Properties

4.1 Introduction

In the previous two chapters it has become clear that the reactivity and the structure of the char are important parameters for the gasification rate. These parameters are determined by the material properties of the char. In turn, these are determined by the material properties of the wood and the pyrolysis conditions, of which the most important is the temperature. This chapter deals with the material properties of both the wood and the char, as well as the pyrolysis procedure.

4.2 Raw Material

The type of biomass investigated in this work is lignocel. Lignocel HB 120 is a commercially available wood flour, commonly used for filter purposes. It is made by grinding hardwood to small fibres, having an average size of 120μm.

The grinding of the wood to small fibres gives rise to a big change (figure 4.1(a)) in structure. The hard wood consists of long (l ~ O(1mm)) hollow cells, the tracheids. In between these cells, large voids (d ~ O(10μm)) are present, the vessels [14]. During the grinding, most of the wood structure is destroyed. The lignocel fibres (4.1(b)) consist of fragments of the tracheids, in which no pore structure on the scale of μm's is recognizable.

The chemical composition of the hard wood is retained during the grinding. The composition of hard wood can be split up in extractables and components of the cell walls of the tracheids. The extractables (resins, volatiles, oils, waxes etc.) are derived from the living cell. The cell wall components can be subdivided in holocellulose and lignin. Holocellulose is the main constituent of the cell wall and consists of hydrocarbon polymers. The lignin is a cementing agent for the cellulose fibres. [14]

The elemental composition of the wood (table 4.1) shows that the upper
Figure 4.1: The structure of hard wood (a) [14] versus the structure of lignocel (b)

limit of the carbon yield is approximately half of the mass of the wood. Remarkable is the high oxygen content of the sample.

4.3 Char

4.3.1 Pyrolysis of wood

During the pyrolysis the chemical composition of the wood changes. The organic compounds of the wood undergo chemical reactions, by which hydrogen rich material, gases and tars, are produced. The general reactions can be subdivided into primary and secondary reactions, according to wether

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>53.67%</td>
</tr>
<tr>
<td>H</td>
<td>5.36%</td>
</tr>
<tr>
<td>N</td>
<td>0.00%</td>
</tr>
<tr>
<td>S</td>
<td>0.00%</td>
</tr>
<tr>
<td>O</td>
<td>40.97%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

Table 4.1: Ultimate analysis of lignocel in weight percent on a dry and ash free basis.
they directly affect the solid material or one of the intermediate reaction products.

The nature and extent of many of the reactions involved in pyrolysis is unknown yet. However, it is known that the reactions are influenced by the temperature and period of heating, the heating rate, the ambient atmosphere and the properties of the substrate.

The transformation of the wood during pyrolysis determines the reactivity of the char. This can easily be understood if one keeps in mind that for example the number of active sites per unit surface area is dependent of the crystallinity. The crystallinity will be affected by the chemical reactions, but possibly also by thermal annealing at high pyrolysis temperature. In addition, the presence of functional groups will decrease at higher pyrolysis temperature thus leading to a decrease of the number of active sites.

The transformation of the wood also leads to a change of the structural properties. Some of the constituents of the wood show melting during pyrolysis, whereas others retain their structure up to high temperatures. The degree of crystallinity can increase when the char is kept at an elevated temperature for a certain time. The species that leave the wood during pyrolysis can leave empty spaces in the char and thus give rise to porosity.

It can be concluded that the great number of parameters involved in pyrolysis makes it a complex process. Nevertheless, it is important to have an idea of the processes that occur during pyrolysis, as the the resulting char properties have a big impact on the gasification speed.

4.3.2 Char Preparation

Selection of Pyrolysis Temperature

Although pyrolysis is an important phenomenon with regard to gasification, it is not the main focus of the present work. It was therefore not attempted to grasp the complex phenomena involved in pyrolysis. Instead, it was chosen to produce a series of char under specified conditions. Thus, the choice of the conditions ensures reproducibility of the experiments. With the help of the literature, the effect of the change of the pyrolysis conditions can be qualitatively related to the results of the gasification experiments.

First, a choice was made for the conditions at which the char was prepared, in particular the temperature. This was done by observing the proceeding of pyrolysis as a function of temperature by means of a Thermogravimetric Analyzer (TGA). A TGA consists essentially of a balance in an electrically heated oven. The oven is flushed with a chemically inert gas. During the measurement, the temperature in the oven is increased. The mass balance records the change in mass of the wood due to the release of tars and volatiles.

In our case, a TGA (type TA SDT 2960) with two mass balances was
used. One of the balances contains the sample, whereas the second balance is the reference balance. As the reference balance undergoes the same procedure as the balance containing the sample, the measurement can be corrected for buoyancy effects. The gas used was helium at a flow rate of 50 ml per minute. All samples used in the TGA had a mass of 5-10 mg.

In figure 4.2 a TGA measurement of lignocel is presented. First, the sample was kept at a temperature of $T = 301.5K$ for 45 min to stabilize the balance. It was then heated at a heating rate $\frac{dT}{dt} = 20K \cdot min^{-1}$. At $1173K$, the working gas was changed from helium to air to start combustion. The temperature was kept constant for 20 minutes. After combustion, the mass measured by the TGA is the mineral content of the char.

The curve indicates that pyrolysis starts at $T \sim 550K$. The weight of the sample decreases rapidly with temperature until $700K$. Then, the pyrolysis rate gradually decreases. The TGA curve indicates that a series of char samples prepared at temperatures ranging from 600 K to 1000 K gives a good representation of the different stages of pyrolysis.

**Char Preparation Procedure**

A setup containing an electrically heated oven is used to prepare chars (4.3). The preparation procedure starts with taking the lignocel out of a stove.
Figure 4.3: Sketch of the setup used for char preparation. By adjusting the position of the handle, the sample container can be shifted into or out of the oven.

The stove is used to store the wood powder under standard conditions ($T = 50 \degree C$) to prevent that samples will contain different moisture levels. A different level of moisture could influence the pyrolysis process.

A sample of a fixed amount of $0.100mg$ lignocel is put into the sample container. As the sample temperature during pyrolysis will not be uniform in the sample, using the same amount for each run has to ensure reproducibility of char preparations.

After setting the flow of nitrogen on a fixed value of $\bar{V}$, the sample is brought into the quartz tube. By means of the handle it is shifted to a position just before the opening of the oven. It is carefully checked by means of the thermocouple, connected firmly to the metal sample container, that the sample temperature does not exceed $150 \degree C$, i.e. no pyrolysis can take place.

When the oven temperature, monitored by means of the thermocouple connected to the nitrogen inlet tube, has reached the desired value, the sample container is shifted into the oven. During the pyrolysis, the signal of the sample container thermocouple is recorded (figure 4.4). The measured temperature is assumed to be a measure for the sample temperature. After a residence time $t_{res} = 5min$, the sample is shifted out of the oven. After it has cooled down to a temperature lower than $40 \degree C$, the nitrogen flow is shut down and the sample is removed from the container.

In the preparation procedure, the following quantities are recorded:

- Starting temperature of the sample, $T_{start}$
Figure 4.4: An example of a temperature measurement with the thermocouple attached to the sample container. Sample from series I (see table 4.2).

- Final temperature of the sample, $T_{\text{final}}$
- Hold time, $t_{\text{hold}} = t_{\text{end}} - t_{\text{start}}$
- Heat up time, $t_{90\%} = t(T_{90\%}) - t_{\text{start}}$. Here $T_{90\%} = 0.90(T_{\text{final}} - T_{\text{start}})$
- Heating rate, $r_h = \frac{T_{\text{final}} - T_{\text{start}}}{t_{90\%}}$
- Conversion factor, $f_c = \frac{m_{\text{final}}}{m_{\text{start}}}$

After a pyrolysis experiment, the char is collected and put in a glass sample container. The sample container is then stored in a closed glass jar containing silica gel, preventing the storage environment to become humid.

4.3.3 Produced Char

Four series of char were prepared. Each series consists of three samples, prepared at the same conditions. The sample series I-III were analyzed with the TGA. Unfortunately, this could not be done for series 0 for practical reasons. The analysis procedure can be found in table 4.2. This is a somewhat more complicated analysis procedure than discussed in the previous section. The isothermal steps 2 and 5 ensure that drying and pyrolysis respectively, can finish completely. From the resulting graph, it can be concluded that in
<table>
<thead>
<tr>
<th>Series</th>
<th>( T_{\text{start}}(K) )</th>
<th>( T_{\text{finish}}(K) )</th>
<th>( t_{90%}(s) )</th>
<th>( r_h(\text{Ks}^{-1}) )</th>
<th>( f_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>423</td>
<td>682</td>
<td>84</td>
<td>168</td>
<td>71.6</td>
</tr>
<tr>
<td>I</td>
<td>425</td>
<td>817</td>
<td>61</td>
<td>364</td>
<td>79.0</td>
</tr>
<tr>
<td>II</td>
<td>424</td>
<td>916</td>
<td>49</td>
<td>538</td>
<td>81.6</td>
</tr>
<tr>
<td>III</td>
<td>424</td>
<td>1000</td>
<td>40</td>
<td>777</td>
<td>82.6</td>
</tr>
</tbody>
</table>

Table 4.2: Produced series of char. For all samples, \( t_{\text{hold}} = 5\text{min} \).

<table>
<thead>
<tr>
<th>Step</th>
<th>Phase</th>
<th>Temperature</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stabilizing</td>
<td>( T = 45^\circ\text{C} ) for 45 min</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>2</td>
<td>Drying</td>
<td>( \frac{dT}{dt} = 20^\circ\text{C} )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>( T = 130^\circ\text{C} ) for 20 min</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Pyrolysis</td>
<td>( \frac{dT}{dt} = 20^\circ\text{C} )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>( T = 900^\circ\text{C} ) for 20 min</td>
<td>Oxygen</td>
</tr>
<tr>
<td>6</td>
<td>Combustion</td>
<td>( T = 900^\circ\text{C} ) for 15 min</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: The operating procedure of the TGA

the TGA, the pyrolyses continues at the temperature where it has stopped during the preparation procedure. Due to the more elaborate measurement procedure, the mass of the dry material, as well as of the fixed carbon content can be determined accurately. Consequently, the weight percentage of the volatiles, fixed carbon and ashes/minerals can be calculated (table 4.4). The fixed carbon content increases with increasing pyrolysis temperature, as could be expected.

A typical SEM picture of the char (4.6) shows that the char retains part of the shape of the wood. Some of the parts of the tracheids of the wood are still recognizable. A large part of the char consists of curved plates.

<table>
<thead>
<tr>
<th></th>
<th>Series I</th>
<th>Series II</th>
<th>Series III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatiles</td>
<td>18.1%</td>
<td>12.1%</td>
<td>9.9%</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>68.3%</td>
<td>73.3%</td>
<td>72.7%</td>
</tr>
<tr>
<td>Ash</td>
<td>13.6%</td>
<td>14.6%</td>
<td>17.4%</td>
</tr>
</tbody>
</table>

Table 4.4: Proximate analysis of char samples in weight percent on a dry basis.

53
Figure 4.5: TGA curves for series I to III. Indicated are the drying, pyrolysis and combustion phases.

Figure 4.6: SEM picture of char from series I
4.4 Gas Adsorption Measurements

4.4.1 Principle

When a solid material is placed in a gas, gas molecules interact with the surface molecules by means of Van der Waals forces. Due to the dense packing of surface molecules, the potential near the surface is strong. The strong interaction potential causes formation of a layer of gas molecules on the surface of the solid. Thus, the potential enhancement at the surface explains the existence of the adsorption layer.

Porous solids have an internal surface which can be as large as several hundreds of square meters per gram of the solid, greatly exceeding the external surface. Gas can flow through the pores to the internal surface, where it is absorbed. A larger surface gives rise to more adsorption of gas molecules. Thus, there exists a relation by the surface area and the amount of gas adsorbed. This relation can be employed to measure the magnitude of the surface. In addition, other properties, like pore sizes can be measured by studying adsorption, provided that sophisticated measurement techniques and physical models for the adsorption are used.

The adsorbed amount of gas by a solid is, apart from its material properties and the surface area, dependent of other parameters. An increase of the temperature will give rise to less adsorption of gas. The gas molecules will have a higher kinetic energy, which makes it less likely that they will get stuck in the potential trap near the surface. An increase of the pressure will result in an increase of the fraction of gas molecules, having a low enough kinetic energy to get adsorbed. This will result in a higher amount of adsorbed gas.

A more complicated parameter that can be varied in the experiment is associated with the type of gas used. The amount of adsorbed gas is dependent of the potential of the gas molecules at the surface of the solid. In the general case, not only Van der Waals forces determine this potential. Among the other forces that determine the adsorption are the dipole and quadrupole momentum of the gaseous molecules, which interact with the electric field and the gradient of the electric field, respectively. On the other hand, the properties of the solid influence the adsorption process. The molecules of the solid can also have a dipole or quadrupole moment.[15]

Formally, the dependence of \( n \), the adsorbed amount of gas per unit mass of the solid from the temperature \( T \), the pressure \( p \) and the gas species can be written as

\[
 n = f_{\text{solid}}(p, T, \text{gas}),
\]

(4.1)

in case of a fixed type of solid. A common way of employing this relation experimentally is to keep the temperature of the gas constant, while varying the pressure. This results in

\[
 n = f_{T,\text{solid, gas}}(p).
\]

(4.2)
<table>
<thead>
<tr>
<th>Pore Type</th>
<th>Pore Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>micropores</td>
<td>&lt; 2 nm</td>
</tr>
<tr>
<td>mesopores</td>
<td>2 nm – 50 nm</td>
</tr>
<tr>
<td>macropores</td>
<td>&gt; 50 nm</td>
</tr>
</tbody>
</table>

Table 4.5: Classification of pores according to their diameter

The curve of \( n \) versus \( p \) is called the adsorption isotherm. It is this curve that is generally used to obtain information about the structure of materials.

An important structure property of a material is its pore size (table 4.5). Pores can be characterized on the basis of their diameter. Pores having a diameter larger than 50 nm are named macropores. The size of mesopores ranges from 2 to 50 nm. Micropores are smaller than 2 nm.

The shape of the isotherm is mainly determined by the pore type (figure 4.7). Type I has a strong rise at low pressure, but becomes constant at higher pressures. Close to \( p_0 \), the saturation pressure of the used gas, the isotherm either remains constant or shows a minor increase. This type is related to a microporous structure. Type IV, related to a mesoporous structure shows a hysteresis loop. In this loop, the adsorbed amount at a certain pressure is higher during a pressure decrease than in case of a pressure increase.

The reasons for the close relation that in general exist between pore size and isotherm shape are discussed extensively in Ref. [15]. Here, only the type I isotherm is discussed, i.e. the case of a microporous solid. The small diameter of the micropores, corresponding to only several diameters of the gas molecules, makes that the gas molecule has much neighbours with which it interacts. The combined potential of all surrounding molecules gives rise to a strong potential, much stronger than at the surface. This causes a strong uptake of gas at low pressures: already at low pressures, this potential is high enough to begin the pore filling. The pores are filled completely after a small increase of the pressure. Consequently, no further uptake takes place and the isotherm becomes constant, which explains the plateau in the isotherm.

### 4.4.2 Experimental Setups

Isotherms can be measured with commercially available gas adsorption measurement devices. For the experiments presented here, the ASAP2010 (Micromeritics) was used.

A sketch of the front panel of the ASAP 2010 is depicted in figure 4.8. At the right side of the ASAP the sample analysis port is located. In the picture, a sample tube is connected to the port. Under the sample tube, a dewar is placed on the elevator. The dewar can be raised automatically. It can be filled with a liquid to keep the sample at a desired temperature.
Figure 4.7: Three isotherm types, indicated by type number in the upper left corner of the graphs. From left to right: isotherm corresponding to micropores, mesopores and macropores.[15]

In the middle of the machine, a cold trap is installed. A cold trap is used to clean the analysis gas from moisture and oil used to lubricate the vacuum pump. By means of leading the gases through a U-shaped tube which is put in liquid nitrogen, the contaminations condense and stay in the curved part of the tube.

At the left of the machine, sample preparation ports are installed. Here, the sample can be heated under vacuum conditions to degas it, i.e to remove remainders of gases left on their surface. In the picture, two sample tubes have been installed. The samples are heated by the heating mantle, which temperature can be adjusted at the control panel.

The ASAP is controlled by a personal computer. An overview of the vacuum system is given on the computer screen (figure 4.9). The vacuum pumps are controlled by valves 1 and 2. In between valve two and the vacuum pumps, a constriction is present. This allows for fine adjustments of the pressure. The flow of analysis gas is controlled by valves 4 and 5. Also here a constriction is present. By opening valve 7 and nine, gas is led to the sample. The other valves and parts of the machine have not been used in the experiments discussed in this work.

4.4.3 Selecting the Analysis Gas

The gas most commonly used for measuring isotherms is nitrogen. The measurement is then performed at 77 K. Nitrogen offers several advantages compared to other gases: [15]:

- The variation of interaction potential over the surface of most solids is not too high compared to the thermal energy of the nitrogen molecule. Therefore, the nitrogen atoms are rather mobile on the surface. They don’t have the tendency to pile up locally, which guarantees the formation of distinct adsorption layers.
Figure 4.8: Sketch of the front panel of the ASAP 2010 measurement system. [16]

Figure 4.9: Sketch of the ASAP 2010 measurement system. The analysis gas is indicated by 'A'. [16]
• Nitrogen is chemically inert towards most solids.

• At 77 K the saturation pressure of nitrogen is near atmospheric pressure, which enables measurement of the isotherm from near-vacuum pressure to saturation pressure.

• The shape of the nitrogen molecule is not far removed from spherical symmetry, which makes it simple to calculate the area taken by a monolayer.

Furthermore, nitrogen is not expensive and safe to use.

In the literature, various results of analysis for microporous chars solids can be found. These include porosity measurements of coal and coal char ([17],[18]), activated coal ([19], [20], [21]) pyrolyzed biomass ([22]) and pyrolyzed polymers ([23]). In these papers, it is argued that nitrogen at 77K cannot reach the micropores. Diffusion in the tested materials is considered to be an activated process. This means that, similar to chemical reactions, a minimum temperature is required to start it.

A possible explanation for the activated diffusion is the presence of local constrictions in the pores. When the width of a constriction is very close to the diameter of a molecule, the molecules will encounter an energy barrier to their passage through the constriction, so that the entry rate through the constriction will have a positive temperature coefficient [15].

Following the explanation by means of activated diffusion, an increase of the temperature would solve the problem. This means, however, that also the working gas has to be changed. The adsorption of nitrogen gas on a solid and condensation of nitrogen gas to a liquid are related phenomena. If the critical temperature of the gas is exceeded during an experiment, the number of adsorbed molecules will diminish. The critical temperature of nitrogen is 126.3 K. Experiments at room temperature (~ 298 K) would greatly exceed this value. For CO₂, the critical temperature is 304.2 K, which is above room temperature. Therefore, in the literature cited above, this gas was used for adsorption measurements.

At first, it was tried to perform experiments with nitrogen as analysis gas at 77K, using the chars prepared for this research. However, isotherms with distorted shapes were obtained and the ASAP had difficulties to meet the equilibrium conditions for measurements at the desired pressures. Then, the same approach in the literature was followed, i.e. measuring with carbon dioxide at room temperature.

4.4.4 Measurement Procedure

Before the measurements start, the samples have to be prepared. For each series a sample tube is filled with char, using an amount of 0.100g for each
tube. (This is the minimal amount of material for reasonably accurate adsorption measurements [16]).

The sample is then placed in an electrically heated stove. In the stove, the temperature is 70°C and the pressure < 0.01 Bar. The samples are stored here for more than 24 hours before they are used for the experiments. This routine is used to predry the char, i.e. to remove all the moist adsorbed by the sample.

When a measurement of a sample is performed, it is taken out of the stove. During the transport from the stove to the ASAP2010 the sample is briefly exposed to the air. Then the sample tube is mounted onto the sample analysis port. By means of the computer, valves 1 and 9 are opened to expose the sample to the vacuum. A heating mantle from the preparation port is then clipped onto the sample and set on a temperature of 130°C. Under these conditions it is outgassed for at least four hours. The reason to outgas the sample at the analysis port and not at the sample preparation port is to prevent exposure to the air when the sample is moved from the preparation port to the analysis port.

When the outgassing has finished, the measurement can start. The settings of the measurement are chosen carefully. The ASAP is used to do a free space measurement before the actual analysis starts. The result of this measurement is used to correct for the growing concentration of gas in the sample tube. In this way, only the amount of gas adsorbed by the sample is used to determine the isotherm. In order to perform this measurement, gas is added to the sample. As the char probably is a microporous medium, this would immediately fill all small pores. The result of the outgassing-procedure would then be undone! Therefore, this procedure has to be cancelled in the program 1. The free space can be measured and added in the program manually after analysis of the sample.

In order to determine the (p, n) combinations for microporous samples, the ASAP 2010 offers the incremental dose mode. In this mode, the machine gives a fixed dose (in the present case set at 12 cm³ STP) and then measures the pressure. This procedure is repeated, until - for the present measurements - the pressure becomes 1 · 10⁵ Pa. In the measurement procedure the saturation pressure of CO₂ at room temperature (T ~ 293 K) was taken to be 5.772 · 10⁵ Pa and the density of the liquid was 7.71 · 10² kg · m⁻³ [24].

4.4.5 Measurement Results

For the raw material and chars 0 to II, adsorption measurements were performed at room temperature (T = 293 K). The resulting isotherms can be found in figure 4.11. From the curve, it can be seen that the raw material (RM) adsorbs only little carbon dioxide. The

---

1In fact, both the options 'backfill sample before analysis' and 'free space measurement' have to be put off. For more details, see the manual [16]
series of char adsorb more carbon dioxide with increasing pyrolysis temperature. The shape of the curve resembles the curve for a microporous medium, but the plateau at higher pressures is not visible.

The increasing adsorption with pore size can be explained with an increase of the porosity of the char with increasing pyrolysis temperature. Admittedly, the measurements do not exclude the possibility that the medium has also macropores, as the plateau at higher pressures is not visible. It should be noted that the saturation pressure of carbon dioxide (5.772 \times 10^6 Pa) greatly exceeds the atmospheric pressure. The ASAP cannot reach pressures higher than 10^5 Pa, which unfortunately means that this plateau is impossible to observe. However, the experience with the standard measurement technique with nitrogen as well indications from the literature about adsorption measurements with chars cited above is considered as a sufficient basis to assume that the chars are microporous.

4.4.6 Adsorption theory for a microporous medium

Dubinin [25] developed a theory to relate the adsorption isotherm to the pore structure. Therefore, he defines the maximal differential molar work of adsorption $\Delta A$, equal, with a minus sign, to the variation of the in the Gibb's free energy of adsorption $-\Delta G$:

$$ A = -\Delta G = RT \ln \left( \frac{p_s}{p} \right). $$

(4.3)

Here, $p_s$ is the saturation pressure of the used gas.

Assuming that the adsorbate is in a highly compressed state, its density can be assumed to be equal to the density of the liquid that condenses when the pressure gas pressure is increased. The degree of filling,

$$ \theta = V_i/V_p, $$

(4.4)
can then be defined, where $V_i$ is the volume of the liquid in the pores and $V_p$ is the total pore volume.

The degree of filling of the micropores can be related to $A$, which can be written formally as:

$$\theta = f(A/E). \tag{4.5}$$

Here, $E$ is named the characteristic energy of adsorption. It is a parameter used to make the differential molar work of adsorption dimensionless. By finding the function $f$, the degree of filling can be related to the gas pressure.

Dubinin proposed to use the Weibull distribution for the expression for $f$. This results in

$$F(A/E) = 1 - \exp\{-A/E\}^n. \tag{4.6}$$

which is known as the Weibull distribution. At $A = 0$, $F(A/E) = 1$. On the other hand, as $p/p_s$ decreases in the range of very low equilibrium pressures, $A$ reaches very high values and $F(A/E)$ tends to zero. Therefore $F(A/E)$ represents the unfilled fraction of micropores, i.e., $1 - \theta$:

$$F(A/E) = 1 - \theta = 1 - \exp\{-A/E\}^n. \tag{4.7}$$

Accordingly, the degree of filling can be expressed as:

$$\theta = \exp\{-A/E\}^n. \tag{4.8}$$

This equation can be expressed as

$$V_i = V_p \exp\left\{\left[-\frac{RT}{E} \ln \left(\frac{p_s}{p}\right)\right]^n\right\}. \tag{4.9}$$
and is generally referred to as the Dubinin-Ashtakov (DA) equation. By fitting this equation to the measured isotherms, the micropore volume $V_p$ can be determined. In this formula, $E$ and $n$ are considered to be fitting parameters.

**Application of the DA-equation**

The DA-equation describes the isotherms rather well (4.12). A plot of $\ln(V_i)$ versus $A^n$ follows a straight line, as predicted by equation 4.9. The resulting pore volumes, as well as the values for $E$ and $n$, are printed in table 4.6.

Unfortunately, no density measurement of the produced chars are available. This means that the pore volume cannot be converted to porosity.

The quantities $E$ and $n$ change considerably for the different samples. Most likely, this is related to the change of the material properties in the pyrolysis process. As could be expected, the total pore volume increases from raw material to char, series I. Remarkably, the total pore volume decreases for series II. This could be related to shrinking or breaking of the particles.
Table 4.6: Results of the fit procedure of the DA equation to the measurement data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E(kJ \cdot mole^{-1})$</th>
<th>$n$</th>
<th>$V_p(cm^3g^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM</td>
<td>17.02</td>
<td>1.6044</td>
<td>0.0389</td>
</tr>
<tr>
<td>Series 0</td>
<td>21.07</td>
<td>1.8041</td>
<td>0.1418</td>
</tr>
<tr>
<td>Series I</td>
<td>24.68</td>
<td>1.9695</td>
<td>0.1579</td>
</tr>
<tr>
<td>Series II</td>
<td>27.77</td>
<td>2.1708</td>
<td>0.1509</td>
</tr>
</tbody>
</table>

with increasing pyrolysis temperature. It could also be related to an error in the measurement procedure. A reproducibility test would be suitable to determine this.

**4.4.7 Discussion of the Interpretation of the Isotherms**

The use of the theory of Dubinin is not without some difficulties. The main difficulty is the obsceness of its underlying foundations. It is a mixture of thermodynamics and empirical rules, instead of a clear description of physical phenomena. This makes it even difficult to estimate weather application of the theory is correct in the present work.

A second difficulty arises due to the treatment of the theory in the literature. In the literature, difficulties of the theory are often ignored, while application of the equations is widespread. This means that the interpretations of the measurements are not performed rigourously according to the theory. For instance, the adsorbed amount of gas not is only used to calculate the pore size, but it is also used to calculate the surface corresponding to its conversion to one monolayer. As the pores are very narrow, this would correspond to the internal surface of the used material. On the other hand, Dubinin explicitly advises not to do so. He argues that the conception of the surface area of a solid body is a macroscopic notion. In colloid chemistry the question also arises of the lower limit of dimensions of colloid particles, beyond which the conception of a surface between the disperse phase and the dispersion medium loses its physical significance. This lower boundary of the colloid particle size is estimated to be 1 to 2 nm and practically coincides with the linear size of micropores. Some authors accept this and use the term 'apparent surface'[22]. Other authors have the opinion that the 'apparent' surface measured with CO$_2$ is the 'absolute' surface [17].

In trying to understand the process that occurs during the adsorption of gasses by char, new ideas regarding its physics arose. One of these ideas [26] is that the process of adsorption of carbon dioxide is similar to the diffusion of liquids into polymers. The carbon in the char has a lamellea-like structure, which make it look like a polymer. The gas could be adsorbed on the surface of the particle and then diffuses inwards. During the diffusion
process, the char particle swells. The effect of swelling has been observed for polymers. The structure properties of the char change. Therefore, the measured adsorption is would be no longer a reliable indication for the porosity of the particle.

4.5 Conclusions

The material properties of the wood and the pyrolysis conditions determine the gasification rate of the char. To be able to perform reproducible gasification experiments, the wood properties and the pyrolysis conditions of the char have to be known. By means of the literature about pyrolysis and additional experiments for char characterization, the results of the gasification experiments can then be explained by the char properties.

By means of a TGA curve of pyrolysis of lignocel, it was observed that pyrolysis starts at around 550 K. At around 1000 K, the pyrolysis is nearly complete, i.e. no further mass loss of the sample was observed. Therefore, the series of samples produced in the temperature range of 600K to 1000K with intervals of 100 K offers a good representation of the different stages of pyrolysis. Proximate analysis has been applied to sample series I to III.

From the SEM pictures of the wood, it became clear that the natural structure of the hard wood is not preserved in lignocel. Conservation of the nerve structure of the wood with pyrolysis thus cannot be an explanation for diffusion effects that are possibly observed in future gasification experiments. From the adsorption measurements with carbon dioxide, it became clear that if the char is porous, it will be microporous. The pores will then be very small, which means that most likely, they play no important role in the reaction.

The characterization of the structure properties of the char by means of adsorption measurements is a difficult task. The experiments are time-consuming and non-standard. The theory of Dubinin is difficult to understand and is often not used in a satisfactory way in the literature. In addition, the underlying physical measurement could be more related to diffusion of a liquid into non-porous material than to the diffusion of a gas into the micropores of a solid.

The adsorption of a large amount of gas by the char means that also at atmospheric conditions gasses or moisture could get trapped in the pores. As the degassing of the sample takes extreme conditions (vacuum, elevated temperature) the effect of the storage of the char in a closed environment together with silicagel could prove to be unnecessary, as gases and moist will always be trapped in the material.
Chapter 5

Gasification Results

To be added.
Chapter 6

Conclusions and Recommendations

The aim of this study was to investigate the effect of diffusion on the gasification rate of a wood derived particle. Some theoretical and experimental work was carried out to help to clarify this matter.

It was shown that a simple, numerical model can describe the interplay of reaction and diffusion in the gasification of a porous char particle. Some important phenomena regarding diffusion and reaction could be included in the model. By applying the theory of the dusty gas model, both bulk diffusion, Knudsen diffusion and all intermediate cases can be described by the gasification model. Application of Langmuir-Hinselwood kinetics in the reaction source term of the model implies that also the CO₂ inhibition effect is included.

It was observed that, due to the interplay of reaction and diffusion, two different gasification regimes can be distinguished. In the reaction controlled regime, the characteristic time of reaction is much larger than the characteristic time of diffusion. In the diffusion controlled regime, the opposite situation occurs. The Second Damköhler number, a dimensionless parameter related to the model equations, reflects the ratio of the characteristic time of diffusion over the characteristic time of reaction. This means that in case the Damköhler number is much smaller than one, gasification is in the reaction controlled regime. A Damköhler number much higher than one indicates that gasification is performed in the diffusion controlled regime.

The diffusion controlled regime and the reaction controlled regime each have distinct features. In the reaction controlled regime, the partial pressures of all gases are nearly constant as functions of the radial coordinate. In the diffusion controlled regime, the reaction occurs only in a thin boundary layer, just below the surface.

The model enables to study variation of the partial pressures of the gases present in the ternary mixture, i.e. nitrogen, carbon dioxide and carbon
monoxide. By choosing for a fixed partial pressure of carbon dioxide and carbon dioxide, the reaction rate was kept constant. By varying the partial pressure of the chemically inert nitrogen, only the mean free path of the gas molecules involved in the reaction is varied. This means that under the described conditions it is possible to influence only the diffusion speed.

The effect of the variation of the diffusion velocity is different in both gasification regimes. In the reaction controlled regime, only a minor effect occurs. The reaction is the slowest step, which means that a decrease of the diffusion rate will not have a large effect on the gasification rate. On the other hand, in the diffusion controlled regime, the apparent gasification rate is determined by the diffusion velocity. Here, the increase of the partial pressure of nitrogen causes the reaction rate to decrease considerably.

The model is useful for the interpretation of the data. In the time-independent case described by the model, the diffusion controlled regime can be recognized by the decrease of the apparent reaction rate when nitrogen is added to the mixture. In experiments, adding nitrogen results in longer gasification times.

Further development of the model in the future would be a justified activity. Although the experiments with char derived from lignocel will probably show no diffusion effects caused by porosity, diffusion is certainly important for larger wood particles. There are some interesting possibilities to improve the model. Of these possibilities, including the time-dependent pore structure is probably the most interesting. In addition, a more complex gasification environment, which includes steam, could be implemented. Also, the model could be extended with a heat balance to make it suitable for larger char particles. Extension of the model could lead to more quantitative and realistic predictions of gasification rates.

In parallel to the development of the model, the material properties of the char were investigated. Attention was mainly focussed on determination of the porosity of the char. First, porosity of the char could partly be related to the nerve structure of wood, as part of the wood structure is retained during pyrolysis. Second, the exhaust of gases and tars during pyrolysis can cause the formation of pores. In this case, molecules that leave the char, leave behind open spaces.

If pores related to the nerve structure of wood are present, nerves should be visible in the lignocel particles. As these pores would have a size in the order of $10\mu m$, they should be visible on SEM pictures. However, this was not the case. Instead, it is concluded that the nerve structure of wood is destroyed when it is grinded to lignocel particles.

Gas adsorption measurements were performed to determine whether the pyrolysis process indeed resulted in porosity. The results of these experiments have shown that most likely, the char contains only micropores. These pores have diameters of the order of $1nm$, which, most likely, makes it too difficult
for molecules of the reactant gas to enter them at a sufficiently high rate.

For char, problems arise with the standard adsorption measurement method. This method involves nitrogen as a working gas and a measurement temperature of 77K. The reason for the failure of this measurement technique is not entirely clear yet. The literature suggests that this is caused by the fact that diffusion into the micropores is considered to be an activated process, i.e. a process having a positive temperature coefficient. This implies that a higher temperature has to be chosen for the adsorption measurements. However, the critical temperature of nitrogen is too high for adsorption measurements at room temperature. Therefore carbon dioxide at room temperature has to be used.

The theory of Dubinin was used to determine the pore volume of the char. The physical basis of this theory is somewhat obscure and in the literature, its terminology is not always used rigourously. In addition, there are doubts whether the volume filling of the pores is the correct physical mechanism to describe the isotherm. This makes the application of Dubinin's theory and the measurement of properties of microporous char more to a subject of research itself than to a readily available measurement technique.

Because only part of the $CO_2$ isotherm can be recorded because of limitations of measurement conditions of the used apparatus, the existence of a plateau in the curve of the isotherm could not be shown. This means that the existence of mesopores cannot be excluded definitively (all be it that the literature strongly suggests that only micropores are present). Therefore it is recommended to try to obtain at least one measurement with nitrogen at 77K, even though such a measurement is time consuming and brings about practical hurdles.

Some preliminary experiments in the grid reactor have resulted in a curve of the characteristic time of reaction versus the temperature. The curve shows the existence of two regimes. In the regime at low temperature, a fit of the Arrhenius equation gives an activation energy that is in agreement with the literature. Therefore, in this regime, it seems that pure kinetics are measured. In the regime corresponding to high temperatures, diffusion could play a role. This would then not be related to diffusion in char pores (which, most likely, does not occur) but either to diffusion of gases from the environment to a boundary layer surrounding the pile of char, or diffusion in the inter-particle space in the char pile.

It is recommended to investigate the occurrence of two regimes further, by starting experiments in which the mixture composition is varied. In this way, it could be tested whether diffusion plays a role in this phenomenon. At the same time, some back-of-the-envelope calculations could be performed to estimate the extent of these effects.

In addition, it is advised to proceed the experiments with the various series of char that were prepared. Trying to understand the results with
the help of literature data available on the complex issue of pyrolysis could lead to interesting new hypothesis, which could in turn be tested in the laboratory.

It can be concluded that a step forward has been made in describing the role of diffusion in gasification processes. In general, a better understanding was obtained from the interplay of reaction and diffusion in a porous medium. In particular, this work is of help to interpret the results of experiments in the grid reactor. Despite the achieved progress, some interesting features remain to be studied.
Appendix A

Charsamples

In table A.1, the prepared chars are listed. The different runs have been combined to four series, to which is referred in this report.

<table>
<thead>
<tr>
<th>Series</th>
<th>Sample Number</th>
<th>$T_{\text{start}}(K)$</th>
<th>$T_{\text{final}}(K)$</th>
<th>$t_{90%}(s)$</th>
<th>$r_{h}(K/min)$</th>
<th>$f_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>30</td>
<td>423</td>
<td>663</td>
<td>80</td>
<td>162</td>
<td>70.7</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>424</td>
<td>708</td>
<td>77</td>
<td>199</td>
<td>73.7</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>423</td>
<td>674</td>
<td>94</td>
<td>44</td>
<td>70.4</td>
</tr>
<tr>
<td>I</td>
<td>21</td>
<td>423</td>
<td>807</td>
<td>58</td>
<td>357</td>
<td>78.2</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>430</td>
<td>821</td>
<td>60</td>
<td>352</td>
<td>79.3</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>423</td>
<td>822</td>
<td>56</td>
<td>384</td>
<td>79.4</td>
</tr>
<tr>
<td>II</td>
<td>24</td>
<td>423</td>
<td>923</td>
<td>-</td>
<td>-</td>
<td>81.1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>423</td>
<td>912</td>
<td>48</td>
<td>549</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>425</td>
<td>913</td>
<td>50</td>
<td>527</td>
<td>81.2</td>
</tr>
<tr>
<td>III</td>
<td>27</td>
<td>423</td>
<td>1004</td>
<td>39</td>
<td>804</td>
<td>82.9</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>425</td>
<td>999</td>
<td>40</td>
<td>774</td>
<td>81.9</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>423</td>
<td>996</td>
<td>41</td>
<td>754</td>
<td>82.9</td>
</tr>
</tbody>
</table>

Table A.1: Prepared chars
## Appendix B

### Model Parameters

In tables (a) to (c), all model parameters are listed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal surface area $S_m(m^2kg^{-1})$</td>
<td>1.83 \cdot 10^6</td>
<td>-</td>
</tr>
<tr>
<td>Surface Density of active sites $N_t(m^{-2})$</td>
<td>6.02 \cdot 10^5</td>
<td>-</td>
</tr>
<tr>
<td>Porosity $\epsilon(-)$</td>
<td>0.5d0</td>
<td>-</td>
</tr>
<tr>
<td>Tortuosity $\tau(-)$</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>Char Density $\rho(kg \cdot m^{-3})$</td>
<td>400</td>
<td>[27]</td>
</tr>
</tbody>
</table>

(a) Char properties.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$M(g \cdot mol^{-1})$</th>
<th>$V_F(m^3mol^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$</td>
<td>44</td>
<td>26.9 \cdot 10^{-6}</td>
</tr>
<tr>
<td>$CO$</td>
<td>28</td>
<td>18.0 \cdot 10^{-6}</td>
</tr>
<tr>
<td>$N_2$</td>
<td>28</td>
<td>18.5 \cdot 10^{-6}</td>
</tr>
</tbody>
</table>

(b) Gas properties. All data taken from [24].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Frequency factor</th>
<th>$E_a(kJ \cdot mol^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_1$</td>
<td>$1.3s^{-1}Pa^{-1}$</td>
<td>165</td>
</tr>
<tr>
<td>$j_1$</td>
<td>$3.6 \cdot 10^{-6}s^{-1}Pa^{-1}$</td>
<td>20.8</td>
</tr>
<tr>
<td>$i_2$</td>
<td>$3.23 \cdot 10^{7}s^{-1}$</td>
<td>236</td>
</tr>
</tbody>
</table>

(c) Kinetic parameters. Data taken from [8]