The influence of particle size distribution on bio-coal gasification rate as related to packed beds of particles

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Abstract

This thesis is a part of a collaboration between Höganäs AB and Luleå University of Technology, aiming at replacing fossil process coal with bio-coal in their sponge iron process. The difference in gasification reactivity, i.e. reaction rate, between fossil coals and bio-coals is the major challenge in the endeavor to decrease the climate impact of the existing process. The goal of this thesis is to develop a model of reaction rate for bio-coals in relation to particle size distribution. Different particle size distributions were combined and tested to see how that affects the effective reaction rate.

Within the scope of this work, gasification reactivities of different materials, including coal, cokes, and bio-coals, were determined. Three bio-coals were selected to study the effect of particle size distribution on reactivity. Kinetic parameters were determined by using thermogravimetric analysis in the temperature range of 770-850 °C while varying CO₂ partial pressure between 0.1-0.4 atm. The effect of particle size on the reaction rate was investigated by using particles with diameter between 0.18 and 6.3 mm. The effect of particle size distribution on the reactivity of bio-coal in a packed bed was carried out in a macro thermogravimetric reactor with a constant bed volume of 6.5 cm³ at 980 °C and 40% (vol.) of CO₂.

The experimental investigation in three different rate-limiting steps was done for one bio-coal sample, i.e. Cortus Bark bio-coal. The activation energy of the bio-coal was 187 kJ mol⁻¹, and the reaction order was 0.365. For the internal diffusion control regime, an increase in particle size resulted in low reaction rate. The effective diffusivity calculated from the Thiele modulus model was 1.41*10⁻⁵ m² s⁻¹. For the external diffusion control regime, an increase in particle size increased the reaction rate up to a certain point where it plateaued at >1 mm. By choosing two discrete particle size distributions, where a smaller average distribution can fit into a larger average distribution the reaction rate was lowered by 30% compared to only using a single narrow particle size distribution. This solution decreased the difference of apparent reaction rate in a packed bed between the bio-coal and anthracite from 6.5 times to 4.5 times.

At the moment the model is not generalized for all bio-coals. However, the developed methodology can be routinely applied to assess the different bio-coal samples. One possible error can be that pyrolysis influences the gasification rate for bio-coal that is pyrolyzed below the temperature of the gasification test. There is a clear correlation between particle size distributions, bulk density, and apparent reactivity. By mixing two distributions the reaction rate of Cortus Bark was reduced from 6.5 times the reaction rate of anthracite to 4.5.
Acknowledgements

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# Table of contents

1. **Introduction**
   
   1.1. Background ................................................................. 6
   
   1.2. Sponge iron process for metal powder production ............... 7
   
   1.3. Problem ........................................................................... 8
   
   1.4. Aim and objectives ....................................................... 8
   
   1.5. Limitations ................................................................. 9

2. **Theory** ................................................................. 10
   
   2.1. Boudouard reaction ....................................................... 10
   
   2.2. Rate limiting steps ....................................................... 10
   
   2.2.1. *Chemical control (Regime I)* ..................................... 11
   
   2.2.2. *Internal diffusion control (Regime II)* ....................... 11
   
   2.2.3. *External diffusion control (Regime III)* .................... 11
   
   2.3. Intrinsic reaction rate .................................................. 11
   
   2.4. Effectiveness factor ..................................................... 13
   
   2.5. Porosity of particles and of the packed bed ..................... 13
   
   2.5.1. *Packed bed* .............................................................. 14

3. **Material and methods** .................................................. 16
   
   3.1. Material information .................................................... 16
   
   3.2. Preparation and initial measurements ................................ 17
   
   3.2.1. *Sample preparation* ................................................ 17
   
   3.3. Intrinsic reactivity measurement (Regime I) ..................... 22
   
   3.3.1. *Calculation of reaction rate constant from random pore model* ...... 22
   
   3.3.2. *Calculation of kinetic parameters* ................................ 24
   
   3.4. Apparent reactivity measurement in the internal diffusion control regime (Regime II) ....................................................... 24
   
   3.4.1. *Diffusion model* ...................................................... 24
   
   3.5. Apparent reactivity measurement in the bulk diffusion control regime (Regime III) ....................................................... 25

4. **Results and discussion** .................................................. 26
   
   4.1. Material selection ........................................................ 26
   
   4.2. Material data ............................................................... 27
   
   4.2.1. *Density measurements* ............................................. 27
   
   4.2.2. *Particle size and distribution analysis* ....................... 28
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Physical quantity</th>
<th>[unit]</th>
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<tr>
<td>α</td>
<td>Concentration of reactant</td>
<td>[mol m(^{-3})]</td>
</tr>
<tr>
<td>A</td>
<td>Pre-exponential factor</td>
<td>[-]</td>
</tr>
<tr>
<td>C(_0)</td>
<td>Initial reactant concentration</td>
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</tr>
<tr>
<td>d</td>
<td>Diameter</td>
<td>[m]</td>
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<tr>
<td>(\rho_{C_0})</td>
<td>The density of carbon material</td>
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<tr>
<td>D</td>
<td>Diffusivity</td>
<td>[m(^2) s(^{-1})]</td>
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<tr>
<td>ε</td>
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<td>[-]</td>
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<td>E</td>
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<td>[kJ mol(^{-1})]</td>
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<tr>
<td>k</td>
<td>Rate constant</td>
<td>[s(^{-1})]</td>
</tr>
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<td>(L_o)</td>
<td>The initial length of the pores per unit volume</td>
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</tr>
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<td>Characteristic length</td>
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1. Introduction

1.1. Background
The Paris agreement says that the goal is to keep the global temperature rise below 2 °C (UNFCCC, 2015). To reach that, it is necessary to stop adding new greenhouse gases into the atmosphere.

A big contributor to greenhouse gas emissions is the steel industry. In steel production, coal is used as a reduction agent for removing oxygen from an oxidized form of iron (iron ore). The steel industry contributes globally between 4 and 7% of all anthropogenic CO₂ emissions (Arens, 2010).

It is not sustainable to continue using fossil coal in the steel industry. That is for two reasons. Firstly, high-quality coal is depleted faster than it is replaced. That means that it will get harder to find it over time. Secondly, by burning coal, a surplus of carbon is introduced to the atmosphere.

One way to decrease the surplus of generated CO₂ is by replacing fossil coal with bio-coal, i.e. charcoal from biomass, in steel production. That way, the carbon is already in circulation. As long as less is used than what is replenished by the growth of the forest, it is sustainable. One difference between fossil-coal and bio-coal is the time it takes to replace it. As shown in Figure 1-1. The short carbon cycle is the one that is absorbed by the annual growth of forest, plants etc. While the long carbon cycle is a by-product of geological processes. By using fossil fuels carbon is added that has not been in the atmosphere for millions of years and such increase the total amount of carbon in circulation. Bio-fuels, on the other hand, are already in the short cycle. By using biofuels in a sustainable way, humans can decrease their climate impact more quickly by utilizing the more forgiving short carbon cycle.

![Figure 1-1. The different carbon cycles. (National Research Council, 2012)](image-url)
This thesis is written as part of a collaboration between Höganäs AB and Luleå University of Technology. The collaboration spans four years and focuses on the sustainable production of metal powder by replacing fossil coal with bio-coal (Umeki, Five million granted for research on fossil-free steel production, 2018). Bio-coal does not add to the greenhouse problem the same way fossil coal does by utilizing the short carbon cycle. As long as the source biomass is not overconsumed, then the natural growth rate of biomass gives a net-zero accumulation of carbon in the atmosphere. Bio-coal can be produced from many different types of biomass materials; although in the context of fossil coal replacement usually woody biomass from trees is utilized. The different types of trees influence the properties of the bio-coals. In general, the time it takes for a forest to grow is less than 100 years. While all fossil coal that is used today started forming 350 million years ago (Planète Énergies, 2015)

1.2. Sponge iron process for metal powder production

The sponge iron process produces iron with high porosity that is called sponge iron. The raw materials are magnetite ore concentrate (Fe₃O₄) and a reduction mix containing coke and anthracite. (Hernebrant, 2015)

The production process of sponge iron is shown in Figure 1-2. The reduction mix and iron ore are placed in the same capsule. But they are not intermixed as can be seen in Figure 1-2 (18) and (19). The reduction mix functions first to reduce the oxygen in the iron ore and then subsequently to protect the newly reduced sponge iron from reoxidation in the latter stage of the process.

![Figure 1-2. Schematic over the sponge iron process at Höganäs AB (Umeki & Robinson, Evaluation of bio-coal quality for the application in sponge iron production, 2019)](image)

The packed capsules are sent via railcars into the kiln where they travel through three zones: a pre-heating zone, a firing zone and a cooling zone. In the hottest zone, the firing zone, the temperature can reach 1200 °C. The entire process takes around 3
days and is governed predominately by endothermic reactions. That means that the process needs a net input of extra energy that is provided by burning natural gas (Umeki & Robinson, Evaluation of bio-coal quality for the application in sponge iron production, 2019) (Hernebrant, 2015). The majority of carbon in the reduction mixture does not react directly with oxygen in the iron ore. Instead, it reacts with CO₂ through the Boudouard reaction to create CO:

\[ C(s) + CO_2(g) \rightarrow 2CO(g) \tag{1:1} \]

The first carbon material to react in the reduction mixture is anthracite. Anthracite has a higher reaction rate than coke and is used to help start the reactions. Coke react at higher temperatures and later in the process. (Hernebrant, 2015)

The CO generated from the Boudouard reaction then reacts with the magnetite ore in two steps as can be seen in equations (1:2) and (1:3):

\[ Fe_3O_4(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g) \tag{1:2} \]
\[ FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g) \tag{1:3} \]

There needs to be an excess of carbon in the process so that there is always CO left even in the cooling zone. The different materials in the reduction mix have different reaction speeds. Anthracite reacts earlier and faster than coke. After the anthracite has reacted, there is still coke left to act as a protection layer for the iron against the elevated atmospheric oxygen in the kiln cooling zone that otherwise would re-oxidize the sponge iron. (Hernebrant, 2015)

1.3. Problem

The major challenge hindering a direct switch to bio-based reduction agents in the sponge iron process is that fossil coal and bio-coal do not have the same physical and chemical properties. Physically, fossil coal is typically much denser than bio-coal, and chemically, fossil coal is mineral-based giving a certain type of ash composition while bio-coal is organic in origin leading to some very different elemental contents in its ash composition. The relevant difference for this thesis is that bio-coal has a much lower density and reacts much faster than fossil coal. If the coal reacts too fast, then all coal will be depleted before the iron ore is fully reduced to sponge iron. Furthermore, some coal content is also required as a protective shield from reoxidation of reduced sponge iron in the latter stages of the process.

Fossil coal and bio-coal are not directly interchangeable without making some modifications of either the bio-coal material or the process layout. For Höganäs AB the preferable goal is to make this switch with as few modifications to the process as possible. To do that, the bio-coal needs to have certain properties. It needs to have low reactivity, low volatile content and have no significant volume change during the process. (Umeki & Robinson, Evaluation of bio-coal quality for the application in sponge iron production, 2019)

1.4. Aim and objectives

The aim of this work is to create a model to describe the effect of particle size distribution on gasification rate of bio-coal in packed beds using small scale experiments.
Gasification rate is the reaction rate of coal or bio-coal gasification. It is a measurement of how fast the gasification reaction occurs. In this case, gasification is the reaction of converting coal into CO (g) with CO$_2$ (g), which is shown in Eq. 1.1.

1.5. Limitations
The economics were not factored in the analysis. Time limitations demanded that the major focus was on one bio-coal sample (Cortus bark) and then fewer tests for two other samples. That also means that there was no time to do the exact same study for fossil coal. Instead, anthracite was used as reference material in some specific experiments.

The furnace used here is not equipped to reach as high a temperature, 1200 °C, as that in the real process. Instead, a lower temperature was used, and this changes the equilibrium of the predominant Boudouard reaction, but this can be compensated for by controlling the continuous removal of CO from the process.

The particle shapes were not considered in this thesis.
2. Theory

2.1. Boudouard reaction
The Boudouard reaction describes the major reaction coal is going through during the process at Höganäs to generate CO.

At high temperature, a mixture of C and CO$_2$ reacts and creates CO according to equation (1:1).

At 1200 °C, the maximum temperature in the real process, the chemical equilibrium is shifted almost completely to the right side of equation (1:1) where close to all C and CO$_2$ have reacted with each other to form CO. (Tangstad, Beukes, Steenkamp, & Ringdalen, 2019)

![Figure 2-1. Equilibrium pressure of CO and CO$_2$ with graphite (Tangstad, Beukes, Steenkamp, & Ringdalen, 2019)](image)

2.2. Rate limiting steps
The limiting factors for the gasification of coal change depending on the scale of the experiment. These conditions refer to different reaction regimes, namely chemical control, internal diffusion control, and external diffusion control. A visual representation of those regimes can be seen in Figure 2-2. It is important to note that the scale for each regime can change depending on pressure, temperature and porosity of particles.

![Figure 2-2. Visual example of the different regimes.](image)
2.2.1. Chemical control (Regime I)
The simplest regime to calculate the gasification rate is under chemical control. This can be achieved with a small sample volume and small particle size when the temperature is not too high. For this size, there are no limiting factors other than the chemical reaction.

At this size and lower temperature, it is assumed that there is no internal diffusion in the particle and that the entire particle is reacting at the same time.

2.2.2. Internal diffusion control (Regime II)
For regime II either the particles are too large, or the temperature is too high so that the previous assumption that there is no internal diffusion is wrong. For this regime, only part of the particle has access to the reactant gas CO$_2$. This is because reaction at the particle surface is too fast to allow CO$_2$ to reach into the particle core and react at the same time. In the core, there is a volume that is not reacting because there is no CO$_2$ in the gas phase.

In this regime the assumption is that it takes time for the CO$_2$ to reach the core. But that outside the particle the concentration of CO$_2$ is constant.

For this size the reaction rate varies with particle diameter. The smaller the size is, the closer the reaction rate will be to the ideal regime I scenario. Meanwhile, the larger the particle is, the smaller proportion of the volume can react at a given time. For large particles the unreactive core gets larger compared to the volume that can react.

2.2.3. External diffusion control (Regime III)
For regime III, similar to regime II, the assumption of constant CO$_2$ concentration throughout the bulk is wrong because here layers of multiple particles stacked on top of each other work to partially block the access of CO$_2$ gas to individual particles. The gas need to diffuse into the stacked layers before the internal diffusion can begin.

In this regime the assumption is that the gas needs to fully diffuse both into the bed of multiple particles before it reaches the surface of all the individual particles but also it needs to diffuse inside each individual particle.

For this regime, a larger particle diameter will make it easier for the gas to pass through the voids between the particles and allow deeper diffusion into the particle bed. But on the other hand, larger particle diameters should lead to slower rates of internal diffusion so the overall gas diffusion behavior is not readily apparent.

2.3. Intrinsic reaction rate
To keep track of the progression of gasification over time, a relation between how much bio-coal has reacted at each time is needed. It is expressed by the rate of change in normalized progress of reaction, X, so-called conversion. Conversion is zero when no bio-coal has reacted and conversion is one when all the bio-coal has reacted. This is shown in equation (2:1).

$$\frac{dX}{dt} = f(X) * k$$ (2:1)

Where dX/dt is the conversion rate, f(X) is a model for active surface area and k is the rate constant. For bio-coal, a random pore model shown in equation (2:2) fits best.

(Mandapati, o.a., 2012)
\[ f(X) = (1 - X) \sqrt{1 - \psi \ln(1 - X)} \]  

Where \( X \) is conversion and \( \psi \) is the structural parameter for the particle.

The rate constant, \( k \), can generally be described by the function of partial pressure of \( \text{CO}_2 \) and temperature in the following form (Strand & Leteng, 2013):

\[ k = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot P_{\text{CO}_2}^n \]  

\( R \) is the universal gas constant, \( E \) is the activation energy for the reaction, \( T \) is the temperature in Kelvin, \( P \) is the partial pressure of \( \text{CO}_2 \) and \( n \) is the reaction order. \( A \) is a pre-exponential constant for which it is difficult to get an accurate value by experimentation.

To find the pre-exponential factor \( A \), the equation (2:3) is needed. It is easier to see the relationship between factors when it is linear. To get a linear relationship, then the logarithmic expression of equation (2:3) is used:

\[ \log(k) = \log(A) - \frac{E}{R} \cdot \frac{1}{T} + n \cdot \log(P_{\text{CO}_2}) \]  

As can be seen in equation (2:4), in order to solve for factor \( A \) one can make the other terms zero. In order to make the logarithmic \( \text{CO}_2 \) concentration equal to zero, it needs to be 100% \( \text{CO}_2 \), which can be achieved during the experiment.

But for the term that includes temperature, it is more difficult to make it equal to zero. The temperature would need to be so high for this factor to be ignored requiring extrapolation outside practical experimental limits. This gives large error values with even small errors in experiments.

Instead, by setting a reference point, factor \( A \) can be removed. Then the final equation is:

\[ k = k_{\text{ref}} \cdot \exp\left(-\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \cdot \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}_2,\text{ref}}}\right)^n \]  

The method for derivating equation (2:5) from (2:3) is given in Appendix 1.

### 2.3.1. Structural parameter \( \psi \)

The structural parameter can be calculated through equation (2:6). (Bhatia & Perlmutter, 1980) (Everson, Neomagus, & Kaitano, 2011)

\[ \psi = \frac{4\pi L_0 (1 - \varepsilon_{p,0})}{S_0^2} \]  

\( L_0 \) is the initial length of the pores per unit volume, \( S_0 \) is the initial surface area per unit volume and \( \varepsilon_{p,0} \) is the initial particle porosity. The measurement of \( S_0 \) or \( L_0 \) is out of scope in this thesis. \( \psi \) will instead be approximated through experimentation. See section 3.3.1 for description. Future explanation of the porosity is in section 2.5.

Because \( S_0 \) or \( L_0 \) cannot be measured the equation is modified to get the relationship for the material in terms of \( \psi \) and starting porosity:
\[
\frac{L_o}{S_0^2} = \frac{\psi}{(1 - \varepsilon_{p,0}) \cdot 4\pi}
\]  

(2.7)

2.4. Effectiveness factor

According to Fogler (2019) the effectiveness factor, magnitude ranging from 0 to 1, indicates the relative significance of diffusion and chemical limitations. The effectiveness factor is defined as:

\[
\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction if entire volume was exposed to surface conditions}}
\]  

(2.8)

Where \( \eta \) is the internal effectiveness factor. The internal effectiveness factor also measures how far into the particle the reactant diffuses. When the internal effectiveness factor is 1, the reaction is entirely controlled by chemical reactions. If the internal effectiveness factor is small (\( \eta \ll 1 \)), then the reaction is controlled by internal diffusion. (Fogler, 2019)

Usually, the internal diffusion factor refers to Thiele modulus, which is a measure of the ratio of surface reaction rate to the diffusion through the particle. Bischoff (1965) defined the Thiele modulus as:

\[
\phi = \frac{1}{\eta} = \frac{L_c \cdot r_{int}(C_0)}{\sqrt{2}} \cdot \left[ \int_0^{C_0} D(\alpha) \cdot r(\alpha)d\alpha \right]^{-\frac{1}{2}}
\]  

(2.9)

Where the relationship (\( \phi \)) is determined by characteristic length (\( L_c \)) or particle diameter in this case, the reaction rate (\( r_{int} \)) with the initial concentration of reactant (\( C_0 \)). The diffusivity (\( D \)) and reaction rate (\( r \)) are integrated over the concentration of reactant (\( \alpha \)).

The intrinsic reaction rate \( r_{int}(C_0) \) of an n-order reaction can be written as:

\[
r_{int}(C_0) = \frac{dC}{dt} = k_{int} \cdot C^n
\]  

(2.10)

Where \( k_{int} \) is the intrinsic rate constant and \( n \) is the reaction order.

By modifying (2.9) with (2.10) and (2.5), the Thiele modulus for the Boudouard reaction (1:1) can be written as (2.11):

\[
\phi = L_c \cdot \frac{n + 1}{\sqrt{2 \cdot D_{eff}}} \cdot k_{ref} \cdot \exp \left( -\frac{E}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \cdot \frac{P_{CO_2}^{n-1}}{P_{CO_2}^{n-1}_{ref}} \cdot \frac{\rho_{C_0}}{M_{wc}} \cdot RT
\]  

(2.11)

Where \( \rho_{C_0} \) is the density of carbon material used, and \( M_{wc} \) is the molecule weight of particle and \( D_{eff} \) is effective diffusivity.

For step by step calculation see Appendix 2.

2.5. Porosity of particles and of the packed bed.

The porosity describes the fraction of the void space in the material. It can range from 0-1. There are two kinds of porosity relevant to this thesis, i.e. the internal porosity of a single particle and the porosity of the packed bed caused by voids between particles.
\[ \varepsilon_p = 1 - \frac{\text{Envelop density}}{\text{True density}} \]  
\[ \varepsilon_b = 1 - \frac{\text{Particle volume}}{\text{Total volume}} = 1 - \frac{\text{Bulk density}}{\text{Envelop density}} \]  

Where \( \varepsilon_b \) is the porosity for the packed bed and \( \varepsilon_p \) is the porosity for the particle.

The difference between bulk, envelop and true density is explained in section 3.2.1.3, Density measurements.

2.5.1. Packed bed

As long as the particle size distribution is narrow enough so that it can be approximated as one having the same particle size for each particle, the porosity stays the same in the packed bed no matter what the average value for the particle size distributions is. The ratio between void and particles is the same.

The gap between the particles increase with the diameter of the particles. With a larger gap, the reaction gas can penetrate the bed more easily, i.e. a higher diffusivity, than with a small gap. Smaller particles have smaller gaps between them, which means a lower diffusivity. (Cussler, 2009)

To change the bed voids, smaller particles can be inserted to fill the voids between the larger particles.

To simplify the calculation of packed bed porosity, it is assumed that each particle is spherical. The simple cubic packing as in the control volume that contains unity spheres is shown in Figure 2-3. They have the same diameter and that that diameter is \( d_{\text{large}} \). From these assumptions the porosity can be calculated:
Figure 2-3. How the particles are assumed to be packed.

\[ \varepsilon_{\text{bed}} = 1 - \frac{\text{Particle volume}}{\text{Total volume}} \]

\[ \varepsilon_{\text{bed}} = 1 - \frac{4\pi d^3}{3 \cdot 2^3} \rightarrow 1 - \frac{4\pi d^3}{3 \cdot 2^3} \rightarrow \]

\[ \varepsilon_{\text{bed}} = 1 - \frac{\pi}{3 \cdot 2} \]

\[ \varepsilon_{\text{bed}} = \frac{6 - \pi}{6} \approx 0.48 \quad (2:14) \]

To reduce the internal void, one way is to use as large intermediary particles as possible that fill out the gap between primary particles. The largest diameter inside the void between particles \( d_{\text{small}} \) can be calculated:

\[ d_{\text{small}} = \sqrt{d_{\text{large}}^2 + d_{\text{large}}^2 + d_{\text{large}}^2 - d_{\text{large}}} \quad (2:15) \]

To get the ratio between the large diameter and the small diameter, equation (2:15) is divided with \( d_{\text{large}} \):

\[ \frac{d_{\text{small}}}{d_{\text{large}}} = \frac{d_{\text{large}}\sqrt{3} - d_{\text{large}}}{d_{\text{large}}} \]

\[ \frac{d_{\text{small}}}{d_{\text{large}}} = \frac{\sqrt{3} - 1}{1} = \sqrt{3} - 1 \approx 0.44 \quad (2:16) \]

By inserting smaller particles that have a diameter 44% of \( d_{\text{large}} \), the decrease in bed porosity can be determined by the following relationships

\[ \varepsilon_{\text{bed}} = 1 - \frac{4\pi d_{\text{large}}^3}{3 \cdot 2^3} \left(\frac{d_{\text{small}}^3}{d_{\text{large}}^3} + \frac{d_{\text{small}}^3}{d_{\text{large}}^3} \right) \]

\[ \varepsilon_{\text{bed}} = 1 - \frac{4\pi}{3 \cdot 2^3} \left( d_{\text{large}}^3 + d_{\text{small}}^3 \right) / d_{\text{large}}^3 \quad (2:17) \]

Inserting the equation (2:16):

\[ \varepsilon_{\text{bed}} = 1 - \frac{4\pi}{3 \cdot 2^3} \left( d_{\text{large}}^3 + \left(\sqrt{3} - 1\right) d_{\text{large}}^3 \right) / d_{\text{large}}^3 \]

\[ \varepsilon_{\text{bed}} = 1 - \frac{\pi}{6} \left(1 + \left(\sqrt{3} - 1\right)^3 \right) \]

\[ \varepsilon_{\text{bed}} = 1 - \frac{\pi}{2} \left(2\sqrt{3} - 3\right) \approx 0.27 \quad (2:18) \]

That means that by inserting an additional smaller particle size distribution, the theoretical bed void can be halved (from 0.48 to 0.27).
3. Material and methods

3.1. Material information
Initially there were 10 different samples including 1 fossil coal, 2 fossil cokes, and 7 bio-coals.

Table 3-1. List of name and production procedure for the different coals. (Robinson, 2020)

<table>
<thead>
<tr>
<th>Fossil coal</th>
<th>Material data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>Anthracite coal</td>
</tr>
<tr>
<td>High quality coke</td>
<td>High quality metallurgical coke</td>
</tr>
<tr>
<td>Low quality coke</td>
<td>Lower quality metallurgical coke</td>
</tr>
<tr>
<td>Bio-coal</td>
<td>Material data</td>
</tr>
<tr>
<td>MEVA</td>
<td>Spruce powder, pyrolyzed at T ≈ 1000°C, t &lt; 10 s</td>
</tr>
<tr>
<td>Harads 1</td>
<td>Birch chips, pyrolyzed at T ≈ 650 °C, t ≈ 60 min, sampled after a few hours (at the beginning of the operation)</td>
</tr>
<tr>
<td>Harads 2</td>
<td>Birch chips, pyrolyzed at T ≈ 650 °C, t ≈ 60 min, sampled after a day (at the steady operation)</td>
</tr>
<tr>
<td>BBQ as-is</td>
<td>Standard barbecue charcoal</td>
</tr>
<tr>
<td>BBQ extruded</td>
<td>Extruded barbecue charcoal, pyrolyzed at T ≈ 450 °C</td>
</tr>
<tr>
<td>Cortus Bark</td>
<td>Crushed extrudates of pyrolyzed Bark, Bark pyrolyzed at T ≈ 1100 °C, t ≈ 20-30 min</td>
</tr>
<tr>
<td>Cortus Pellets</td>
<td>Crushed extrudates of pyrolyzed wood Pellets, Pellets pyrolyzed at T ≈ 1100 °C, t ≈ 20-30 min</td>
</tr>
</tbody>
</table>

From these samples three bio-coals and one fossil coal were selected for further testing. The criteria were their reaction rate and to include one extruded material. Each sample was tested once by the same method as described in 3.3, Intrinsic reactivity measurement (Regime I) to get an approximation of their reaction rate. Then, their reaction were normalized and the time was compared to each other.
3.2. Preparation and initial measurements

3.2.1. Sample preparation

The preparation of each sample was done according to DIN 51701-3: 2006 Testing of solid fuels - Sampling and sample preparation. Samples were received from Höganäs AB.

Bulk density and moisture content were measured on the as-received samples. The samples were then pre-dried in an oven at 40 °C for 12 h. Bulk density and moisture content were measured again after drying. Then the samples were separated for a different test. The following characteristics of the samples were examined:

1. Envelope density
2. True density
3. Particle size distribution
4. Higher heating value
5. Ultimate analysis
6. Proximate analysis
7. Intrinsic reactivity
8. Apparent reactivity of as-received samples
9. Apparent reactivity of sieved samples

For a graphic view, see Appendix 3. Graphical representation of the preparation.

3.2.1.1. Drying

The drying was done in an oven at 40 °C for 12-14 h. Wet material is the sample as received. After it has dried in the oven it is called “dry” even if there still is small amounts of moisture in it.

3.2.1.2. Sample separation

Each sample was delivered in one big container with around 300 g. That was divided into eight equal-sized samples by using a rotary sample divider (Retsch PT100). During the separation, a sample was put in the hopper and was fed into the dividing head by means of vibration. The dividing head was rotated at 110 rpm during the separation. For a test that demanded a smaller amount, 1/8 of the received sample was weighed and put into the divider again until the target was reached. The target was ~2 g for the reactivity measurement at Regime I. If more than one bottle was used from the previous division, the bottle on the opposite side was picked.
3.2.1.3. Density measurements

![Bulk](image1.png) ![Envelop](image2.png) ![True](image3.png)

Figure 3-1. The difference between bulk, envelop and true density. (Phounglamcheik, 2019)

**Bulk density**

Bulk density of the samples was determined by measuring the volume and mass of the samples according to analogue VDLUFA-Method A 13.2.1. The sample was put into a graduated cylinder with a volume of 500 ml and accuracy of ±5 ml. The volume was measured after compressing the cylinder 10 times through tapping the bottom. Then the mass was measured by using an analytical balance with an accuracy of ±1 mg. Bulk density was then calculated based on mass and volume. To make certain that the variation of properties are negligible inside the container, each sample was measured three times at their predetermined locations (at the top, middle and bottom) in the container.

**Envelope density**

In order to measure the envelope density, the voids between the particles should be filled with a filler material. Al₂O₃ was used as filler in this work. Table 3-2 shows the particle size distribution of Al₂O₃.

Around 15 ml of Al₂O₃ was filled into a graduated cylinder (25:0.5 ml) and was tapped 10 times. The initial mass and volume were measured. Then approximately 3-5 ml of a sample was added into the cylinder. The solids were mixed manually by covering the top and shake the container by repeatedly turning it upside down and roll it on the table. This procedure was carried out slowly in order to avoid fragmentation of the bio-coal. The final mass was measured after the sample were completely covered. The cylinder was then tapped 10 times. Then the volume increase could be measured. The envelope density was calculated by the ratio of the mass and volume differences as shown in equation (3:1)

\[
\text{Envelop density} = \frac{\Delta m}{\Delta V}
\]

Table 3-2. Particle size distribution for Al₂O₃.

<table>
<thead>
<tr>
<th>Size range</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;2 mm</td>
<td>&lt;2%</td>
</tr>
<tr>
<td>&lt;0.063 mm</td>
<td>&lt;28%</td>
</tr>
<tr>
<td>&gt;0.063 mm</td>
<td>&gt;72%</td>
</tr>
</tbody>
</table>

The samples with relatively large particle size were selected in this analysis in order to minimize experimental error due to the particles those are smaller than the filler
material. However, experimental error become larger if the particle size of the sample material is smaller than 0.143 mm (according to an estimation based on assumption described in Section 2.5.1). To make certain that the variation of properties are negligible inside the container, each sample was measured three times at their predetermined locations (at the top, middle and bottom) in the container.

**True density measurement**

True density analysis of the samples was done using Micrometrics AccuPyc II 1340 gas displacement pycnometry system with helium as the medium. Prior to the analysis, each sample was prepared by drying at 105 °C to remove the moisture in the particles. In the analysis, as the helium gas filled in both the internal and the external voids of the particles, the true density of the particles was calculated by the instrument based on the principle of volume displacement.

### 3.2.1.4. Particle size distribution

The particle size distribution was measured in two steps. The first step was the coarse range, i.e. 1 – 7.1 mm. That was done according to ASTM C 136 – 01. A stack of sieves with mesh aperture widths of 7.1 mm, 6.3 mm, 5.0 mm, 4.0 mm, 3.15 mm, 2.0 mm, and 1.0 mm and Retsch AS200 mechanical sieve shaker were used in this step. For this portion between 20 – 70 g of the test sample was put into the stack and was sieved for 15 min with the sieve shaker set at 45%. Then the mass of the different sections was measured. That gave the mass fractions based on size distributions. If more than 2% of the original mass was missing, then the resulting data and remaining material were discarded, and a new test had to be done.

The second step, i.e. particle size below 1 mm, was done by using Retsch Camsizer XT. After the first step, the finer particles below 1 mm had been extracted. They were put into the feed hopper and moved into the Camsizer by means of vibration and vacuum pressure. The particles passed in front of a LED light and were captured by two CCD cameras. The digital images were recorded and processed by a built-in algorithm. That led to a size distribution based on the captured images of the particle geometry.

### 3.2.1.5. Higher Heating Value (HHV)

Higher heating value is how much energy you get by cooling the combusted products down to room temperature (25°C) and condensing any water vapor. The higher heating value was measured by using a bomb calorimeter, IKA C200. It operates on the principle of complete adiabatic combustion under pure oxygen at 30 bar. The HHV was calculated by the temperature increase of the water bath where the combustion chamber was submerged. Each material was tested with a 1 g sample with a size distribution <1 mm.

The energy density can then be calculated by:

$$HHV \left( \frac{MJ}{m^3} \right) = HHV \left( \frac{MJ}{kg} \right) \times \text{bulk density} \left( \frac{kg}{m^3} \right)$$  \hspace{1cm} (3:2)

### 3.2.1.6. Ultimate analysis

Elemental carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) content of each sample was determined using EuroVector EA3000 which operates based on combustion (for CHNS analysis) or pyrolysis (for O analysis) and followed by gas
chromatography with helium as the carrier gas. For each CHN, O, and S analysis, the experiment started with the construction of a calibration curve as reference data using standard compounds, which was acetanilide for CHN and O analysis, and sulphanilamide for S analysis.

Once the equipment was calibrated, samples were prepared by placing 0.5-2.5 mg of the ground sample in the designated capsule for the specific analysis - tin capsules for CHN and S analyses and silver capsules for O analysis. The mass of the elements in the sample should be inside the elementary range of the calibration materials to minimize the errors. Based on the element retention time, peak and area below the curve were measured, and the elemental contents of the elements in the sample could be calculated by Callidus software coupled to the instrument.

**3.2.1.7. Proximate analysis**

**Moisture content**
Moisture content is the amount of water in the sample. The moisture content was measured with Mettler Toledo Moisture Analyzer MJ33 based on thermogravimetric principles. Around 1 g of material was used in each test. The sample was heated to 105 °C. Then the moisture content was determined by measuring the mass loss during the drying process. Each sample was tested three to four times.

\[
\text{Moisture content} = 1 - \frac{m_{\text{final}}}{m_{\text{initial}}} \, [%] \tag{3:3}
\]

**Volatile content**
Volatile matter (VM) of each sample was determined based on thermogravimetric (TG) principle, according to DIN 51720: Determining the volatile matter content of solid fuels. For each sample, approximately 1 g of ground sample was put in a ceramic crucible (bottom dia. x height ≈ 2 cm x 4 cm) with a lid. The crucible was then placed in a preheated macro-TG reactor at 900 ± 5 °C under nitrogen atmosphere (N₂ flow rate of 7 L min⁻¹) for 30 minutes, or until a constant mass was achieved, the mass of the sample being constantly monitored. The volatile matter content was then calculated according to equation (3:4) as follow.

\[
VM = 1 - \frac{m_{\text{final}}}{m_{\text{initial}}} \, [%] \tag{3:4}
\]

Where, m is the mass of the sample in [g].

**Ash content**
The determination of ash content was performed based on the thermogravimetric principle according to DIN 51719: Testing of solid fuels – Solid mineral fuels – Determination of ash content. For each sample, approximately 2 mg of a ground sample with particles <1 mm was put in a sample tray and was heated up in a ThermoGravimetric Analysis (TGA) reactor through two heating phases while constantly monitoring the mass of the sample/tray.

In the first heating phase, the sample was heated up from 30 to 105 °C with a heating rate of 5 °C min⁻¹ under nitrogen atmosphere (N₂ flow rate of 50 mL min⁻¹) until a constant mass was reached (mass difference less than 0.05%).
In the following heating phase, fossil coal and bio-coal were heated to different temperatures. The bio-coal samples were heated up to 550 °C while the fossil coal were heated to 815 °C with a heating rate of 5 °C min\(^{-1}\) under oxygen-enriched atmosphere, i.e. 20\% (vol.) of O\(_2\) with the same total volume flow (50 mL min\(^{-1}\)). The different temperature standards come from different ash content. Certain elements in biomass ash are volatile at temperatures above 550 °C.

Once the targeted temperature in the second phase was reached, the temperature was held for 30 minutes or until a constant mass was achieved. At this point, all the organic matter was supposed to be completely combusted and converted into gaseous products and water vapor, thus the ash content of the sample was determined based on the remaining mass on the crucible as presented in equation (3:5):

\[
\text{Ash content} = \frac{m_{\text{final}}}{m_{\text{initial}}} \quad [\%] \tag{3:5}
\]

Where, \(m\) is the mass of sample in [g].

**Fixed carbon**

The value for fixed carbon in bio-coal can be calculated knowing the moisture content, ash content and volatile matter (Speight, 2015).

\[
\text{Fixed carbon} = 100\% - \text{Moisture} - \text{Ash} - VM \quad [\%] \tag{3:6}
\]

Fixed carbon is what Höganäs AB want in their processes. Because VM reacts fast and is burnt off too early in the sponge iron process, it does not contribute significantly to heat generation or iron ore reduction (Robinson, 2020).
3.3. Intrinsic reactivity measurement (Regime I)

For the intrinsic reactivity experiment, a TGA8000 and a Gas Mixing Device (GMD) from PerkinElmer was used. The schematic diagram of TGA8000 can be seen in Figure 3-2. The sample tray is hung on a hook connected to an analytical scale inside the reactor. The gas flow comes from the top and exits at the bottom of the reactor chamber. The sample tray is surrounded by heating elements.

All samples were measured once, and the reaction rate and structural parameter ($\psi$) were approximated by curve fitting. From an initial 10 samples, 3 samples were picked by the criteria mentioned in Section 3.1. They were tested in 8 different conditions. Each condition was repeated 3 times for each sample, i.e. 45 tests in total. For the different test conditions, see Table 3-3. The variation of CO$_2$ concentrations in the gas mix was tested at two different temperatures so they could be compared to each other.

Around 1 mg of the sample with a particle diameter <75 μm was used in this analysis. The test started at 30 °C and temperature was increased by 10 °C min$^{-1}$ in a pure nitrogen environment. During the entire test, the total gas flow was 50 mL min$^{-1}$. At the target temperature, the gas composition was changed from pure nitrogen to a pre-determined mixture of CO$_2$ and N$_2$. The considered reaction was the Boudouard reaction, as shown in (1:1). The test was in an isothermal environment until the weight loss had stopped.

![Figure 3-2. Schematic of the TGA](image)

Table 3-3. Experimental conditions for intrinsic reactivity measurement.

<table>
<thead>
<tr>
<th>CO$_2$ = 10%</th>
<th>CO$_2$ = 20%</th>
<th>CO$_2$ = 40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=850 °C</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>T=830 °C</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>T=800 °C</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>T=770°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.1. Calculation of reaction rate constant from random pore model

The apparent reaction rate constant, $k$, was calculated from the random pore model, referring to equation (2:1) and (2:2), as can be written as:

$$\frac{dX}{dt} = k \times (1 - X) \times \sqrt{1 - \psi} \times \ln(1 - X)$$  \hspace{1cm} (3:7)

After integrating equation (3:7), it will become:
\[
\left(\frac{2}{\psi}\right) \times \left[\sqrt{1 - \psi \ln(1 - X)} - 1\right] = k \times t
\]  
(3:8)

The structural parameter, \(\psi\), was estimated from the experimental data using the reaction time between a starting point (SP) and 80% (SP \(\leq X \leq 0.8\)). 80% was chosen because for the last \(~10\%\) of the weight the reaction rate was not stable. This is because a small variation in initial ash content affects the reaction rate significantly. The starting point is the same as the percentage of volatile matter for the sample. That is because the VM is released fast in the reaction and not according to the Boudouard reaction.

\[
\frac{\left[\sqrt{1 - \psi \ln(1 - X)} - 1\right]}{\left[\sqrt{1 - \psi \ln(1 - 0.8)} - 1\right]} = \frac{t}{t_{X=0.8}}
\]  
(3:9)

The accuracy of the parameter fitting was tested by the following relationship,

\[
Rsqr = 1 - \sqrt{\frac{\sum_{1}^{n} \left(\frac{dx}{dt}_{exp} - \frac{dx}{dt}_{model}\right)^{2}}{n}}
\]  
(3:10)

The best fitted structural parameter gave the closest value to 1.

With \(\psi\) the \(k\) value can be calculated by finding the slope of the reaction rate curve in the experiment as can be seen in Figure 3-3.

![Mass balance over time](image)

Figure 3-3. K value is the same as the rate of change.
3.3.2. Calculation of kinetic parameters.

In order to determine kinetic parameters, the logarithmic form of the rate expression, equation (2:5), was applied, which can be written as

$$
\log (k) = \log(k_{\text{ref}}) + \frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) + n \cdot \log \left( \frac{P_{CO_2}}{P_{CO_2,\text{ref}}} \right)
$$

(3:11)

The reference point is chosen from Table 3-3. $P_{CO_2}$ at 20% and temperature is tested at two points, either $T_{\text{ref}}$ at 800 °C or $T_{\text{ref}}$ at 850 °C. That is tested by comparing the test results to the theory through equation (3:11). The reference temperature is chosen to be as high as possible and still not having internal diffusion occur for the experiment at that temperature. To find out the values for $E$ and $n$, an interpolation is performed with the test data from the conditions described in Table 3-3.

3.4. Apparent reactivity measurement in the internal diffusion control regime (Regime II)

The same equipment (TGA and GMD) as for intrinsic reactivity measurement was used.

The selected particle size distributions were:

- 6.3-4 mm
- 3.15-2 mm
- 1-0.8 mm
- 0.4-0.315 mm
- 0.212-0.18 mm

A single layer of the sample was put into the crucible with the goal to cover the base of the crucible as can be seen in Figure 3-4. That means that different mass was used depending on the particle size. The test started at a temperature of 30 °C and increased rapidly to 850 °C with a heating rate of 415 °C min$^{-1}$ under pure nitrogen. At target temperature, the gas was switched from pure nitrogen to a predetermined mixture of 40% CO$_2$ 60% N$_2$ the total volume flow was constant at 50 mL min$^{-1}$. The actual test is in an isothermal condition until >50% of the weight is lost. From that the effectiveness factor is calculated with equation (2:8).

3.4.1. Diffusion model

The decrease in reaction rate from diffusion was modeled using Thiele modulus, equation (2:11):

$$
\phi = L_e \cdot \frac{n + 1/2 \cdot D_{\text{eff}} \cdot k_{\text{ref}}} {E/R} \exp \left( - \frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \cdot \frac{n-1}{n} \frac{P_{CO_2}^{n-1}}{P_{CO_2,\text{ref}}^{n-1}} \cdot \frac{\rho_{CO_2}}{\rho_{CO_2,\text{ref}}} \cdot M_{CO_2} \cdot RT
$$

(2:11)

As long as temperature and pressure are constant then the square root is a constant. That means that equation (2:11) can be simplified:
\[
\frac{\phi}{L_c} = \text{Constant} \tag{3:12}
\]

\[
\text{Constant} = \sqrt{\frac{n + 1}{2 \cdot D_{\text{eff}}} \cdot k_{\text{ref}} \cdot \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \cdot \frac{P_{\text{CO}_2}^{n-1}}{P_{\text{CO}_2\text{ref}}} \cdot \frac{P_{\text{CO}_2}}{M_{\text{w}}} \cdot RT} \tag{3:13}
\]

From the Constant the value of \( D_{\text{eff}} \) can be separated out:

\[
D_{\text{eff}} = \frac{n + 1}{2 \cdot \text{Constant}^2} \cdot k_{\text{ref}} \cdot \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \cdot \frac{P_{\text{CO}_2}^{n-1}}{P_{\text{CO}_2\text{ref}}} \cdot \frac{P_{\text{CO}_2}}{M_{\text{w}}} \cdot RT \tag{3:14}
\]

3.5. Apparent reactivity measurement in the bulk diffusion control regime (Regime III)

For external diffusion experiments, a macro-TG reactor was used. Every test was done once.

The schematic diagram of the macro-TG reactor can be seen in Figure 3-5. The reactor is an externally heated stainless-steel cylinder (grade 304). The internal diameter of the reactor is 40.5 mm and 360 mm in the length of the heating zone. A ceramic crucible (2 cm in diameter and 4 cm in height) connected with an analytical scale was hung from the top of the reactor chamber. The reactor temperature was measured by a Type N thermocouple placed at the center of the reactor and 1 cm below the sample crucible. The carrier gas entered the reactor from the bottom and left at the top with volatile gases generated during the experiment.

The size ranges for the material were the same for external diffusion as it was for internal diffusion. Prior to the experiment, the macro-TG is set at a target temperature of 1100 °C before any gas is turned on. With the gas turned on the temperature stabilizes around 980 °C. The total gas flow is 5 L min\(^{-1}\). That is split into 3 L min\(^{-1}\) N\(_2\) and 2 L min\(^{-1}\) CO\(_2\) for a concentration of 40% (vol.) CO\(_2\). Then, the sample was lowered down manually into the reactor. The recording of the temperature started before the sample was lowered. The mass of the sample was recorded after the sample was placed inside the reactor. (N\(_2\))

To test the external diffusion, the volume of the samples was kept at around 6.5 cm\(^3\) while the particle size distribution changed.

![Figure 3-5. Macro- TG schematic](image)
4. Results and discussion

4.1. Material selection

The first tests in Regime I was to see the initial reaction rates for the different bio-coal samples.

As can be seen in Figure 4-1. The bio-coals react at a different speeds compared to each other. Three different materials were chosen for further testing: Harads coal, Cortus Bark and extruded BBQ. This selection includes one extruded material, two materials from the grouping of slowest reaction rates and one material with an intermediate reaction rate.

![Conversion of bio-coal and Anthracite at 850 degrees and 20% CO2](image)

Figure 4-1. First test to see how the bio-coal ranked between each other. A fossil coal, anthracite, is the slowest one.

After two hours anthracite had reached ~10% of conversion compared to bio-coals that was over 60%.

In Figure 4-1 the slowest bio-coal material is BBQ as-is. But this result was not available when the materials were picked for further testing.
4.2. Material data

4.2.1. Density measurements

The different density measurements have been summarized in Figure 4-2. In Table 4-1 the data has been summarized. In the table, there is also data for the particle porosity and bed porosity.

<table>
<thead>
<tr>
<th>Density</th>
<th>Anthracite</th>
<th>Cortus Bark</th>
<th>Extruded BBQ</th>
<th>Harads 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (dry)</td>
<td>972</td>
<td>572</td>
<td>382</td>
<td>176</td>
</tr>
<tr>
<td>Envelop Density</td>
<td>1389</td>
<td>783</td>
<td>761</td>
<td>480</td>
</tr>
<tr>
<td>True density</td>
<td>1718.8</td>
<td>1901</td>
<td>1565</td>
<td>1548</td>
</tr>
<tr>
<td>Particle porosity</td>
<td>19%</td>
<td>59%</td>
<td>51%</td>
<td>69%</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>30%</td>
<td>27%</td>
<td>50%</td>
<td>63%</td>
</tr>
</tbody>
</table>

Figure 4-2. Measurement of density.

Table 4-1. Different densities for material and their particle void and bed void.

The theory in equation (2:14) and (2:18) showed that a single particle distribution should have a bed porosity of 44% and an optimal dual distribution should have a bed porosity around 27%. Compared to that, Anthracite and Cortus bark samples show bed porosity close to the expected value for a dual distribution at 30 and 27%, respectively. While the bed porosity of Extruded BBQ and Harads 2 samples are
much higher than the theoretical value. This different in the latter samples may occurred due to the particle shape of the samples are different from sphere.

4.2.2. Particle size and distribution analysis

The coarse particle size distribution of dried samples is summarized in Table 4-2 and can also be visualized in Figure 4-3.

The fine particle size distribution can be seen in Figure 4-4.

Table 4-2. Coarse particle size distribution of dried samples. The percentage is of initial mass.

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Anthracite</th>
<th>Cortus Bark</th>
<th>Extruded BBQ</th>
<th>Harads 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;7.1 mm</td>
<td>3.90%</td>
<td>0.45%</td>
<td>93.57%</td>
<td>16.50%</td>
</tr>
<tr>
<td>&gt;6.3 mm</td>
<td>5.40%</td>
<td>2.06%</td>
<td>1.12%</td>
<td>4.90%</td>
</tr>
<tr>
<td>&gt;5.0 mm</td>
<td>8.40%</td>
<td>4.05%</td>
<td>0.00%</td>
<td>12.60%</td>
</tr>
<tr>
<td>&gt;4.0 mm</td>
<td>8.80%</td>
<td>6.27%</td>
<td>0.26%</td>
<td>12.30%</td>
</tr>
<tr>
<td>&gt;3.15 mm</td>
<td>6.70%</td>
<td>4.92%</td>
<td>0.17%</td>
<td>8.30%</td>
</tr>
<tr>
<td>&gt;2.0 mm</td>
<td>14.70%</td>
<td>7.49%</td>
<td>0.06%</td>
<td>13.20%</td>
</tr>
<tr>
<td>&gt;1.0 mm</td>
<td>17.20%</td>
<td>10.43%</td>
<td>0.28%</td>
<td>13.70%</td>
</tr>
<tr>
<td>&lt;1.0 mm</td>
<td>34.80%</td>
<td>64.32%</td>
<td>4.53%</td>
<td>18.30%</td>
</tr>
</tbody>
</table>

Figure 4-3. Coarse particle size distribution of dried sample. Same distributions as in Table 4-2
Figure 4-4. Fine particle size distribution by dry basis. Percentage is from total amount of photographed particles. The initial sample is from the fraction below 1 mm in the course particle distribution test.

As can be seen in Figure 4-3 and Table 4-1. Extruded BBQ is dominated by its extrusion and has a singular particle that is much larger than the other. That leads to that the BBQ has the second highest bed void. Harads does not have such obvious reason in the particle distribution. To see the aspects ratio for particles <1 mm see Appendix 4.

Cortus Bark differs from the other samples in that it had around 65% of total mass below 1 mm while the other materials had much smaller amount below 1 mm.

4.2.3. Ultimate analysis

The ultimate analysis comparison can be seen in Table 4-3.

Table 4-3. Ultimate analysis of pre-dried samples.

<table>
<thead>
<tr>
<th></th>
<th>Anthracite</th>
<th>Cortus Bark</th>
<th>Extruded BBQ</th>
<th>Harads 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>82.2% ± 0.5%</td>
<td>82.4% ± 0.8%</td>
<td>84.7% ± 1.1%</td>
<td>91.5% ± 0.1%</td>
</tr>
<tr>
<td>H</td>
<td>1.8% ± 0.1%</td>
<td>0.5% ± 0.0%</td>
<td>2.5% ± 0.0%</td>
<td>2.1% ± 0.0%</td>
</tr>
<tr>
<td>N</td>
<td>0% ± 0.0%</td>
<td>0.5% ± 0.2%</td>
<td>0.4% ± 0.4%</td>
<td>0.4% ± 0.3%</td>
</tr>
<tr>
<td>O</td>
<td>2.7% ± 0.1%</td>
<td>5.8% ± 0.2%</td>
<td>9.2% ± 1.4%</td>
<td>3.2% ± 0.3%</td>
</tr>
<tr>
<td>S</td>
<td>1.1%</td>
<td>0.023%</td>
<td>0.04%</td>
<td>-</td>
</tr>
</tbody>
</table>

There were no signal for Sulphur in the experiments of bio-coals. Instead the values for Cortus Bark and extruded BBQ come from Robinson Ryan at Höganäs (2020, April). The missing percentages is ash.
The total carbon content is a measure of how useful the sample could be in the sponge iron process. As carbon is the primary reducing agent.

4.2.4. Proximate analysis

The result from proximate analysis is shown in Table 4-4.

Table 4-4. Proximate analysis of samples.

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Anthracite</th>
<th>Cortus Bark</th>
<th>Extruded BBQ</th>
<th>Harads 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (wet)</td>
<td>3.1% ± 0.4%</td>
<td>1.7% ± 0.2%</td>
<td>3.5% ± 0.2%</td>
<td>1.5% ± 0.4%</td>
</tr>
<tr>
<td>Moisture content (dry)</td>
<td>0.7% ± 0.1%</td>
<td>0.9% ± 0.1%</td>
<td>1.2% ± 0.1%</td>
<td>1.4% ± 0.1%</td>
</tr>
<tr>
<td>Volatile Matters</td>
<td>8.0% ± 1.3%</td>
<td>2.0% ± 0.5%</td>
<td>17.0% ± 1.0%</td>
<td>11.0% ± 1.4%</td>
</tr>
<tr>
<td>Ash at 815 °C</td>
<td>10.3% ± 0.9%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash at 550 °C</td>
<td></td>
<td>11.6% ± 0.3%</td>
<td>2.2% ± 0.2%</td>
<td>1.7% ± 0.1%</td>
</tr>
<tr>
<td>Fixed carbon (wet)</td>
<td>78.7%</td>
<td>84.7%</td>
<td>77.3%</td>
<td>85.8%</td>
</tr>
<tr>
<td>Fixed carbon (dry)</td>
<td>81.1%</td>
<td>85.5%</td>
<td>79.5%</td>
<td>85.8%</td>
</tr>
</tbody>
</table>

The weight adjusted for removal of volatile matter was used as starting point (SP) for the kinetic parameter tests. Cortus Bark has much lower volatile content than the other Bio-coals. Extruded BBQ has the lowest fixed carbon of all the tested samples.

4.2.5. Higher heating value analysis

The result from the bomb calorimeter is shown in Figure 4-5. The energy density is calculated by using the result from Table 4-1.
For the Höganäs sponge iron process, if a reduction agent has both a high HHV and reasonably high density means that the process will need less extra energy input from for example natural gas. Furthermore, a high HHV means low endothermicity for the Boudouard reaction. Because each batch is packed in a fixed capsule the energy density is the important value. From Figure 4-6 it is shown that Cortus Bark only provides ~60% of the energy anthracite does. That means that Höganäs would need to add more external energy to compensate.
4.3. Regime I (Kinetic parameters of bio coal)

4.3.1. *Cortus Bark*

The intrinsic parameters for Cortus Bark can be seen in Figure 4-7 through to Figure 4-8. To find the activation energy (E) the Arrhenius plot, representing the logarithmic reaction rate against the inverse temperature, for Cortus Bark is used.

Figure 4-7. Arrhenius plot for the tested temperatures for Cortus Bark.

The reaction order can be found by doing the interpolation against the reaction rate and concentration of CO\textsubscript{2} in Figure 4-8.

Figure 4-8. Comparing different concentration of CO\textsubscript{2} at and T=850 °C for Cortus Bark.

All the values for the model of intrinsic reaction rate of Cortus Bark is summarized in Table 4-5.
Table 4-5. Model values for Cortus Bark

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cortus Bark</strong></td>
<td><strong>Units</strong></td>
<td><strong>Value</strong></td>
</tr>
<tr>
<td>$k_{ref}$</td>
<td>1/min</td>
<td>0.0051</td>
</tr>
<tr>
<td>$T_{ref}$</td>
<td>°C</td>
<td>850</td>
</tr>
<tr>
<td>$pCO_{2ref}$</td>
<td>atm</td>
<td>0.20</td>
</tr>
<tr>
<td>$E$</td>
<td>kJ/mol</td>
<td>187</td>
</tr>
<tr>
<td>$R_{sqr} E$</td>
<td>-</td>
<td>0.852</td>
</tr>
<tr>
<td>$n$</td>
<td>-</td>
<td>0.365</td>
</tr>
<tr>
<td>$R_{sqr} n$</td>
<td>-</td>
<td>0.895</td>
</tr>
<tr>
<td>$\psi_{avg}$</td>
<td>-</td>
<td>3.568</td>
</tr>
</tbody>
</table>

4.3.2. Extruded BBQ

This is the same data set as for Cortus Bark shown for extruded BBQ. For extruded BBQ, the fastest reaction speed at 850 °C starts to show diffusion effects. As can be seen from Figure 4-9, the highest temperature at 850 °C starts to experience internal diffusion. The relation between log($k$) and $T^{-1}$ should be linear according to the theory shown in equation (3:11). For $T^{-1}$ at $8.9 \times 10^{-4}$ and $9.05 \times 10^{-4}$ the average value for log($k$) is almost the same. That means that it is not the intrinsic reaction rate that is the limiting factor at that point. Because of this, the interpolation is based on the temperature interval 770-830 °C instead, as seen in Figure 4-10.

Figure 4-9. Arrhenius plot for the tested temperatures for extruded BBQ.
Figure 4-10. Interpolation from 770-830 °C to find the activation energy for extruded BBQ.

As can be seen in Figure 4-11 it is not as easy to create a model for extruded BBQ as for Cortus Bark. That can also be shown from Rsqr in Table 4-6. One reason for that might be that the results from extruded BBQ could change widely between tests. The consistency in the results was low. One possible explanation for lack of consistency can be because of uncertainty in the experiment caused by equipment failure, gas impurity, or human error.

All the values for the model of intrinsic reaction rate of Extruded BBQ is summarized in Table 4-6.
Table 4-6. Model values for extruded BBQ.

<table>
<thead>
<tr>
<th>Extruded BBQ</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{ref} )</td>
<td>1/min</td>
<td>0.0035</td>
</tr>
<tr>
<td>( T_{ref} )</td>
<td>°C</td>
<td>800</td>
</tr>
<tr>
<td>( pCO_{2ref} )</td>
<td>atm</td>
<td>0.20</td>
</tr>
<tr>
<td>( E )</td>
<td>kJ/ mol</td>
<td>138</td>
</tr>
<tr>
<td>( Rsqr E )</td>
<td>-</td>
<td>0.703</td>
</tr>
<tr>
<td>( n )</td>
<td>-</td>
<td>0.419</td>
</tr>
<tr>
<td>( Rsqr n )</td>
<td>-</td>
<td>0.524</td>
</tr>
<tr>
<td>( \psi_{avg} )</td>
<td>-</td>
<td>0.868</td>
</tr>
</tbody>
</table>

4.3.3. Harads 2

This is the same data set for Harads 2 as it is for Cortus Bark and extruded BBQ. Here there is an even larger drop at 850 °C. For explanation how to see where internal diffusion start to occur see 4.3.1.

Figure 4-12. Arrhenius plot for the tested temperatures for Harads 2.
Figure 4-13. Interpolation from 770-830 °C to find the activation energy for Harads 2.

Figure 4-14. Concentration of CO₂ at T=800 °C for Harads 2.

All the values for the model of intrinsic reaction rate of Harads is summarized in Table 4-7.

Harads 2 is the same as for extruded BBQ and not as easy as to create a model for as Cortus Bark. The problems also be caused by the same sources (equipment failure, gas impurity, or human error) as mentioned previously for extruded BBQ.
Table 4-7. Model values for Harads 2.

<table>
<thead>
<tr>
<th>Units</th>
<th>Harads 2</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ref}$</td>
<td>1/min</td>
<td>0.0039</td>
</tr>
<tr>
<td>$T_{ref}$</td>
<td>°C</td>
<td>800</td>
</tr>
<tr>
<td>$pCO_{2ref}$</td>
<td>atm</td>
<td>0.20</td>
</tr>
<tr>
<td>$E$</td>
<td>kJ/ mole</td>
<td>165</td>
</tr>
<tr>
<td>Rsqr E</td>
<td>-</td>
<td>0.842</td>
</tr>
<tr>
<td>n</td>
<td>-</td>
<td>0.153</td>
</tr>
<tr>
<td>Rsqr n</td>
<td>-</td>
<td>0.145</td>
</tr>
<tr>
<td>$\psi_{avg}$</td>
<td>-</td>
<td>0.830</td>
</tr>
</tbody>
</table>

Harads 2 has much lower fit for reaction order, Rsqr n, than the other materials.

4.3.4. Analysis of kinetic parameters

Table 4-8. Summary of different model parameters.

<table>
<thead>
<tr>
<th>Units</th>
<th>Cortus Bark</th>
<th>Extruded BBQ</th>
<th>Harads 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ref}$</td>
<td>1/min</td>
<td>0.0051</td>
<td>0.0035</td>
</tr>
<tr>
<td>$T_{ref}$</td>
<td>°C</td>
<td>850</td>
<td>800</td>
</tr>
<tr>
<td>$pCO_{2ref}$</td>
<td>atm</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>$E$</td>
<td>kJ/ mole</td>
<td>187</td>
<td>138</td>
</tr>
<tr>
<td>Rsqr E</td>
<td>-</td>
<td>0.852</td>
<td>0.703</td>
</tr>
<tr>
<td>n</td>
<td>-</td>
<td>0.365</td>
<td>0.419</td>
</tr>
<tr>
<td>Rsqr n</td>
<td>-</td>
<td>0.895</td>
<td>0.524</td>
</tr>
<tr>
<td>$\psi_{avg}$</td>
<td>-</td>
<td>3.568</td>
<td>0.868</td>
</tr>
<tr>
<td>Particle porosity</td>
<td>-</td>
<td>59%</td>
<td>51%</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>-</td>
<td>27%</td>
<td>50%</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>-</td>
<td>2.0% ± 0.5%</td>
<td>17.0% ± 1.0%</td>
</tr>
<tr>
<td>Pyrolysis temperature</td>
<td>[°C]</td>
<td>1100</td>
<td>450</td>
</tr>
</tbody>
</table>

As can be seen in Table 4-8 only Cortus Bark could be modeled by a linear interpolation for equation (2:4). Cortus Bark had Rsqr above 0.8 for both parameters while the other two had one of their parameters, reaction order, at Rsqr<0.5. From the analysis of the materials and the initial condition there are two possible sources of error. The volatile matter content and/or the pyrolysis temperature used during the creation of the material. Other than these two errors there may be human errors in the test or unknown errors.
Cortus Bark has a low volatile matter content at 2% while extruded BBQ and Harads 2 have 17% and 11% volatiles respectively. The volatile matter content is compensated for by starting the measurements for Regime I at a point after the volatiles have disappeared. The measurements started after the mass had decreased the same amount as the volatiles in the material.

For the pyrolysis, Cortus Bark has been heated to 1100 °C while Harads 2 was only heated to 650 °C and extruded BBQ was only heated to 450 °C. That means when the operation temperature during kinetic testing is at 800 °C, pyrolysis reactions can conceivably start again in Harads 2 and extruded BBQ. A supporting argument for this hypothesis is that extruded BBQ has even lower pyrolysis temperature than Harads 2 and that the resulting data from extruded BBQ is even less consistent with the theory. It is recommended to do more analysis on this relationship.

![Distribution of $\psi$ values for constant T](image)

Figure 4-15. $\psi$ distribution at T=800 and 850 °C with varying CO$_2$ concentration.

As seen in Figure 4-15. The different samples have a different $\psi$ dependence on temperature, with Cortus Bark having the least temperature dependence of $\psi$. Assuming the initial particle porosity is constant between different trials of the same material, results lead us to conclude that the pore structure is changing with temperature for the other materials, extruded BBQ and Harads 2, according to equation (2:7).
The results in Figure 4.15 come from measuring kinetic parameters with particle size <75 μm. For this scale reactions should occur uniformly throughout the particle. So the shape properties should not significantly influence the reactions more than the Chemical reaction.

The reason Cortus Bark is more stable at higher temperatures can be because its origin comes from treatment at a much higher pyrolysis temperature. So, when pyrolysis temperatures for the other test samples are much lower than 800 °C, it is conceivable that some pyrolysis reactions occur during the kinetic analysis at ≥ 800 °C thereby contributing to a more dramatic change in their pore structure.

The results can also be uncertain due to errors caused by equipment failure, gas impurity, or human error.

4.4. Regime II (Effect of particle size on internal effectiveness factor)
Only Cortus Bark was tested for this regime because it has most reliable kinetic data from regime I. Figure 4.16 shows how the change in average particle size distribution influences how fast the particle reacts when particles are exposed to the same surface conditions.

![Graph](image)

**Figure 4-16. Effectiveness factors change for Cortus Bark material for a single layer with changing particle size distribution.**
Figure 4-17. Thiele modulus for Cortus Bark at T= 850 °C and p_{CO2} = 20%. The test show particle size distributions.

The slope for the Thiele modulus interpolation in Figure 4-17 give the constant from equation (3:12). That constant is 0.2979 with a Rsqr 0.8534. Equation (3:14) allows the calculation of effective diffusivity D_{eff}. The values for E, \( n \), \( T_{\text{ref}} \) and \( P_{\text{CO2,ref}} \) are from the model in regime I. R is the universal gas constant and T and \( P_{\text{CO2}} \) are the temperature and concentration used during the experiment. \( M_{\text{wc}} \) is the molar weight for the material and \( \rho_{C0} \) is the envelop density. \( M_{\text{wc}} \) can be calculated by using the ultimate analysis to calculate the molar weight.

Table 4-9. Value for diffusion effect in Cortus bark.

<table>
<thead>
<tr>
<th>Thiele modulus</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R )</td>
<td>[J kg^{-1}K^{-1}]</td>
<td>8.314462</td>
</tr>
<tr>
<td>( \rho_{C0} )</td>
<td>[kg m^{-3}]</td>
<td>783</td>
</tr>
<tr>
<td>( M_{\text{wc}} )</td>
<td>[kg mol^{-1}]</td>
<td>0.0128</td>
</tr>
<tr>
<td>( D_{\text{eff}} )</td>
<td>[m^2 s^{-1}]</td>
<td>1.41*10^{-5}</td>
</tr>
</tbody>
</table>

To get a more accurate reading on Thiele modulus, a narrower range of particle distributions would be needed.

4.5. Regime III (Effect of particle size distribution on apparent reactivity)

Because of lack of time, only Cortus Bark was tested for the regime III. Here, external diffusion refers to the diffusion into a packed bed to a point where the gas reaches the surface of all particles.
As seen in Figure 4-18 the small particles have small effectiveness factor which means it is harder for the external diffusion into the packed bed. Figure 4-19 shows that by mixing two different particle size distributions one can reduce the reaction rate of a packed bed more than by merely decreasing the particle size of a single distribution.

Figure 4-18. Effectiveness factor changes in a packed bed for Cortus Bark material for different particle size distributions.

Figure 4-19. Effectiveness factor for mixed particle size distributions for Cortus Bark.
Figure 4-20. Bulk density (bar diagram) for the regime III and the calculated bed porosity (line diagram) for Cortus Bark.

Figure 4-21. Comparison in reaction rate of Cortus Bark with Anthracite

As seen in Figure 4-21 combining the particle distributions decreased the reaction rate. That is because it combines the qualities of both the large particles with
increased internal diffusion and the small particles that have higher bulk density. The bimodal distribution also reduces the bed porosity and increase the bulk density as can be seen in Figure 4-20 which also slows down external diffusion.

Figure 4-19 show that the change in reaction rate is noticeable but miniscule between the different bimodal mixtures. That means if it is cheaper to keep the Bio-coal particles larger at the size mix of 6.3-5 and 4-3.15 mm instead of grinding the distribution down to 6.3-4 and 0.18-0.212 mm then there is not that big of increase in reaction rate.

5. Conclusion
For bio-coal that has been pyrolyzed at <800 °C it is difficult to evaluate the Bouduard reaction kinetics because there will always be an interaction with side reactions due to devolatilization. Bio-coal samples should preferably be completely devolatized before conducting kinetics testing in order to more clearly give an indication for suitability as reduction agent in the Höganas sponge iron process, where carbon sources are evaluated based on their fixed carbon content. At the moment the model created is not generalized to work for all bio-coals. It can only successfully simulate one of the tested samples. To make the model applicable for other types of bio-coal, the source of errors needs to be narrowed down.

By mixing the particle size distributions carefully according to the theory there is a possibility to greatly reduce the reaction rate of bio-coal in packed beds. The reactivity was highly affected by both internal and external diffusion. And there is a clear correlation between particle size distributions, bulk density, and apparent reactivity. But only mixing two separate particle distributions and not doing anything else is not enough to reach the low reactivity level of anthracite. At the end of this thesis the reaction rate of Cortus Bark was reduced from 6.5 times the reaction rate of anthracite to 4.5. That is a decrease with 30% from the first test. That is the same if the smaller particle size distribution of the two was either 0.18-0.212 mm or 4-3.15 mm.

If a recommendation has to be made of what material should be used in the process at Höganas AB at this point from the three materials that were tested. Then it becomes Cortus Bark because it is reacting as expected and was tested fully. But no recommendation can be made for what the optimal bio-coal for Höganas is until the errors in the model has been narrowed down in order to test several other types of bio-coals. Also only one sample was tested fully and only three were tested for kinetic reactivity. One recommendation that can be made is to pyrolyze the bio-coal at a temperature higher than the temperature chosen for kinetic analysis to avoid interference from devolatilization reactions.

Changing from anthracite to any other bio-coal tested in this thesis would mean that at least 40% of the energy in anthracite is lost and need to be replaced through external means.
6. Future work

The problem with the model can depend on pyrolysis temperature. In this thesis different sources for each material were used. To test the influence of the pyrolysis temperature only one source should be used but it should be prepared at different temperatures.

The results from the bimodal particle size distributions show that increasing the packing density of the material can lower the reaction rate for a packed bed. How much more would the reaction rate be lowered if the theoretical density limit could be reached? Another thing not studied in this work was how the materials as-received mixture reacted. According to Figure 4-20 the as-received distribution has higher bulk density than a single particle size distribution, but lower than any of the bimodal ones so the reaction rate should be somewhere in between.

From the miss in the beginning of the thesis the barbeque charcoal were not tested even though the first test showed that it has slower reaction time than the extruded one. Why did the extrusion speed up the reaction rate for the bio-coal?

In this thesis the volume change for bio-coal were not considered during the reaction. But for Höganäs AB that was one of the criteria and that should be studied to make certain particle size distribution does not influence the volume change.
7. References


Appendix 1. Replacing that pre-exponential factor with a reference point.

To remove the constant A, a reference point is decided.

\[ k = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot P_{CO2}^n \]  
\[ k_{ref} = A \cdot \exp\left(-\frac{E}{R \cdot T_{ref}}\right) \cdot P_{CO2ref}^n \]

By dividing \( k \) with \( k_{ref} \) A is removed

\[ \frac{k}{k_{ref}} = A \cdot \frac{\exp\left(-\frac{E}{RT}\right)}{\exp\left(-\frac{E}{R \cdot T_{ref}}\right)} \cdot \frac{P_{CO2}^n}{P_{CO2ref}^n} \]

That can be simplified to:

\[ k = k_{ref} \cdot \exp\left(-\frac{E}{R \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}\right) \cdot \left(\frac{P_{CO2}}{P_{CO2ref}}\right)^n \]
Appendix 2. Calculation of Thiele modulus.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_c$</td>
<td>Characteristic length</td>
<td>[m]</td>
</tr>
<tr>
<td>$k_{int}$</td>
<td>Intrinsic kinetic coefficient</td>
<td>$\left[ \frac{1}{s} * \frac{m^3}{mol} \right]^{n-1}$</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial reactant concentration</td>
<td>$[mol]$</td>
</tr>
<tr>
<td>$D_{eff}$</td>
<td>Effective diffusivity</td>
<td>$[m^2/s]$</td>
</tr>
</tbody>
</table>

From Bischoff (1965) Thiele modulus was defined as:

$$\varphi = \frac{1}{\eta} = \frac{L_c * r_{int}(C_0)}{\sqrt{2}} * \left[ \int_0^{C_0} D(\alpha) * r(\alpha)d\alpha \right]^{-\frac{1}{2}} \quad (1)$$

With the rate equation of $n^{th}$ order being:

$$r_{int}(C_0) = \frac{dC}{dt} = k_{int} * C^n \quad (2)$$

By inserting (2) into (1):

$$\varphi = \frac{L_c * k_{int} * C_0^n}{\sqrt{2}} * \left[ D_{eff} * k_{int} \int_0^{C_0} C_0^n dC \right]^{-\frac{1}{2}} \rightarrow$$

$$\varphi = \frac{L_c * k_{int} * C_0^n}{\sqrt{2}} * \left[ D_{eff} * k_{int} * \left( \frac{C_0^{n+1}}{n+1} \right) \right]^{-\frac{1}{2}} \rightarrow$$

$$\varphi = \frac{L_c * k_{int} * C_0^n}{\sqrt{2}} * \left[ D_{eff} * k_{int} * \left( \frac{C_0^{n+1}}{n+1} \right) \right]^{-\frac{1}{2}} \rightarrow$$

$$\varphi = \frac{L_c * k_{int} * C_0^n}{\sqrt{2}} * \left[ \frac{1}{D_{eff} * k_{int} * \frac{n+1}{C_0^{n+1}}} \right] \rightarrow$$

$$\varphi = L_c \sqrt{\frac{k_{int}}{2 * D_{eff}}} * \frac{C_0^n * n+1}{\sqrt{C_0^{n+1}}} \rightarrow$$

$$\varphi = L_c \sqrt{\frac{k_{int}}{2 * D_{eff}}} * \frac{C_0^{n-1} * (n+1)}{C_0^{n+1}} \rightarrow$$

$$\varphi = L_c \sqrt{\frac{(n+1)}{2 * D_{eff}}} \frac{k_{int} * C_0^{n-1}}{\sqrt{C_0^{n+1}}} \quad (3)$$

Testing solution by unit cancelation for (3).
\[- = m \frac{s - 1}{m^2} \left( \frac{m^3}{mol} \right)^{n-1} \frac{mol}{m^3} \]

Modify (3) with (2) by doing:

\[ k_{\text{int}} \cdot C_0^{n-1} = \frac{k_{\text{int}}}{\frac{r_{\text{int}}(C_0)}{C_0}} \]

Final solution:

\[ \varphi = L_c \frac{(n + 1) \cdot r_{\text{int}}(C_0)}{2 \cdot D_{\text{eff}} \cdot C_0} \]

By inserting the model for bio-char (6) and a definition of initial concentration (7) into the Thiele modulus model (5) an expression of Thiele modulus for bio-char can be created.

\[ r_{\text{int}} = k_{\text{ref}} \cdot \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \cdot \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}_2\text{ref}}} \right)^{n} \cdot \frac{\rho_{\text{C}_0}}{M_{\text{W}_\text{C}}} \]

\[ C_0 = \frac{P_{\text{CO}_2}}{RT} \]

\[ \phi = L_c \sqrt{\frac{(n + 1) \cdot k_{\text{ref}} \cdot \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \cdot \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}_2\text{ref}}} \right)^{n} \cdot \frac{\rho_{\text{C}_0}}{M_{\text{W}_\text{C}}}}{\frac{P_{\text{CO}_2}}{RT}}} \]

\[ \phi = L_c \sqrt{\frac{(n + 1) \cdot k_{\text{ref}} \cdot \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \cdot \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}_2\text{ref}}} \right)^{n} \cdot \frac{1}{P_{\text{CO}_2}} \frac{\rho_{\text{C}_0}}{M_{\text{W}_\text{C}}} \cdot RT}} \]

The final model:

\[ \varphi = 1/\eta = L_c \sqrt{\frac{n + 1}{2 \cdot D_{\text{eff}}} \cdot k_{\text{ref}} \cdot \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \cdot \frac{P_{\text{CO}_2}^{-1}}{P_{\text{CO}_2\text{ref}}} \frac{\rho_{\text{C}_0}}{M_{\text{W}_\text{C}}} * RT} \]

Sample preparation

- Sample as received (<500 g)
- Take ~300 g of sample by quarter-sampling method
  - Bulk density measurement
  - Moisture content measurement
- Dry the sample at 40 °C for 12 hr
  - Bulk density measurement
  - Moisture content measurement
- Divide the sample to 8 bottles

Quarter-sampling method
- Moisture analyzer (take 1-2 g of sample)
- Rotary divider
  - Measuring cylinder 500 ml (for bulk density; use ~300 g of sample)

Physical characterization

- Bottle #1 of representative sample
  - Envelop density measurement
  - Measuring cylinder 25 or 50 ml (for envelop density)
  - ***Repeat every analysis 2-3 times

- Bottle #2 of representative sample
  - True density measurement
  - He pycnometer

- Bottle #3 of representative sample
  - Particle size distribution (PSD)
    - Step 1: Sieving (7 - 1 mm)
    - Step 2: CAMsizer (< 1 mm)
Chemical characterization

- Sample grinding (< 1 mm)
- Ultimate analysis (CHNOS)
- Higher heating value (HHV)
- Ash content
  - Coal: 815 °C
  - Bio-coal: 550 °C
  - Open crucible
- Volatile matter
  - At 900 °C
  - Close crucible

***Repeat every analysis 2-3 times

Reactivity in Regime I

- Bottle #5 of representative sample
- Divide sample to small bottle (~ 1-2 g)
- 1 vial of representative sample
- Grind sample to < 75 μm
- Reactivity measurement in TGA

Kinetic parameters measurement in TGA
- $T = 750, 800, 900$ °C
- 1-2 mg of sample
- Thin layer of sample
- 20, 40, 60% of CO$_2$

***Repeat every analysis 2-3 times

Reactivity in Regime III

- Bottle #6 of representative sample
- Sieving sample
- Large particle (4-5 mm)
- Small particle (150-250 μm)
- Measurement of reactivity and volume after conversion in macro TG

Precise macro TG

$T = 1100$ °C
$= 300$ K/min
Open crucible
Sample mass is dependent on volume of crucible
60% of CO$_2$
Appendix 4. Aspect ratio for below 1 mm.