Pyrolysis of Wood Chips

Influence of Pyrolysis Conditions on Charcoal Yield and Charcoal Reactivity

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Abstract

At a steel mill, charcoal from biomass is a potential substitute to coal as a reducing agent in the Blast Furnace. The steel industry accounts for 5 % of the global CO₂ emissions. Charcoal, being a renewable fuel, has the potential to mitigate the steel industry’s contribution to global warming. If charcoal were to replace the pulverized coal injected into one of Sweden’s two blast furnaces an estimated 1,13 Mton raw biomass per year would be required, this is equivalent to 2,5 % of the total available biomass in Sweden the year 2020 . If this is to be realized, a well optimized pyrolysis process for charcoal production would be required, a process with high charcoal yield that minimize the biomass consumption.

This report presents a study on pyrolysis of wood chips. The two main objectives of this work have been to find pyrolysis conditions, applicable in a real process, that increase the charcoal yield and also to investigate how the reactivity of the charcoal is affected by these conditions. A hypothesis with two approaches has been proposed and evaluated experimentally.

It has been proposed that the charcoal yield is increased if the tar found in the pyrolysis gases are condensed and returned to impregnate the ingoing wood before undergoing a second pyrolysis step. Or, the charcoal yield is increased by letting the tar impregnate the outgoing charcoal before the two undergoes a second pyrolysis step.

The hypothesis has been evaluated in a laboratory where pyrolysis has been conducted on chips from fir wood together with bio-oil. The bio-oil has been used to resemble tar.

It has been concluded that by recycling tar the charcoal yield is increased. Pyrolysis of fir wood at 340 °C yields 32 % charcoal. If the wood is impregnated before the pyrolysis with an amount of bio-oil equivalent to a tar yield of 25 % the charcoal yield is increased to 37,7 %. It is possible to say, with 80 % confidence, that pyrolysis of wood and bio-oil gives a higher charcoal yield if the two undergoes pyrolysis while being in contact with each other instead of being separated. The charcoal yield is not increased by pyrolysis of charcoal impregnated with bio-oil. There is no difference in reactivity between charcoals from impregnated wood and plain wood.
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1. Introduction
Carbon is one of the fundamental elements in biological matter and the carbon cycle is one of three major cycles, next to the water and nitrogen cycles, which makes life on planet earth possible. In the cycle, carbon is exchanged between the atmosphere, biosphere, pedosphere, hydrosphere and geosphere by a series of chemical processes. Since the industrial revolution, human activity has interfered the normally stable cycle. With the extensive use of fossil fuels, humans have caused an imbalance, mainly in the atmosphere, where the level of carbon has risen due to the release of, for the most part, carbon dioxide and methane. The process of burning fossil fuels is carbon positive, as more carbon is emitted into the atmosphere than what is subtracted from it via photosynthesis of plants in the bio- and hydrosphere.

With the ongoing climate change, renewable fuels are getting more attention. Renewable fuels from biomass are in contrast to fossil fuels carbon neutral. This is because the carbon has recently been stored in the biomass and the fuel can therefore be seen as a part of the natural carbon cycle.

In Sweden biomass such as wood and forest residues are used as energy sources both in its pure form and as refined and processed high quality fuels. As a step towards a society less dependent on fossil fuels there are today possibilities to have cars, trucks and busses with engines powered by bioethanol, biodiesel or biogas. And with its access to hydro and nuclear power, Sweden is able to provide its electricity demand by electricity free from fossil fuels. There is however industries that are today completely dependent on fossil fuels e.g. cement, plastic and steel industry.

Producing steel requires large amount of carbon and heat for the reduction and smelting of iron oxide. In the process a high rank bituminous coal with high carbon content and high heating value is used as fuel, supplying the necessary heat and carbon. The process emits CO$_2$, and globally the steel industry accounts for 5 % of the total greenhouse gas emissions. Sweden’s two steel mills accounts for 11 % of the nation’s total CO$_2$ emissions (1) (2). Focus is therefore directed on alternative and renewable reducing agents, so called bio-reducers. One suggested approach is to partly replace the coal with charcoal from wood biomass.

Charcoal is produced from wood in a thermal process known as pyrolysis. In Sweden, charcoal is mainly used as a barbecue fuel and the demand for it is therefore relatively low. Today there is only one company in Sweden producing charcoal on an industrial scale (3). If the Swedish steel mills were to introduce charcoal in the process a completely new industry would have to arise producing and delivering vast amounts of charcoal to meet the demand. Studies estimate that replacing 33 % of the coal used at one of Sweden’s two steel mills with charcoal would require 1,13 Mton raw dry biomass per year which equals 2,5 % of the total available biomass, year 2020 (4). The study is based on the assumption that 35 wt% of the biomass can be converted to charcoal. Evidently, less biomass would be required if the pyrolysis process could be optimized, with improved charcoal yield. Theoretically, the maximum charcoal yield from wood is around 50 %, but most commercial pyrolysis plants have char yields of 25 – 37 wt% (5).
2. Objectives
The scope of this project has been within research on charcoal production. The aim is to lay a basis for future research. The two main objectives are:

1. To find pyrolysis process scheme and conditions, applicable in a real process, that increases the charcoal yield.

2. To evaluate how the reactivity of the charcoal is affected by these pyrolysis conditions.

3. Background

3.1 Wood biomass
In energy engineering the term biomass is mostly used to describe living or recently living plant based matter that is not suitable as food but can serve as a source of energy. Typical biomass used for energy production is agricultural waste, forest residue, sawdust and wood chips. In Sweden the use of biomass based fuels has been on a steady incline since the early 1990s, much due to taxation on CO₂-emissions and increased energy tax, which biofuels were spared from. In 2013 biofuels accounted for 23 % of Sweden’s total energy supply where the three main consumers were industry, district heating and households. A majority, 41 %, of the biofuels came from unrefined wood, however, the share of fuels from refined wood and other types of biomass is growing. The transport sector has in the past ten years increased its use of biofuels such as biodiesel and biogas (6).

3.2 Pyrolysis of wood
One of the oldest methods to upgrade wood to a higher quality fuel is pyrolysis; thermal decomposition of organic matter at high temperatures in the absence of oxygen. Historically this technique was used to produce charcoal from wood. Before the industrial revolution where coal became the main fuel, charcoal was an important fuel in for example metallurgy and cooking. At that time the production took place in charcoal pits with limited possibilities to control the process, unlike today where pyrolysis is practiced industrially with possibilities to control the process thoroughly. Figure 1 shows an example of an industrial pyrolysis process.

![Continuous pyrolyzer developed by Framatome.](image)

Figure 1. A continuous pyrolysis process (7).

Pyrolysis of wood begins at around 300 °C. It is at this temperature that cellulose, the main constituent of wood, begins to break down in its glycosic linkages to form smaller and lighter molecules. Both hemicellulose and lignin, the other main components in wood, begins to decompose at lower temperatures, 225 and 250 °C respectively. Although the lignin begins to decompose at temperatures below 300 °C it is more stable and less reactive than the other components, see Figure 2. Wood is a heterogeneous material and the product formation and composition of wood pyrolysis is not possible to fully predict (8). However, pyrolysis of wood will
always yield char, liquid and gases, how much of each depends on the wood characteristics and pyrolysis conditions.

![Thermogravimetric analysis (TGA) of cotton wood and its components, Xylan is a type of hemicellulose (7).](image)

### 3.2.1.1 Yield
The yield of products, for example char or tar, is measured as a fraction between the mass of the product and initial mass of the wood:

\[
Y = \frac{m_2}{m_1}
\]

Where \( m_1 \) denotes the initial mass of the feedstock and \( m_2 \) the final mass of a product. The yield is always between 0 and 1 but may be expressed in percent, in that case 0 to 100 wt%.

### 3.2.1.1 Char
Char is a generic term for carbonized solid fuels. It is the solid residue remaining after complete pyrolysis and it is characterized by high carbon content. It is common to specify the type of char e.g. charcoal when the char originates from biomass or coal char when referring to charred coal.
Charcoal production is favored at slow pyrolysis; low temperatures, 300-450 °C, a process that requires low heating rates and relatively long residence times, from minutes up to several hours. Charcoal produced at low temperature has less wt% fixed carbon and contains more volatile matter compared to charcoal produced at higher temperatures, 500-800 °C (7).

### 3.2.1.2 Tar
Some of the gaseous products formed in pyrolysis will condense at room temperature to a sticky, dark and oily substance commonly referred to as tar. The chemical composition of tar formed in wood pyrolysis is complex and depends on the fuel characteristics and pyrolysis conditions. It does however always consist of heavier hydrocarbons such as Levoglucosan (C_{6}H_{10}O_{5}) (8). Tar is like char, a generic term. It can be produced from i.e. wood, peat or coal. Tar from biomass pyrolysis can be processed to bio-oil.

The yield of liquid products is highest in fast pyrolysis. Fast pyrolysis is in the temperature range of 500 °C and above and is characterized by short residence times and high heating rates. (7).

### 3.2.1.3 Gases
The lighter gases consist mainly of CO, CO_{2} and CH_{4}. In a pyrolysis process these gases are normally recycled back to the process and combusted to supply the heat needed for the pyrolytic reactions (7).

### 3.2.2 Means to maximize charcoal yield
High quality charcoal is characterized by high carbon content and low volatile matter, properties best achieved in high pyrolysis temperatures where the yield is low. It is therefore desired to find methods how to produce charcoal with high yield and high carbon content.
Theoretically the maximum possible charcoal yield would be reached if all the carbon in the wood got fixed during pyrolysis, for most wood that would mean 45-50% (9). Practically this is not possible to achieve and
industrial processes rarely reach above 37%. Research has shown that it is possible to approach the theoretical yield by carrying out the pyrolysis in a closed environment at elevated pressure (5). Enclosing the wood prevents the heavier molecules formed, such as Levoglucosan, from escaping the reactor and condense. When kept among the reacting wood these molecules continues to decompose into char and lighter gases. Higher moisture content has also been linked to higher charcoal yields. It is believed that moisture favors the formation of Levoglucosan (5).

3.3 Charcoal in the steel industry

The steel industry is an industry heavily dependent on fossil fuel, mainly in the form of coal. Steel production accounts for 5% of the global CO$_2$ emissions and focus is being put on finding alternative production methods and alternative fuels in the process to replace the coal. One alternative is to replace part of the coal with charcoal from biomass. Charcoal, being a renewable fuel, has the potential to mitigate the steel industry’s contribution to global warming.

3.3.1 Overview of blast furnace process

A Blast Furnace (BF) is a 20-30 meter high, cylindrical steel construction with a brick coating inside. It is the main technology used to produce pig iron; the raw material for steel. The smelting of iron ore in a BF is a countercurrent process where the raw material is fed at the top and hot air is supplied near the bottom. It is common to inject a supplementary fuel together with the hot air, often pulverized coal. The raw material consists of iron ore and limestone in 1-4 cm pieces and coke in pieces of 2,5-10 cm. The lime stone is used to bind impurities entering the furnace with the iron ore and coke such as sulfur and silica. Coke is a product from pyrolysis of coal. In a BF, coke does not only serve as a fuel and reducing agent, but is also with its porosity and strength the scaffold supporting the burden from above and allowing the hot gases to flow upwards. It normally takes six to eight hours for the iron ore and limestone to go from a solid state at the top to a liquid state at the bottom where the finished product is emptied in regular intervals, see Figure 3.

The smelting process includes a great number of chemical reactions occurring at different temperatures. Below, some of the main reactions are listed. The overall reduction reaction of iron ore (Hematite) is:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$  \[1\]

The reduction is done by carbon monoxide which is a product of incomplete combustion of coke:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$  \[2\]

Even though there is an excess of carbon some carbon dioxide will form through:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$  \[3\]

At the bottom of the BF the temperature is high enough for the Boudouard reaction:

$$C(s) + CO_2(g) \leftrightarrow 2CO(g)$$  \[4\]

The Boudouard reaction is crucial in a BF, if controlled properly this reaction will lower the fuel consumption in the furnace. But if the reaction rate becomes too high the fuel consumption will increase since this reaction requires energy (11).
3.3.2 Charcoal as reducing agent
In the 1700s coke began to replace charcoal as reducing agent in metallurgy. Coke, with its high mechanical strength enabled the large sized blast furnaces used in modern steel production. Replacing coke completely with charcoal in a modern large BF is not possible. There are three main approaches to decrease coal consumption by using charcoal:

- Partly replace coke by charcoal
- Blend charcoal with coal before the coke production, making bio-coke
- Inject pulverized charcoal instead of coal with the hot air blast

Injecting pulverized charcoal does not change the coke properties and is considered a promising method to reduce coal consumption. Studies estimate that replacing the pulverized coal used at one of Sweden’s two steel mills with charcoal would require 1.13 Mton raw dry biomass per year which equals 2.5 % of the total available biomass, year 2020. The heating value of charcoal is generally lower than that of bituminous coal and a larger mass of charcoal would be required. The lower ash content is favorable but the higher alkali content in the ash might cause problems. Charcoal is more reactive than coal, something that can affect the flame characteristics (4).

3.4 Charcoal gasification in CO₂
The chemical and physical properties differ between charcoals produced under different pyrolysis conditions. Low temperature charcoals have less fixed carbon, more volatile matter and tend to be less porous than charcoals produced at high temperature. These are properties affecting a charcoal’s behavior in a combustion environment. One experimental method to evaluate this is gasification in CO₂; reaction between a solid carbonous fuel and CO₂ at high temperatures (>700 °C). The reaction between solid carbon and carbon dioxide gas is relatively slow. In a laboratory, this enables the mass loss over time of the carbonous matter, e.g. charcoal, to be measured with good precision.

3.4.1 Reactivity
By gasification in CO₂ the Boudouard reaction [4] is studied. There are several parameters that influence the rate at which this reaction occurs. The reaction rate can be increased by:

- Increasing temperature
- Increased pressure
- Higher fraction of CO₂
- The presence of catalytic substances within the solid
- Accessibility of carbon
- Particle size

By keeping temperature, pressure, particle size and CO₂ fraction constant it is possible to evaluate how the reactivity differs between different charcoals.

3.4.1.1 Properties influencing reactivity
The reaction between carbon and carbon dioxide is a solid-gas reaction. If the carbon source is a char particle it is evident that the structure of the particle will influence the possibilities for the CO₂ to react with the carbon found at the char surface. A more porous structure increases the possibilities for the CO₂ to diffuse into the particle enabling a larger surface area for the reaction to take place hence increasing the reaction rate.

Within the ash of the char there might be compounds having a catalytic activity on the reaction. Biomass fuels often contain alkali metals such as Na and K, which tend to work as a catalyst in the reaction between C and CO₂. A catalyst will lower the activation energy for the overall reaction and thereby increasing the reaction rate.

If the ash content is high a layer of ash might form on the surface of the particle hindering the CO₂ to reach the carbon resulting in a lower reaction rate.

3.4.1.2 Conversion
In char gasification experiments the mass loss of the char particle is monitored, this data is useful for further analysis. The reactivity among different charcoals can be evaluated by comparing their conversion behavior, the conversion is defined as:

\[ X = \frac{m_1 - m_f}{m_1 - m_2} \]  (eq. 2)
Where \( m_i \) is the initial mass, \( m_t \) is the mass at a certain time and \( m_f \) is the final mass when no further mass loss is taking place. The value of \( X \) is between 0 (no reaction) and 1 (100% reacted).

### 3.4.1.3 Conversion rate

The conversion rate \( dX / dt \) is the derivative of \( X \) with respect to the time \( t \). The conversion rate gives information about how fast the reaction is occurring at a certain conversion degree.

### 3.4.2 Kinetic models

Data obtained from char gasification experiments can be used for further analysis. There are many mathematical models for char gasification that describes the conversion rate \( dX / dt \) as a function of the conversion \( X \):

\[
\frac{dX}{dt} = k \cdot f(X) \tag{eq. 3}
\]

Where \( k \) is a rate constant dependent on pressure and temperature. \( f(X) \) is the reaction model concerning the change of reaction rate as a function of conversion.

For charcoal gasification the Extended random pore model has been used successfully in previous studies (12) (13):

\[
f(X) = (1 - X) \sqrt{1 - \psi \ln(1 - X)} (1 + \theta^p) \tag{eq. 4}
\]

In eq. 4 \( \psi \) is a surface parameter describing the initial porosity and pore structure of the particle. \( \theta = cX \) where \( c \) and \( p \) are empirical constants.

The extended random pore model suggests that the reaction rate is governed by pore growth within the structure of the particle. The last term \( (1 + \theta^p) \) is the extension of the original random pore model and serves to compensate for an increase in conversion rate occurring at high conversions due to the effect of catalytic compounds in the char.

### 4. Hypotheses

Research on char yield from biomass pyrolysis show that the yield is increased if the pyrolysis is carried out in a closed environment, at elevated pressure. Addition of moisture to the feedstock has shown to favor the yield as well. The yield is increased by keeping the tar in a vapor phase for further decomposing together with the reacting wood.

There are a few disadvantages if this method were to be implemented in an industrial scale. By keeping the process sealed the pyrolysis gases could not be used to supply the necessary heat and heat would have to be supplied by an external fuel source. Closed environment would require a batch wise process which is hard to scale up. Adding moisture to the feedstock would greatly increase the heat demand. However, the tar is a carbon-rich asset not to be neglected if maximized char yield is desired and the hypothesis of this thesis is related to the method mentioned above.

### 4.1 Increasing charcoal yield by recycling tar

The formulation of this hypothesis has been done by taking into account an industrial process, the basis have been a continuous process like the one shown in Figure 1. With recycling tar the idea is to add a condensation step after the gas extraction where the tar within the gases is condensed. The tar can then be returned back to the process for further pyrolysis and thereby increasing the total yield. How the tar can be returned to the pyrolysis has been suggested by two different approaches.

#### 4.1.1 Pyrolysis of wood impregnated with tar

In this approach it is suggested that the total char yield is increased if the condensed tar goes through the pyrolysis process while being adsorbed on the ingoing wood. Practically this would be done by impregnating the wood with tar before the pyrolysis. Figure 4 shows a simple process flow chart of this approach.
4.1.2 Pyrolysis of charcoal impregnated with tar

This approach suggests that the total char yield is increased if the condensed tar goes through the pyrolysis process while being attached to charcoal. Practically this would be done by impregnating the outgoing charcoal with tar and then let the impregnated charcoal go through a second pyrolysis step. Figure 5 shows a simple process flow chart of this approach.

Figure 4. Pyrolysis process with recycling tar by impregnating wood.

Figure 5. Pyrolysis process with recycling tar by impregnating charcoal.
5. Method

The hypotheses were evaluated experimentally in a laboratory. It was investigated how the total charcoal yield is affected by impregnating wood and charcoal with tar before pyrolysis. The final charcoal was then put through gasification experiments in order to evaluate how the reactivity is affected by the impregnation methods.

5.1 Material

5.1.1 Fir wood chips

The wood used in the experiments came from debarked chips of Norway Spruce, it is one of the two most common species in Sweden. The wood chips were donated by the sawmill Stenvalls Trä AB in Luleå, Sweden. At the sawmill, the wood chips are a rest product and are therefore not cut to meet specific requirements. This result in a variety of shapes and sizes, Figure 6 shows the shape of the chips used in the experiments. They have a mean weight of 4 g.

![Figure 6. The type of wood chip used in the experiments.](image)

5.1.2 bio-oil

Bio-oil from Fortum’s pyrolysis plant in Joensuu, Finland was used in the impregnation experiments to represent tar. This is because the possibilities to collect the tar produced in the laboratory are limited. The bio-oil was produced in a fast pyrolysis process were the feedstock were forest residue, wood chips and sawdust (14).

5.1.3 Injection coal

In the gasification experiments, bituminous coal from SSAB in Luleå Sweden, was used as a reference to get a perception of how the reactivity of charcoal compares to that of coal char.

5.2 Equipment

5.2.1 Thermogravimetric analysis (TGA)

The pyrolysis and gasification experiments were monitored by a Thermogravimetric analysis (TGA). TGA is a method to measure how a sample is physically and chemically changed as a function of time or temperature. The available laboratory setup in this project enabled to measure the weight loss as a function of time. The TGA equipment can be seen in Figure 7.
The reactor chamber is heated electrically with a maximum heating rate of 2 °C/min, the equipment is therefore suitable for isothermal TGA. Maximum available temperature is 900 °C. The sample can be hung in a wire which is connected to a balance that logs the weight every two seconds. The data is stored in a computer connected to the balance. At the bottom there is an inlet for gas, a heating tape is wrapped around the gas pipe enabling preheating of the gas up to 300 °C. A thermocouple measures the temperature at the center point of the chamber. At the top of the reactor there is an inlet for nitrogen gas that may be used for quenching samples before they are brought out. The exhaust gases are removed by a ventilation hose via an exhaust pipe.

5.2.2 Electric Sieve Shaker
An electrical sieve shaker was used to separate charcoal particles between 250 – 300 µm before gasification experiments.

5.2.3 Scanning Electron Microscope
A scanning electron microscope was used to take photos of the structure of the surface of different chars.

5.3 Experimental procedure
The experimental procedure is explained in this section in chronological order. Every experiment was conducted three times for repeatability.

5.3.1 Pretreatment of wood chips
The wood chips have a moisture content of 12-13 wt% when delivered from the sawmill. The chips selected for experiments were dried for 24 hours at 105 °C in a drying cabinet and then stored in a low humidity cabinet.

5.3.2 Pyrolysis of wood chips at temperature range
As an initial step the influence of pyrolysis temperature on charcoal yield and conversion rate was evaluated. This was done by performing pyrolysis wood chips at 12 different fixed temperatures ranging between 300 to 800 °C. The results were used as a basis to find pyrolysis conditions where the charcoal yield and conversion time was satisfactory for producing charcoal for impregnation experiments later on.

5.3.3 Pyrolysis of wood chips impregnated with bio-oil
In this part experimental data was gathered for evaluation of the approach to the hypothesis described in 4.1.1. The wood chips were impregnated with bio-oil before pyrolysis. Table 1 lists the experiments done in this section.
Table 1. Experiments with impregnated wood, X represents 3 repeated experiments. - means no experiment done. Ratios Wood/Oil is defined as percentages of the total mass of the impregnated wood chip.

<table>
<thead>
<tr>
<th>Wood/Oil</th>
<th>300 °C</th>
<th>320 °C</th>
<th>340 °C</th>
<th>360 °C</th>
<th>380 °C</th>
<th>400 °C</th>
<th>425 °C</th>
<th>450 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>90/10</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80/20</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>75/25</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The bio-oil was applied on the wood with a brush, see Figure 8. After weighing a dry wood chip, the amount of bio-oil required to reach a desired impregnation ratio was calculated. Bio-oil was then applied evenly on the wood chip under continuous weighing until the mass equaled the calculated value within 0.1 % of error margin. Pyrolysis at different temperatures was done with a constant impregnation ratio of 80/20 to evaluate how the charcoal yield of impregnated wood is affected by pyrolysis temperature. Wood chips with different impregnation ratios were then pyrolyzed at 340 °C to investigate if the total char yield is affected by letting the bio-oil and wood convert while in contact with each other rather than separately.

![Figure 8. Impregnation method.](image)

5.3.4 Pyrolysis of charcoal impregnated with bio-oil
The purpose of the experiments in this section was to evaluate the second approach to the hypothesis described in 4.1.2. This was done in the same manner as described in section 5.3.3 with charcoal instead of wood. The charcoal used was produced by pyrolysis of wood chips at 340 °C.

5.3.5 Pyrolysis of bio-oil
To be able to evaluate whether the charcoal yield is affected by the impregnation methods or not it was necessary to conduct experiments on pyrolysis of bio-oil. Pyrolysis was done at the same temperatures used in the impregnation experiments. The amount of bio-oil used for each experiment was 0.5, 1.0 and 1.5 g. To hold the oil a ceramic crucible was used.

5.3.6 Gasification of pulverized charcoals
Gasification experiments were conducted at 900 °C in 50 % CO₂ on selected charcoals from the pyrolysis experiments, Table 2 lists the experiments.

Table 2. Gasification experiments at 900 °C of pulverized chars 250-300 μm, X represents 3 repeated experiments.

<table>
<thead>
<tr>
<th>Char from Pyrolysis temperature</th>
<th>300 °C</th>
<th>340 °C</th>
<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
<th>600 °C</th>
<th>700 °C</th>
<th>900 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>Impregnated wood 75/25</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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Gasification experiments were conducted on chars from wood pyrolyzed at different temperatures in order to investigate how the pyrolysis temperature influences the charcoal reactivity.Chars produced at 340 °C from impregnated wood, impregnated charcoal and bio-oil were used to evaluate how the impregnation affects the reactivity. Char from the bituminous coal was produced by pyrolysis at 900 °C, the gasification of coal char was done to get a reference point for the charcoal reactivity.

The chars were prepared by crushing and sieving to a size between 250 – 300 µm, after sieving the samples were dried for 10 minutes in a drying cabinet at 105 °C before being stored in a low humidity cabinet. In every experiment, 0,1 g of char particles were spread evenly on a platinum mesh with the opening of 225 µm, see Figure 9. The mesh was then mounted on the wire in the TGA equipment.

![Figure 9. Pulverized charcoal on the platinum mesh.](image)

### 5.4 Data analysis

#### 5.4.1 Filtering
The balance used in the TGA setup picks up noise from the surroundings, this is noticeable on data collected in the gasification experiments where the mass of the sample was low, around 0,1 g. Therefore, the data had to be filtered before being analyzed, this was done with the Smooth function available in Matlab, with a smooth factor 0,5 and robust loess.

#### 5.4.2 Pyrolysis data
The data obtained in the pyrolysis experiments were mainly used to calculate the conversion in order to investigate how the conversion time depends on the pyrolysis temperature. The TGA data was not used to calculate the char yields, for these calculations data was taken manually by weighing the samples before and after pyrolysis.

#### 5.4.3 Gasification data
The gasification data was used to calculate the conversion and conversion rate. The difference in reactivity between different chars was evaluated graphically by plotting the conversion \( X \) as a function of time. Kinetic models were investigated by curve fitting on plots of the conversion rate \( \frac{dx}{dt} \) as a function of conversion \( X \).

### 5.5 Elemental analysis
Charcoal samples were sent to the Mikroanalytisches Laboratorium at the University of Wien. Analyses were done to evaluate how the carbon, hydrogen and nitrogen content in the chars are affected by impregnation and pyrolysis temperature.
6. Results and Discussion

6.1 Pyrolysis

6.1.1 Pyrolysis at temperature range

Figure 10 shows the TGA curves from pyrolysis of wood chips at different temperatures. There is a clear difference between the conversion at 300 °C compared to higher temperatures. At 300 °C, the conversion is protracted which can be explained by the fact that cellulose begins to decompose at this temperature. There is also the influence of the slow reacting lignins. The lignin may also be linked to the fact that the wood does not cease to convert even though the main reaction is completed, this applies to all temperatures. However, the change in yield within this section is relatively small, at 300 °C the yield is 37,6 at 25 min compared to 36,6 at 40 min.

It can be seen Figure 10 that both the char yield and conversion time is affected by the pyrolysis temperature. To find a temperature where the char yield is satisfactory within reasonable time pyrolysis were carried out at a range of temperatures. Figure 10 indicates that the influence of a 100 °C increase in temperature is greater at 300 °C compared to higher temperatures, hence the interval 300 – 400 °C was analyzed extra thoroughly. During the experiments the conversion was considered complete when there was no change in mass larger than 0,002 g occurring within 30 seconds time. To minimize the influence of this method on the experimental error the time for 90 % conversion has been used when evaluating how the pyrolysis temperature affects the conversion time. The results from the experiments are presented in Figure 11.
The results in Figure 11 summarize pyrolysis of fir wood chips. It is evident that high yields are favored at lower temperatures where the conversion time is longer. Maximum char yield is achieved at 300 °C where 37 % of fir wood converts to charcoal in 16 minutes. However, the objective of this thesis has been to increase char yield, and to enable enough experiments within the timeframe of the project the evaluation of the hypothesis had to be done at temperatures above 300 °C where the conversion time is shorter. 340 °C was considered a temperature giving high char yields in reasonable time; 32 % in 8 – 9 minutes.

6.1.2 Pyrolysis of bio-oil
During pyrolysis the bio-oil swells and converts to a spongy and crusty char, see Figure 12. The char yield was affected by the amount of bio-oil poured in the crucible; doubling the amount of bio-oil can increase the char yield with up to 10 %. A possible reason for this is that the bio-oil begins to convert at the surface. A larger amount of bio-oil will result in a thicker crust covering the converting liquid at the bottom and the mass transport is hindered. By this the conversion is slowed and more bio-oil is converted to char. To compensate for this every experiment was conducted with 0,5 1,0 and 1,5g bio-oil, this range covers the amount of bio-oil used in the impregnation experiments.

The char yield of bio-oil at different temperatures is shown in Figure 13. The trend is the same as for pyrolysis of wood; the char yield is decreased with increased temperature. Pyrolysis of bio-oil yields 22 % char at 300 °C. It is likely that the yield is higher at temperatures below 300 °C, however, this was not examined in this project. At 340 °C the char yield is 17 %.
Figur 13. Char yield of bio-oil pyrolysis at temperatures 300 – 450 °C. The data points for bio-oil marks the mean value of the three experiments conducted with 0,5 to 1,5 g at each temperature.

6.1.3 Pyrolysis of wood chips impregnated with bio-oil
The bio-oil was applied on the wood with a brush, this method works well with the impregnation ratios 90/10 and 80/20 (wood/oil). But at the higher ratio, 75/25, wood chips from heart wood, the inner core of the stem, are not able to absorb the bio-oil completely. For these experiments chips of sap wood, the outer layer of the stem, had to be sorted out and used. For sap wood chips the maximum impregnation ratio is around 70/30. Figure 14 shows a cross section of an impregnated wood chip. The bio-oil is absorbed at the surface of the chip until the surface is saturated, at this point the oil will not penetrate further into the wood. bio-oil is more easily absorbed on surfaces perpendicular to the wood fibers.

Figure 14. Cross section of a wood chip where the surface has been saturated with bio-oil.

Figure 15 shows how the char yield of wood chips impregnated with bio-oil, at a ratio 80/20, is influenced by the pyrolysis temperature. The fact that the impregnated wood yields more char than plain wood is not surprising, the yield is calculated considering the process described in 4.1.1 were tar is condensed and recycled back to the pyrolysis and (eq. 1) is defined as:

$$Y = \frac{m_{\text{char}}}{m_{\text{wood}}}$$

In this case more of the initial mass is converted to char giving a higher total yield when eq. 1 is used. On an average the char yield is increased with 16 % when the wood is impregnated with bio-oil at a ratio 80/20.
Up to a pyrolysis temperature of around 380 °C there is no visual difference between char from impregnated wood and char from plain wood, except for the surface of the char from impregnated wood looking slightly crystalline. But at temperatures above 380 °C the bio-oil tends to soften and trickle out of the wood before converting, forming crusts of bio-oil char on the surface of the wood char, see figure 16. This could not be avoided by longer impregnation times. This phenomenon is a possible explanation to why the difference in yield between plain and impregnated wood is decreased at temperatures of 380 °C and up.

\[
Y = \frac{m_{\text{char}}}{m_{\text{wood}} + m_{\text{bio-oil}}}
\]

The amount of bio-oil is increasing along the x-axis starting at 0 where wood alone yields 37 % char and reaching 100 % at the right where bio-oil alone yields 17% char. The results from the experiments are plotted in the same graph; all points that are above the solid line are indications that the total yield is increased by the synergy effect of the impregnation. The experimental values are all above the line, a fact better illustrated with Figure 18 which is a zoomed portion of the graph in Figure 17.
The Impregnation limit is marked in the graphs just above 30 %, finding methods to enable higher impregnation ratios is of little significance. In the continuous process described in 4.1.1 a ratio of 70/30 wood/oil corresponds to a tar yield of 43 % which is high for pyrolysis at this low temperature.

With a statistical analysis of the experimental data it is possible to say, with 80 % confidence, that in pyrolysis at 340 °C, wood impregnated with bio-oil at a ratio 75/25 gives a higher char yield than if the same amounts were to be pyrolyzed separately.

6.1.4 Pyrolysis of charcoal impregnated with bio-oil
Figure 19 shows the results from the temperature range experiments on impregnated charcoal. The yield curve for the impregnated charcoal crosses the curve for the wood at 340 °C which is the temperature at which the incoming charcoal was produced. There is a slight increase in char yield at 340 °C and above but it is not as obvious as for the impregnated wood. The reason for this is that the impregnation ratio is based on mass and charcoal is much lighter than wood leading to less bio-oil being impregnated on the charcoal. The initial plan was to base the amount of bio-oil as a fraction of the initial wood mass but the charcoal was not able to absorb such amounts.
Figure 19. Yields after pyrolysis of charcoal impregnated with bio-oil.

In Figure 20 it can be seen that the yield of char from bio-oil is not increased by letting the oil convert while being attached to charcoal. The impregnation limit is a little higher than for wood which is probably because of the more porous structure of the char. In the graph the yield at 0% bio-oil is 96%, this is due to that the charcoal continues to convert during the second pyrolysis step.

Figure 20. Evaluation of impregnation.

6.5 Gasification of pulverized charcoals
All gasification experiments were carried out at 900 °C in 50% CO₂. Before being gasified, the samples were crushed and sieved between sieves at 250 – 300 µm. The wood structure, with long fibers, are noticed when charcoal is crushed. The char splits into thin long splinters as shown in Figure 21. The particle in Figure 21, which is from charcoal produced at 340 °C, is about 1 mm in length but has been separated in the sieving as being 0,25 – 0,3 mm. The particle would have most likely, after sufficient time in the sieve, also passed through the mesh of 250 µm as its width appears to be around 150 µm. The fact that charcoal breaks into flakes of this shape posed some requirements on the sieving procedure. The crushed charcoal was sieved for 1 min at 75% of maximum amplitude and all particles found on the 250 µm mesh after this procedure were considered to be of the proper size.
6.5.1 Reactivity of charcoals from plain wood

In Figure 22 the conversion $X$ is plotted over time for charcoals produced at different pyrolysis temperatures. The conversion rate is increased with increasing pyrolysis temperature. At 50% conversion, $X = 0.5$, the conversion rate for charcoal produced at 700°C is 38% greater than that for charcoal produced at 300°C.

![Figure 22. Gasification of charcoal particles 250 – 300 µm.](image)

The conversion of char from the bituminous coal is compared with charcoal in Figure 23. At $X = 0.5$ the conversion rates of the charcoals are 10 times greater than that of coal char. This can be explained by the difference in physical structure between charcoal and coal char. This is well illustrated by Figure 24. The charcoal to the left has a flaky hollow structure whereas the coal char to the right is dense with few pores. The more porous structure of the charcoal, the larger surface area for the reaction between CO$_2$ and carbon to take place.
6.5.2 Reactivity of charcoals from impregnated wood and charcoal

The reactivity of the chars from impregnated wood and charcoal is not different from charcoal from plain wood, see Figure 25. Char from bio-oil is less reactive. At $X = 0.5$ the conversion rate is 33% less for bio-oil char than for the charcoals. This can be explained by looking at microscope photos in Figure 26 of char from impregnated wood and char from bio-oil. The bio-oil char is less porous than the char from impregnated wood.
6.5.3 Charcoal gasification model fitting

Up until 50% conversion the conversion rate of the charcoals decrease in a linear manner but at $X = 0.5$ the rate evens out before diving to 0 at $X = 0.8$. The extended random pore model fits well with the experimental data for all charcoals produced in this project. Figure 27 shows model fitting for two charcoals. The conversion rate curves together with the model fitting indicate that there is an influence on the conversion by catalytic substances within the char.
6.5.4 Volatile matter in charcoals

When the charcoal is lowered into the heated chamber of the TGA equipment volatile matter is released within the first seconds. In the experiments, the sample was lowered by hand carefully to not cause shaking and spillage, a procedure taking 5 – 10 seconds. The volatile release happened within this time and could therefore not be seen on the TGA data as the data logging could be started only after the sample was hanging freely in the chamber. But since every sample was weighted before the experiment the initial data from the TGA could be used to estimate the mass of volatile matter released. Figure 28 shows the estimated volatile matter for charcoals produced at different temperatures. The error bars marks 90 % confidence intervals for the estimated values. The volatile matter is high for charcoals produced at low temperatures and decreases in a linear manner as the pyrolysis temperature is increased.

Figure 27. For 340 °C char: $\psi = 1 \ c = 1,3 \ p = 4$ For 500 °C char: $\psi = 0,5 \ c = 1,2 \ p = 4,5$

![Charcoal gasification, model fitting, Extended Random Pore Model](image)

![Gasification at 900 °C](image)

Figure 28. Volatile matter in charcoal from fir wood.
6.6 Elemental analysis

The results from the elemental analysis of charcoals are presented in the graphs in Figure 29. The carbon content is increased with increasing pyrolysis temperature for all chars hence the hydrogen and oxygen content is decreased. The only clear influence of the impregnation is the values for impregnated charcoal 80/20 at 300 °C. This is due to the charcoal used to impregnate was produced at 340 °C.

Figure 29. Elemental analysis of chars.
7. Conclusions
The two main objectives of this work was to find pyrolysis conditions, applicable in a real process, that increase the charcoal yield and also to investigate how the reactivity of the charcoal is affected by these conditions. It has been proposed that the charcoal yield is increased if the tar found in the pyrolysis gases are condensed and returned to impregnate the ingoing wood before undergoing a second pyrolysis step. Alternatively, the charcoal yield was proposed to be increased by letting the tar impregnate the outgoing charcoal before the two undergoes a second pyrolysis step. This has been evaluated experimentally by pyrolysis of fir wood chips impregnated with bio-oil, which has been used to resemble tar. The following conclusions can be drawn:

- The highest charcoal yield from pyrolysis of plain wood chips was at 300 °C where 37 % of the wood was converted to char.

- By impregnating wood chips with bio-oil at a mass ratio of 80/20 the char yield is increased by 16 %. This has been confirmed at pyrolysis temperatures between 300 – 450 °C.

- It can be concluded, with 80 % confidence, that the char yield in pyrolysis at 340 °C of wood and bio-oil at a ratio 75/25 is higher if the two undergoes pyrolysis while being in contact with each other rather than separately.

- The char yield is not increased by pyrolysis of charcoal impregnated with bio-oil.

- The reactivity of charcoal decrease with increasing pyrolysis temperature.

- The reactivity of the charcoals is not affected by the impregnation methods.

Future Work
To fully evaluate the hypothesis experiments should be done with tar produced in the laboratory from the same feedstock. The conversion of tar should be studied at lower temperatures than 300 °C to see if it would be beneficial to the total char yield if the tar is converted separately at a lower temperature. An analysis of the pyrolysis gases is needed to see how the tar condensation will affect the remaining gases and their possibilities to supply enough heat to sustain a continuous pyrolysis process.
8. References


4. Injecting Different Types of Biomass Products to the Blast Furnace and Their Impacts on the CO2. Wang, C, o.a., o.a. Luleå : u.n., 2015.


