

Optimization of Biomass Materials for use in the Sponge Iron Process

Master Thesis for Degree in Master of Science in Chemical Engineering

Author: Elin Hernebrant

Supervisors: Dr Ryan Robinson (Höganäs AB) and Professor Jan-Olle Malm (LTH)

Examiner: Professor Sven Lidin

Department of Chemistry

Centre for Analysis and Synthesis

Lund University

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Abstract

This master thesis was a project in cooperation with Höganäs AB. The aim was to increase the apparent density (AD) of two biomass chars, by three different agglomeration methods. The reason for the investigation is that biomass char could be used as a reducing agent in the sponge iron process at Höganäs AB. The goal was to exchange anthracite in the reduction mixture to agglomerated biomass char. Biomass char is a more environmentally friendly alternative to anthracite. The fact that the price of anthracite of good quality is also increasing, which makes it necessary to find an alternative material.

A characterization of the biomass chars was performed at first, where the specific surface area, higher heating value and composition of the biomass chars were determined. Extrusion, tumble agglomeration and granulation in a planetary mixer were performed in order to increase the AD of the biomass chars. A binder was necessary in all agglomeration methods, which is why a preliminary binder investigation took place. Four different organic polymers and one inorganic binder have tested in this investigation. In order to see if the AD had increased and what properties that might have an effect on the AD, an evaluation of the agglomerates was performed. The evaluation included measuring the AD, determining the particle size distribution, moisture content and the reactivity of the agglomerates. The final experiments were made in a pilot scale process, which is similar to the sponge iron process, in order to see how an increase in AD could affect the reduction.

The agglomerates made in the extruder resulted in the highest AD. The result was expected since extrusion is a high-pressure method compared to the other methods. A surprising result was, however, the increase in reactivity of the agglomerates made in the extruder. The agglomerates made by tumble agglomeration and granulation decreased in reactivity.

Acknowledgement

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Table of Contents

1 Introduction	1
1.1 Presentation of the Project	1
1.2 Aim	1
1.3 Scope	1
1.4 Limitations	2
1.5 Background	2
1.5.1 Höganäs AB	2
1.5.2 The Sponge Iron Process	2
1.5.3 Previous Study	4
2 Literature Survey	6
2.1 Biomass	6
2.1.1 Raw Biomass	6
2.1.2 Composition of Biomass	6
2.1.3 Biomass Treatments	8
2.1.3.1 Pyrolysis	8
2.1.4 Comparison between Biomass and Fossil Materials	9
2.1.5 Biomass Char as a Reducing Agent	11
2.2 Agglomeration Theory and Technology	11
2.2.1 Agglomeration Mechanism	11
3 Implementation	14
3.1 Material	14
3.2 Characterization	15
3.3 Agglomeration Methods	16
3.3.1 Pretreatment of the Biomass Chars	16
3.3.2 Preliminary Binder Investigation	17
3.3.3 Agglomeration	20
3.3.3.1 Extrusion	20
3.3.3.2 Tumble Agglomeration	21
3.3.3.3 Granulation	21
3.4 Methods for Evaluating Agglomeration Results	22
3.4.1 Apparent Density	22
3.4.2 Reduction Value	22
3.4.3 Particle Size Distribution	22
3.4.4 Compression Strength	22

3.4.5 Reactivity Test	23
3.4.6 Moisture Content	23
3.5 Tests in Pilot Scale	24
4 Results	26
4.1 Characterization Results	26
4.2 Pretreatment Results	27
4.3 Binder Determination	27
4.4 Agglomeration Results	28
4.4.1 Choice of Binder	28
4.4.2 Extrusion	29
4.4.3 Tumble Agglomeration	29
4.4.4 Granulation	31
4.5 Results from the Agglomeration Evaluation	33
4.6 Pilot Tests Results	37
5 Discussion	41
6 Conclusion	45
7 Future Work	46
Appendix 1	
Appendix 2	
Appendix 3	
Appendix 4	
Appendix 5	

1 Introduction

1.1 Presentation of the Project

This master thesis is a project in association with Höganäs AB and is a continuation on a previous study [1]. In the previous study [1], different biomass chars were investigated for the use as a reducing agent, instead of fossil material, in the sponge iron process at Höganäs AB. The reason for the investigation is the environmental aspect of biomass chars and also the fact that the reducing agent that is used today becomes more and more expensive. The main environmental benefit with biomass compared to fossil materials is that biomass are renewable if new plants or trees are planted after harvesting.

The results from the previous study [1] showed that it is possible to use biomass chars as a reducing agent. The high reactivity and the small amount of sulfur in biomass chars are some of the advantages. Some problems arose, however, with the exchange to biomass char, such as the low apparent density (AD) (g/dm^3). The low AD resulted in poor reduction compared to the reduction with current reducing agent. AD is a density measurement, where the total volume of the material is taken into account [2]. The total volume also includes the space between particles when the material is placed in a beaker of specific volume [2]. The low AD also made it difficult to fit all reducing agent that is necessary in the process. The sponge iron process and the previous study will be explained further in the report.

The purpose of this master thesis is therefore to increase the AD by different agglomeration methods and determine which AD that is optimal for biomass char, when acting as reducing agents. The agglomeration methods going to be performed are extrusion, tumble agglomeration and granulation in a planetary mixer. For all agglomeration methods, a binder will be necessary and to determine which binder that is suitable for each method, a preliminary binder investigation will be done.

1.2 Aim

The aim of this master thesis is to optimize two different biomass chars by increasing the AD. The goal is to reach an AD that is higher than non-agglomerated biomass char, yet lower than the AD of the reducing agent that is used today, to utilize the high reactivity of biomass chars. Furthermore, determine which properties of the agglomerates that are necessary for the use as a reducing agent in the sponge iron process at Höganäs AB.

1.3 Scope

Three different agglomeration methods will be performed in order to increase the AD of two different biomass chars. A preliminary binder investigation will be performed in order to determine which and how much binder that is going to be used in the agglomeration methods. It was initially planned that two levels of AD should be reached for each agglomeration method. However, due to difficulties in controlling the AD during the experiments, shortage of material and lack of time, only one level of AD will be reached for each method. For the experiments in the extruder, only one of the materials will be used due to shortage of material. This means that

it will result in five samples in total. These five samples will be evaluated to determine AD, particle size distribution, reduction value, compression strength, reactivity and moisture content. A characterization of the biomass chars will also be performed, which include determination of the composition of the biomass chars, surface area and higher heating value (HHV). The final tests will take place in a pilot plant, in a process that is similar to the sponge iron process.

1.4 Limitations

The project will not include any economic evaluation.

1.5 Background

1.5.1 Höganäs AB

According to “Stawfordska Sällskapet – Historikgruppen för Höganäs AB” [3], Eric Ruuth and Carl Bagge founded Höganäs Stenkolsverk in 1797. Höganäs Stenkolsverk was working with coal mining and in the future years, they also manufactured a variety of other products, such as bricks, salt glazed pottery and sanitary ware [3]. In 1903, Höganäs Stenkolsverk became Höganäs-Billesholm AB after a merging of the two companies Höganäs Stenkolsverk and Billesholm-Bjuvs AB [3]. Then in 1910, the sponge iron process was built and ready to use [3]. Since 1966, the company’s name is Höganäs AB [3].

Today, Höganäs AB is the leader of production of metal powder in the world [4]. There are various type of metal powders suitable for different applications. Metal powders can for example be used in sintered components, surface coating and metal injection molding [5].

The headquarters of Höganäs AB is located in Höganäs in northwestern of Skåne in Sweden. Höganäs affiliates can also be found in other parts of the world, for example Brazil, India and United States [5].

1.5.2 The Sponge Iron Process

The sponge iron process is a process for producing sponge iron, which is porous iron [1]. The raw material used for producing sponge iron is magnetite ore concentrate (Fe_3O_4), which is the material that will become reduced [1]. The reduction mixture consists of coke and anthracite [1]. Figure 1.1 shows the process scheme over the sponge iron process.

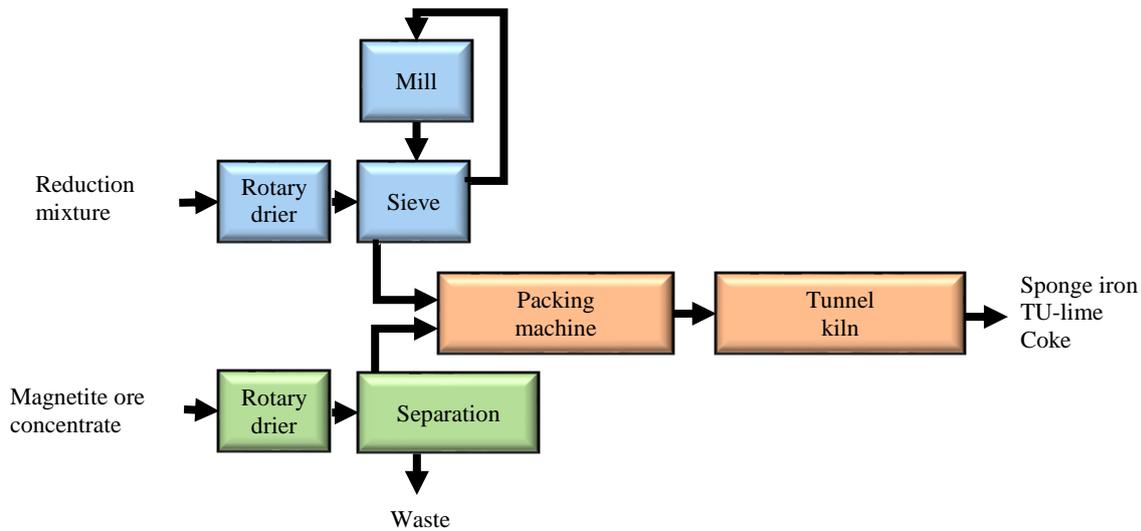


Figure 1.1. The sponge iron process at Höganäs AB (Adapted from [1]).

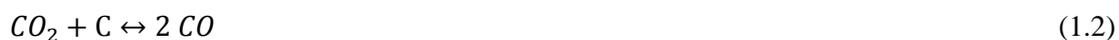
The reduction mixture and magnetite ore concentrate enter separate rotary driers [1]. After drying, large particles in the reduction mixture will be sorted out during sieving and crushed [1]. The magnetite ore concentrate will enter a magnetic separation after drying, because only ferromagnetic material is used in the process [1]. Further, the reduction mixture and the magnetite ore concentrate are placed in capsules [1]. The materials are distributed in a certain pattern in the capsules by a packing machine [1].

When the capsules are filled, they will be placed on a cart and enter a tunnel kiln [1]. The cart will travel through three zones in the tunnel kiln; the pre-heating zone followed by a firing zone and a cooling zone [1]. The temperature in the firing zone will reach approximately 1200°C [1].

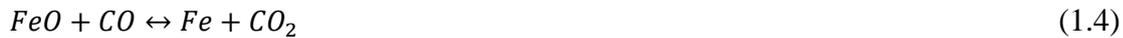
While in the tunnel kiln, a lot of chemical reactions occur. At rather low temperatures, volatile hydrocarbons are released, followed by oxidizing of coal when the temperature has increased (1.1) [1].



Carbon dioxide (CO₂) will in turn react with anthracite in the reduction mixture at first, because anthracite is more reactive than coke, and afterwards with coke in the Boudouard reaction (1.2) [1]. The reason for the higher reactivity of anthracite is because of the longer decay period compared to coal [6]. Further, anthracite therefore contains more carbon than coke [6]. Anthracite also contains a larger fraction of volatiles compared to coke, which is due to the more anisotropic structure of anthracite [1].



The product, carbon monoxide (CO), is used to reduce the magnetite ore concentrate, which is done in two steps (1.3)-(1.4) [1]. The first step occurs at approximately 650°C and the second step occurs at approximately 1000°C [1]. Magnetite ore concentrate will at first be reduced to wüstite (FeO) and in a second step to iron (Fe) [1].



The remains of carbon monoxide that will not be used to reduce magnetite ore concentrate is combusted (1.5) [1].



The reduction reactions are endothermic, which means that energy needs to be added in order to keep the temperature stable [1]. This is done by burning natural gas and also by the exothermic reactions (1.1) and (1.5) [1].

In order to have enough carbon monoxide in the cooling zone, there must be an excess of carbon in the process [1]. In addition to reducing agent, coke also work as protection against oxidation of sponge iron if there is an excess of coke, or in fact carbon [1]. Anthracite does not have that property since it is more reactive than coke [1]. At the time when there is a possibility for oxidizing of sponge iron, anthracite is already consumed [1]. It is necessary to have both coke and anthracite in the reduction mixture, due to their different properties [1].

The outcome from the tunnel kiln is sponge iron, which has an iron content of 98 %, and residues from the reduction mixture [1]. The residues can be further separated in order to get coke that can be reused in the reduction mixture and the by-product TU-lime [1]. The sponge iron will get crushed and exposed to further treatments in order to get the final iron powder [1].

1.5.3 Previous Study

Alternative materials to the reducing agent that is used today in the sponge iron process at Höganäs AB, were investigated in a previous study [1]. The alternative materials tested were biomass char from different biomass sources. A characterization was made on the materials to determine for example the moisture content, amount of fixed carbon and volatile matter. Important results from the previous study are presented in Appendix 1. The alternative materials were also investigated in pilot scale, in a process similar to the sponge iron process, to see if it is possible to use them as reducing agents.

The results from the previous study [1] showed that it seem to be possible to use biomass char as reducing agent. Magnetite ore concentrate became reduced and sponge iron was produced. However, all magnetite ore concentrate did not become reduced. The reduction was not as good as when using fossil materials. The AD of the alternative materials was not high enough to

create stability in the capsule, or enough to fit all necessary carbon content in the capsule. The author concluded that the AD should at least be 300 g/dm^3 in order to fit all carbon that is necessary during the reduction in the capsule.

2 Literature Survey

2.1 Biomass

2.1.1 Raw Biomass

Biomass is usually some kind of plant-life, such as trees, crops or plants, but biomass can also be in the form of municipal waste [7]. Sweden has 22.5 million hectares of forest of a total area of 40.8 million hectares [7], which means that 55 % of available land is forest. The forest in Sweden mostly consists of Norway spruce, Birch and Scots pine [7]. The biofuel from forestry can be logging residues, clearing wood and timber that is not going to be used in some kind of industry [2]. Different parts of the tree can be used, including branches, spruce needles, bark and the trunk [2].

Another important source of biomass is agriculture [7]. Usually the biomass consist of some kind of crop [7]. The most frequently used agricultural products in Sweden are Salix [7] (energy wood) [2] and residues of straw [7].

On the market, there are biomass that are commercial and as by-products. By-products that are classed as biomass are generated by for example pulp- and paper industry and sawmills [7]. Bark is for example a by-product from forest industry that is used as a saleable biomass product [2]. A common commercial biomass is wood residues from harvesting [2].

2.1.2 Composition of Biomass

The composition of biomass varies greatly because of the variety of sources. However, the main components in a wood-based biomass are listed below [2, 8]:

- Cellulose
- Hemicellulose
- Lignin
- Extractives

Cellulose is the main component in wood-based biomass, since approximately 50 % is cellulose [9]. Cellulose is a polysaccharide that consists of glucose monomers [9]. It is a semi-crystalline polymer, due to the crystalline cellulosic microfibrils and the amorphous cellulose on the outside of the microfibrils [9]. These microfibrils are further arranged in bundles [9], which can be seen in Figure 2.1.

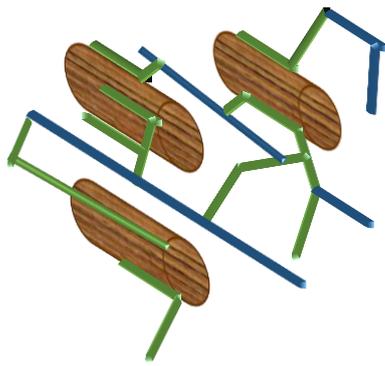


Figure 2.1. Cellulosic bundles (brown), hemicellulose (green) and lignin (blue)
(Adapted from [9] and [25])

Hemicellulose is a branched amorphous polymer [9] that surrounds the cellulose [2], where the monomers in the main chain are xylan [9]. The branches consist of compound such as arabinose, glucose and mannose [9].

Lignin consist of polymers that creates an amorphous network based on phenyl propane monomers [9]. Lignin helps to keep the cellulosic microfibrils together [9]. Other than cellulose, hemicellulose and lignin, biomass also consist of extractives, such as terpenes, fat and phenols [2].

In the purpose of agglomeration, it is also interesting to know the chemical composition of biomass. Table 2.1 shows an example of the chemical composition in biomass based on tree trunk [7].

Table 2.1. An example of the chemical composition of biomass [7].

Substance	Biomass in the form of a tree trunk (wt.-%)
Carbon	51.8
Oxygen	41.8
Hydrogen	6.1
Nitrogen	0.18
Sulfur	0.02
Chlorine	0.02

The amounts in the Table are measured on dried material with no ash. As can be seen in the Table, the main content in biomass is carbon, oxygen and hydrogen.

2.1.3 Biomass Treatments

2.1.3.1 Pyrolysis

Raw biomass needs to be treated, for example by pyrolysis, before it can be used as a reducing agent. The reason is the low energy density and the high moisture content in biomass [7]. The energy density can be calculated by using Equation (Eq.) 2.1.

$$\text{Energy density (J/m}^3\text{)} = \text{HHV (J/kg)} \cdot \text{Mass density (kg/m}^3\text{)} \quad (\text{Eq. 2.1})$$

The HHV defines the amount of energy in a material [10]. There are methods for improving biomass, however, such as pyrolysis, also called dry torrefaction [8]. The result from pyrolysis is a carbonized product in solid state [7], more specifically, biomass char.

In pyrolysis, raw biomass is heated to a temperature between 400°C-500°C [7]. The heating occur in an atmosphere with an inert gas, such as nitrogen [8], in order to make sure no oxygen is present [7]. This will result in three products, which are biomass char, pyrolysis oil and syngas [7].

According to W. Wei et al. [7], depending on temperature and pyrolysis time, the outcome of the reaction will be different. If the temperature is kept low, at approximately 400°C, and the pyrolysis time is long, the amount of biomass char, pyrolysis oil and syngas will approximately be the same. This process is called slow pyrolysis. If the temperature is higher, approximately 500°C, and the pyrolysis time is shorter, more pyrolysis oil is produced and biomass char and syngas are by-products. This process is called fast pyrolysis. According to the authors, there is also a method called gasification, where syngas is the main product and biomass char and pyrolysis oil are by-products. Gasification is performed at high temperature, approximately 1000°C and long pyrolysis time.

Raw biomass is hydrophilic, which can cause sustainability problems [8]. When raw biomass is exposed to water, it will fall apart [8]. The biomass char is on the other hand hydrophobic, due to the pyrolysis, which will increase the biomass char's durability against water [8].

The biomass char produced from pyrolysis consists of approximately 10 wt.-% moisture, compared to approximately 40 wt.-% before pyrolysis [7]. The fixed carbon content, which is the weight loss after combustion in air of a material after the moisture content and volatile matter has been removed [11], is the carbon source that can be utilized in reduction processes [7]. It can be calculated using Eq. 2.2 [12]. The fixed carbon content reaches values between 60-90 % after pyrolysis [7].

$$\text{Fixed Carbon (\%)} = 100 - (\text{Ash (\%)} + \text{Volatile Matter (\%)}) [12] \quad (\text{Eq. 2.2})$$

The volatile matter are gaseous compounds such as hydrocarbons and carbon monoxide [2], which are released during pyrolysis.

In the report, written by M.T. Reza et al. [8], the energy density (GJ/m^3) was also measured before and after treatment. Raw biomass and biomass char almost had the same energy density, approximately 20 GJ/m^3 . The reason is according to the authors that the HHV (MJ/kg) increased during pyrolysis, which means that biomass char have higher HHV than raw biomass. However, the mass density (kg/m^3) of biomass char became lower than raw biomass in their investigation due to pyrolysis. Based on Eq. 2.1, which could be seen in the beginning of this section, the energy density is approximately the same for raw biomass and biomass char.

As written in the Composition of Biomass, section 2.1.2, the main components in wood-based biomass is cellulose, hemicellulose and lignin. Since these components can influence the agglomeration, it is interesting to know if the pyrolysis process affect the composition. Moreover, the composition before and after pyrolysis at 350°C was investigated in the report written by M.T. Reza et al [8]. The biomass used in the investigations was loblolly pine, which consisted of 54 % cellulose, 11.8 % hemicellulose, 25 % lignin, 8.9 % extractives and 0.4 % ash before the pyrolysis. The results in the report showed that both cellulose and hemicellulose decreased during pyrolysis to 18 % and 0 % respectively. In relation to cellulose and hemicellulose, the lignin content increased by pyrolysis and became 80 %. The extractives and ash resulted in 1 % and 0.9 %. According to the authors, the reason for that was that water extractives, hemicellulose and about 65 % of cellulose became volatiles during pyrolysis. The other 35 % of cellulose became solid char.

2.1.4 Comparison between Biomass and Fossil Materials

There are inherent differences between biomass and fossil materials. In the report, written by W. Wei et al. [7], it is described how the fossil fuel can be replaced by biofuel in a blast furnace. Differences between biofuel and fossil coke are explained in the report. The moisture content is one dissimilarity, which can be calculated using Eq. 2.3 [2].

$$\text{Moisture Content (\%)} = 100 - \left(\frac{\text{Dried material}}{\text{Raw material}} \cdot 100 \right) \quad [2] \quad (\text{Eq. 2.3})$$

For raw biomass, the moisture is usually more than 30 wt.-% compared to 2-4 wt.-% for fossil coke [7]. However, as written before in Pyrolysis, section 2.1.3.1, the moisture content of biomass after upgrading treatments decreases to 10 wt.-%, which can be seen in Table 2.2. All the values listed in the Table are results after biomass has been treated in pyrolysis. The values vary a lot depending on which coke or biomass char used, which means that the values in the Table are only one example of a comparison.

Table 2.2. An example of a comparison of important parameters for coke and biomass char [7].

Property	Unit	Coke	Biomass char
Moisture	wt.-%	2-4	10
Ash	wt.-% (dry basis)	10	3
Volatile matter	wt.-% (dry basis)	1-3	20-25
Fixed carbon	wt.-% (dry basis)	85-88	70

Another dissimilarity between fossil materials and biomass char is the ash content. Ash is inorganic non-combustible compounds [2]. Table 2.3 is a list of chemicals that can be found in the ash of biomass char. Biomass char contains less ash but more volatiles, compared to coke. The fixed carbon content is slightly higher for coke than for biomass char. A high carbon content is important because, as written before, it is the carbon that is essential for reduction [7]. The ash content, fixed carbon and volatile matter are based on dried material.

Table 2.3. An example of ash composition in biomass char [7].

Substance	Amount (g/kg sample)
Calcium	4.430
Potassium	2.570
Magnesium	0.910
Manganese	0.580
Phosphor	0.290
Iron	0.076
Silica	0.060
Aluminum	0.025
Titanium	0.019
Sodium	< 0.010

As written before, the values in the Table are only examples and can vary a lot between different types of coke and biomass chars. The HHV is almost the same for coke and biomass char. In the report, written by J. Parikh et al. [10], a correlation has been made that makes it possible to mathematically determine the HHV of biomass chars, using Eq. 2.4.

$$HHV (MJ/kg) = 0.3536 \cdot \text{Fixed Carbon} + 0.1559 \cdot \text{Volatile Matter} - 0.0078 \cdot \text{Ash} [10] \text{ (Eq. 2.4)}$$

The amount of impurities in coke and biomass char is also of interest. Fossil materials usually contains more sulfur than biomass chars [7]. However, results from the previous study [1] showed that the potassium content in the ash from the majority of the biomass chars were higher than in the ash in the fossil materials.

2.1.5 Biomass Char as a Reducing Agent

There are both advantages and disadvantages with using biomass char as reducing agent in the sponge iron process. There are not infinite amount of fossil material and if it is possible to replace the reducing agent, there will be no dependency on fossil materials [7]. However, there are not an infinite amount of biomass either, unless the material used is recycled and new trees are planted.

Biomass is carbon neutral [7], which means that when biomass char is combusted it does not release any extra carbon dioxide, only the amount that the biomass in the form of tree for example, was taken up during its growth [13]. For this to apply, biomass need to be recycled and new trees need to be planted after harvesting. Otherwise, biomass is not carbon neutral and biomass will not be renewable. If a lot of forest will get harvested, the environment will be negatively affected. It will result in more carbon dioxide released to the atmosphere, because there would not be enough trees and plants that could take care of it through photosynthesis.

There is also another aspect that should be mentioned when it comes to the long term potential adverse effects of an increase of usage of biomass. If the demand for biomass would become much greater, companies selling biomass would probably need more arable land. It could pose a risk that land used for planting food crops is used for planting biofuels instead. It is important to consider the risk and prevent for it to actually happen. There is also a risk that current applications for biofuel get threatened, such as the use for heating houses.

It is important to keep the risks in mind, however, as long as the biomass is used in a sustainable and environmental friendly way, biomass have more benefits than fossil materials.

The reactivity of biomass char was investigated by H-b Zou et al. [14]. Biomass char, coal and coke were tested in their investigation. The biomass char used was carbonized waste wood, which was not compacted before the reduction experiments. In the experiments, the reducing agents reacted with carbon dioxide during heating while the weight change was registered. Results showed that the temperature when the reduction started with biomass char as reducing agent, was lower than the temperature with the use of coal and coke. Furthermore, the reactivity (weight loss/min) of biomass char was higher than the reactivity of coal and coke. According to the authors, the reasons for the low reaction temperature and high reactivity of biomass char are for example because of the high surface area and high content of volatile matter.

There are disadvantages with biomass as well. In the previous study [1], the stability in the capsule during the reduction was not high enough, which is probably due to the low AD of biomass chars compared to fossil materials. The low AD resulted in less material in the capsule, which in turn led to poor reduction [1]. Another thing to consider is the handling of wood-based biomass, which comprises a risk of fire when the material is sufficiently disintegrated [2].

2.2 Agglomeration Theory and Technology

2.2.1 Agglomeration Mechanism

In all the agglomeration experiments that will be performed in this master thesis, a binder will be necessary to keep the agglomerates together. There are several of binders with different

properties. Important is to consider if the binder could affect the process and reduction. The binder should also be environmentally friendly.

Different binders for production of biomass char briquettes were investigated by T. Demus et al. [15]. In their investigation, they tried water as a binder, followed by molasses and polyvinyl alcohol (PVOH). Finally, they tested molasses mixed with water and PVOH mixed with water. The briquette with water and molasses sustained the most pressure in the hydraulic testing press. In summary, a binder with 24 % molasses and 76 % water gave the best results.

During a compaction, or agglomeration, there arises a number of different types of binding mechanisms listed below [16]:

- Solid bridges
- Attraction forces
- Mechanical interlocking bonds
- Adhesion and cohesion forces
- Interfacial forces

Solid bridges occur because of various reasons, such as diffusion of particles, crystallization of a substance, chemical reactions and solidification of binder [16]. Attraction forces are caused by van der Waals' forces for example [16]. The closer two particles come together, the stronger will the attraction forces get [9]. The mechanical interlocking bonds takes place for example when large particles are unfolding and gets trapped in another large particle [16]. Adhesion is caused by viscous binders during agglomeration, which has the ability of creating solid bridges between particles [16]. Moisture in the material could also work as a binder and form cohesive forces and produce a thin adsorption layer that will create interfacial forces [9, 16].

During extrusion, the biomass material is pressed forward by a rotating screw through a die [9]. Biomass particles are therefore pressed against each other, which will cause the attraction forces to become stronger and the material is forced to be compacted [9]. This compaction process will develop heat because of the friction caused by biomass char against the wall of the extruder together with friction internally in the biomass char and the speed of the screw [9]. The heat will cause bridges between the particles followed by interlocking bonds [9].

Tumbling agglomeration can be performed by using a tumbling plate. The plate rotates at a low speed. A small amount of material can be added to the plate followed by spraying of water in order to form nucleates. Material is added at regular intervals and the same applies to water and nucleates will become larger by coalescing [9]. The amount of water added could affect the size of the agglomerates, since much water will result in large agglomerates and vice versa. There is also a possibility that large particles are growing by "consuming" small particles [9].

G. I. Tardos et al. [17] have described the agglomeration mechanism during granulation of powders in a mixer in their report. A binder is continuously added to the powder in the mixer during granulation. Shearing forces will be created by the stirrer, which will help particles to collide. The first step in agglomeration mechanism is the nucleation. The particles will attach to each other because of the binder, which is present on the particle surface. The solvent in the binder should be able to evaporate during the attachment of the two particles. The agglomerates

will grow due to coalescence. When an agglomerate is saturated with binder and collide with another agglomerate, larger agglomerates will form.

In the agglomeration experiments, it is important that a suitable amount of binder is used in order to create nucleates [17]. When nucleates have been formed, there are still a lot of parameters that will influence the stability of the agglomerates, such as the viscosity of binder, the addition rate of binder and the granulation time [17].

Another interesting parameter that could influence the agglomerates is the particle size distribution of the feed. Smaller particles in the feed will result in better durability [16] and could lead to higher density of the agglomerates [9], however, more grinding also leads to higher costs [16]. A recommended particle size distribution is 0.5-0.7 mm [16]. Another suggestion, according to [9], on the feed particle size distribution is presented in Table 2.4.

Table 2.4. Suggestion on feed particle size distribution [9].

Sieve size (μm)	Amount of material on the sieve (%)
+3000	1
+2000	5
+1000	20
+500	30
+250	24
-250	20

3 Implementation

3.1 Material

Two different biomass chars will be used in the experiments, biomass char 1 (BC 1), which is a by-product when producing syngas during pyrolysis, in the same way as in the Literature Survey, section 2.1.3.1. The raw material for producing BC 1 is Salix. Biomass char 2 (BC 2) is a commercial product. The reason for using these materials is because of the result from the previous study [1], where four biomass chars, BC 1, 2, 3 and 4, from different biomass were investigated. Table 3.1 presents some of the results from the previous study [1].

Table 3.1. Some of the results from the previous study [1].

	Anthracite	BC 1	BC 2	BC 3	BC 4
Apparent density (g/dm ³)	810	191	253	232	289
Remaining reduction mixture in the capsule after reduction (%)	54	45	48	46	44
Fixed carbon in the capsule (kg)	17.9	15.2	16.8	16.4	16.7
Ash (% dry basis)	8	4	7	2	15
Fixed carbon (% dry basis)	81	85	64	76	58

The reason for choosing BC 2 in the experiment in this master thesis is because of the slightly higher content of fixed carbon in the capsule, compared to the other materials. According to the results in the previous study [1], BC 4 seemed to have the second highest amount of fixed carbon in the capsule and moreover the highest AD, however, the high ash content that is formed is not preferred. The reason for choosing BC 1 as the second material in the experiments, is because it is a by-product from syngas production, whereas BC 3 is a commercial product.

The appearance of both BC 1 and BC 2 is reminiscent of ground charcoal, which can be seen in Figure 3.1. Both materials have been pyrolyzed, however, BC 1 have been pyrolyzed at a higher temperature, which also gives the material a burned and smoky smell.



Figure 3.1. To the left: BC 1. To the right: BC 2.

The particle size distributions of the materials are compared in Table 3.2.

Table 3.2. Particle size distributions of BC 1 and BC 2.

Sieve size (μm)	Amount of BC 1 on the sieve (wt.-%)	Amount of BC 2 on the sieve (wt.-%)
+800	87.3	20.0
+500	0.5	8.2
+425	1.0	1.6
+300	1.0	6.7
+212	0.6	7.5
+150	0.7	5.6
+106	0.4	5.7
+75	5.1	4.9
-75	3.4	39.8

3.2 Characterization

Two analysis will be performed by an external company, where one is calorimetry in order to determine HHV (kcal/kg) and the other is an analysis in order to determine the elemental composition of the biomass chars. A BET (Brunauer Emmett Teller)-analysis will be performed by Höganäs AB, in order to determine the specific surface area (m^2/kg) of the biomass char particles. All analysis will be performed on the particles that are smaller than 800 μm and larger than 500 μm (-800 μm +500 μm), in order to normalize the samples and improve the comparability.

The HHV will be determined experimentally before agglomeration. A bomb calorimeter will be used to determine HHV. The sample container will be placed inside of the bomb, which is made of stainless steel [18]. During the experiment, water vapor will be produced [18]. In order to condense the formed vapor, a small amount of water will also be added to the bomb [18]. The water will consequently absorb vapor molecules [18]. Afterwards, the bomb will be filled with oxygen, which will cause the pressure inside of the bomb to increase [18]. Furthermore, the bomb is placed inside of the actual calorimeter [18]. A known amount of water will be added into the calorimeter [18]. A thermometer is regularly measuring the temperature of the water [18]. The sample will be ignited and a combustion will take place [18]. Energy (kcal) will therefore be transported as heat to the water outside the bomb, per biomass char sample (kg), during combustion (water in liquid phase as product) at a constant volume [19].

Usual methods for determining the composition in coal are proximate and ultimate analysis [11]. The result from the proximate analysis contains the amount of ash, moisture, volatile matter and fixed carbon in the material [11]. The results from the ultimate analysis instead contains the elemental composition of carbon, oxygen, hydrogen, nitrogen and sulfur in the materials [11].

The ash content (% , dry basis) in the materials will be determined by a TGA (thermogravimetric analysis) of the samples. The samples will be heated and combusted and at the same time will the weight change be registered. The weight will become stabilized after combustion, which will be the same as the ash content [11].

In order to determine the composition of carbon, hydrogen and nitrogen in the materials, a CHN analysis equipment will be used. The sample will be combusted in an electric furnace, which is connected to two infrared cells, in order to detect carbon and hydrogen, and one thermal conductivity cell in order to detect nitrogen [20]. The sulfur will be analyzed in a similar way in another equipment, where the sample is combusted in a furnace completely filled with oxygen [20]. The product, sulfur dioxide (SO₂), will be detected by an infrared cell [20]. The oxygen content in the materials will be calculated based on the results from the analysis.

In addition to the ash content and the ultimate analysis, the chlorine content in the materials will also be determined. This will be determined by ion-exchange chromatography. An extraction of ionic species [21] in the biomass char samples need to be performed because only liquid samples are possible to use in ion-exchange chromatography. The liquid sample, the solution, is injected to the ion-exchange equipment [22]. The ion-exchange will take place in a column (stationary phase), which is packed with particles with ion-exchangers (counter ions) [22]. An eluent (mobile phase), which also consists of ion-exchangers, is also passing through the column [22]. The eluted sample will pass through a detector in order to determine the chlorine content [22].

The BET-analysis will take place before and after agglomeration in order to determine the specific surface area of the particles. The specific surface area will be determined by nitrogen gas adsorption. The nitrogen molecules are assumed to form a monolayer on the surface of the particles in the sample [23]. The specific surface area can be calculated based on the amount of nitrogen gas (mol/g solid sample), which is calculated from an adsorption isotherm, the Avogadro number and the cross-sectional area of a nitrogen molecule [23].

3.3 Agglomeration Methods

3.3.1 Pretreatment of the Biomass Chars

The particle size distributions of the two biomass chars are not the same, which could be seen in Material, section 3.1. In order to be able to draw fair conclusions when comparing the results between the materials, the particle size distributions should be more equal. BC 1 will therefore get grinded in a BAC-mill, in order to get similar size distribution as BC 2. The BAC-mill is a combined hammer- and disc mill, which is specially made for Höganäs AB.

BC 2 contains more moisture than BC 1, 25 % and 4 % respectively. By drying BC 2, the conditions will be more equal when making agglomerates. Some analysis that will be done, such as the BET-analysis, also requires a dry material. The drying will take place in a drying cabinet, which can be seen in Figure 3.2, at 90°C.



Figure 3.2. The drying cabinet.

3.3.2 Preliminary Binder Investigation

All agglomeration methods are in need of a binder. In order to determine how much and which binder that is suitable for each agglomeration method, a binder investigation will be made. Binders that will be investigated are organic polymer 1, 2, 3 and 4 as well as an inorganic binder.

According to T.C. Eisele et al [24], the properties of binders can be divided into various groups. Moreover, the organic polymer 1 will create a film due to a chemical reaction on the particle's surface [24]. Due to the chemical reaction, the film will solidify, which will cause the particles to attach to each other [24]. Organic polymer 2, 3 and 4 will create an inactive film on the particle's surfaces instead [24]. The inactive film is caused by the stickiness of the binders [24]. The attachment of the particles are therefore caused by capillary forces, adhesion or cohesion [24]. The inorganic binder will create a chemical matrix, which means a matrix caused by a chemical reaction [24]. The chemical matrix will solidify, like the chemical film [24].

In the binder investigation, only one of the biomass chars will be investigated and it will be BC 2. There is not enough time to investigate both nor enough material of BC 1 to use in the binder investigation and in the large scale agglomeration experiments.

Equipment that will be used in the binder investigation are a tumbling plate, a planetary mixer and a hydraulic press. These methods have been chosen because they are similar to the agglomeration methods that will be performed in larger scale. Agglomerates will be made with each method followed by an investigation of the compression strength and measuring of AD.

The first agglomerates will be made in a tumbling plate, which can be seen in Figure 3.3. The equipment consists of a plate with approximately 1.5 dm high edges, which is fixed to a tripod.



Figure 3.3. The tumbling plate.

Biomass char will be mixed with binder and water as a starting mix. A small amount of the mix will be added to the plate followed by spraying of water. This will be repeated until the material is out. Some of the agglomerates will fall out from the plate when they are large enough. The rest of the agglomerates will be removed from the plate while it is still rotating. Afterwards, the agglomerates will be left to dry.

It can be seen in the Figure that the plate is angled. The smaller the angle, the larger will the pellets become because the pellets will stay and tumble for a longer time in the plate before the pellets fall out.

It needs to be quite damp to get any agglomerates and that is why a humidity meters is placed in the plate.

The planetary mixer that will be used for granulation is an ordinary kitchen machine, which can be seen in Figure 3.4. The biomass char will be mixed with the binder followed by granulation at the highest mixing speed for a short period of time, approximately three minutes. Water will be added if necessary. The agglomerates will be left to dry in air afterwards.



Figure 3.4. The kitchen machine.

Pellets will be made in a hydraulic press. Biomass char will be mixed together with binder and water in the kitchen machine. The pellets will be made by using a press tool, which can be seen in Figure 3.5. Material will be added in the tool with a hole and pressed together by the hydraulic press with 15 tons by the two pistons.



Figure 3.5. Tools for the hydraulic press.

In order to determine how sustainable the agglomerates will become, the compression strength of the agglomerates will be decided. The equipment consists of two load cells, which can be seen in Figure 3.6. The agglomerate will be placed between a stamp and a load cell and crushed using compressed air. This equipment is connected to a measuring instrument, which saves the highest pressure (Newton) reached. It means that it measures the highest pressure the agglomerate can withstand before it breaks.



Figure 3.6. The compression strength equipment.

The most important test is the AD measurement. It will be done by filling a funnel with the material, which can be seen in Figure 3.7. The funnel has a hole with a specific diameter in the bottom. A beaker of known volume and mass will be placed underneath the funnel. The material will flow down and become loosely packed into the beaker. When the beaker is full, the material will be weighed and the AD can be decided. This will be done on the particles of size $-800\mu\text{m} +500\mu\text{m}$, which means that the agglomerates and pellets need to be ground. A mortar will be used to ground and to be sure the particles are in the correct size distribution, sieving will be performed.



Figure 3.7. To the left: the equipment for measuring AD. To the right: the funnel from above.

3.3.3 Agglomeration

Once the binders have been decided, the agglomeration experiments for producing a larger amount of agglomerates can begin. In order to increase the AD of the biomass chars, three different agglomeration methods will be performed. The methods that will be implemented are extrusion, tumble agglomeration and granulation in a planetary mixer. These methods have been chosen because it is three methods that are available and feasible to implement within the time frame.

3.3.3.1 Extrusion

Extrusion is interesting to try, since it could be a possible way to produce agglomerates continuously. It is also a high-pressure method, compared to the other methods, which means that the results from AD measurements are expected to be the highest.

The experiments in the extruder will be performed by an external company. The corresponding experiments to the extrusion made in the Preliminary Binder Investigation is the hydraulic press.

The material will be added to the extruder and pressed forward by a screw using high pressure. The material will be pressed through holes and the result will probably look like cut “spaghetti-like” pellets. No heat will be added during the extrusion.

Unfortunately, for the extrusion experiments, only one of the biomass chars, BC 2, will be used. The reason is that there is not enough of BC 1 to do all three agglomeration methods. Most of the material is necessary for the extruder, compared to the other agglomeration methods, so a decision was made to use the material of BC 1 for the other two agglomeration methods.

Two batches of BC 2 will be prepared for the extruder, which will be prepared in a planetary mixer, which can be seen in Figure 3.8. The mixing tool that is going to be used is a dough hook, which also can be seen in Figure 3.8. It will be mixed for 15 minutes in the planetary mixer. It is difficult to determine if it is the right amount of moisture in the mixtures so more binder will also be prepared, which can be added if necessary.



Figure 3.8. To the left: the planetary mixer. To the right: the mixing tool.

After the material have been compacted in the extruder, it will be left in air to dry.

3.3.3.2 Tumble Agglomeration

Tumble agglomeration will be performed in a tumbling plate in the same way as in the Preliminary Binder Investigation, section 3.3.2.

3.3.3.3 Granulation

The final method is granulation in a planetary mixer, which could be seen in Figure 3.8 above. However, the granulation tool that is going to be used can be seen in Figure 3.9. The planetary mixer will be set to the highest speed. The granulation will be done for a short period of time, approximately three minutes, in the same way as in the kitchen machine. The agglomerates will be left in air to dry.



Figure 3.9. Granulation tool.

3.4 Methods for Evaluating Agglomeration Results

3.4.1 Apparent Density

AD will be measured after the agglomeration experiments and compared with the AD of non-agglomerated material, which was measured in the previous study [1]. This will be done in the same way as in the Preliminary Binder Investigation, section 3.3.2.

3.4.2 Reduction Value

The reduction value is heating value per volume, which can be calculated by using Eq. 3.1.

$$\text{Reduction value [kcal/dm}^3\text{]} = \text{Apparent density} \cdot \text{HHV [1]} \quad (\text{Eq. 3.1})$$

Reduction value is another word for energy density, which means that Eq. 2.1 in Pyrolysis, section 2.1.3.1, is the same as Eq. 3.1. The reduction value is more useful than the HHV since it is based on volume and one capsule in the sponge iron process have a specific volume.

3.4.3 Particle Size Distribution

The particle size distribution will be determined by sieving at the size fractions; 800 μm , 500 μm , 425 μm , 300 μm , 212 μm , 150 μm , 106 μm and 75 μm . The goal is to reach a particle size distribution of the biomass char agglomerates as anthracite, because it is anthracite that will be exchanged to biomass char. The particle size distribution of anthracite can be found in Appendix 1.

3.4.4 Compression Strength

In order to investigate how much pressure the agglomerates can withstand, the compression strength will be determined. This will be done in the same way as in the Preliminary Binder Investigation, section 3.3.2.

3.4.5 Reactivity Test

The reason for investigating the reactivity is because of the higher reactivity of biomass char compared to fossil materials. The reactivity of the biomass chars will be investigated before and after agglomeration in order to see if the agglomeration causes a change in the reactivity. The reactivity will be determined in a thermogravimetric (TG) oven using carbon dioxide.

The material is placed in a basket to make sure as much as possible of the gas is reaching the sample. The basket is placed on a scale in the oven and the weight of the sample will be registered during the experiment. At first, nitrogen is added to begin the experiment in an inert atmosphere. After 10 min, the scale will be reset and carbon dioxide (500 l/h) will be added. At the same time will the oven be heated to 1000°C and kept at 1000°C for approximately 50 minutes. The weight of the sample will decrease as carbon dioxide react with the carbon in the material as in the Boudouard reaction (1.2).



The weight will be registered every ten seconds during the experiment. The scale has a margin of error between ± 1 g, therefore, in order to get a more reliable result, a weight median will be calculated for each three minutes. The weight loss, TG (%), during the experiment, will be calculated by using Eq. 3.2.

$$TG (\%) = \frac{m_0 + m_{median}}{m_0} \cdot 100 \quad (Eq. 3.2)$$

Where m_0 (g) is the start weight of the sample, m_{median} (g) is the registered weight during the experiment, which has been calculated as a median.

The weight loss per minute, DTG (derivative thermogravimetry) (wt.-%/min), will be calculated by using Eq. 3.3.

$$DTG (wt. -\%/min) = \frac{TG (\%) - 100}{t - t_0} \quad (Eq. 3.3)$$

Where t is reaction time (min), t_0 is the time (min) when carbon dioxide is added and 100 means TG (%) at t_0 .

3.4.6 Moisture Content

The moisture content will be determined using an equipment where the sample is weighed and afterwards heated. It will be heated until there is no weight change, meaning that all water has evaporated and the wt.-% moisture can be determined.

3.5 Tests in Pilot Scale

Tests will also be performed in pilot scale, in a process that is similar to the sponge iron process, to investigate if the agglomerated biomass chars are suitable as reducing agents. The pilot test involves a single sagger furnace, which can be seen in Figure 3.10. The materials will be placed in the capsule in the same pattern as in the sponge iron process, which will be done by using a template. The material will be vibrated down in the capsule in order to fit as much as possible of the reduction mixture in the capsule.



Figure 3.10. The single sagger furnace.

The reduction mixture consists of coke and anthracite, which will be the components in the reference. Anthracite will be exchanged to some of the agglomerated biomass chars. The components will be mixed in a cement mixer.

In the Sponge Iron Process, section 1.5.2, the tunnel kiln with its three zones (pre-heating, firing and cooling) was described. The capsule in the oven in pilot scale will not move like in the tunnel kiln, however, the corresponding “zones” can be seen in Table 3.3.

Table 3.3. The course of events in the single sagger furnace.

Process	Time (% of test duration)	Temperature (°C)
Drying	27	Ambient - 1000
Pre-heating	17	Ambient - 1000
Firing	44	1000-1200
Cooling	12	1200-Ambient

In order to make sure all material in the capsule is dried, the experiments will begin with a drying period.

During the experiments, the temperature and the amount of carbon monoxide and carbon dioxide in the oven will be registered.

The results from these tests will hopefully give answer to the question which AD that is optimal for biomass chars when used as reducing agents. Also, how much of the biomass chars that can fit into the capsule and how much of the magnetite ore concentrate that will be reduced by biomass chars.

After the trial in the single sagger furnace, the produced sponge iron will be crushed between two toothed rolls followed by grinding in a disc mill. A magnetic separation will also be done in order to remove non-magnetic material, such as ash.

The sponge iron produced in the single sagger furnace will be analyzed by Höganäs AB in order to determine the composition of iron, oxygen, carbon, nitrogen and sulfur in the materials. The iron composition will be divided into the total amount of iron and metallic iron. The total amount of iron both consist of metallic iron and iron in chemical compounds. The oxygen content will also be divided into two parts, the total amount of oxygen and oxygen that are bound to iron (H₂-loss).

The amount of Fe in the materials will be determined by titration while the amount of oxygen (total), carbon, nitrogen and sulfur will be determined in a similar way as in the Characterization, section 3.2, of the biomass chars. In order to determine the oxygen that are bound to iron, the samples will be heated in an oven in a hydrogen atmosphere.

4 Results

4.1 Characterization Results

In order to be able to investigate the HHV and the composition of the biomass chars, the biomass chars had to be ground into a finer particle sizes than the particle size -800 μm +500 μm . The result from the calorimetry can be seen in Table 4.1.

Table 4.1. Results from calorimetry on non-agglomerated materials.

Sample	HHV (kcal/kg)
Anthracite	7233 [1]
BC 1	7178
BC 2	7148

The result from TGA, ultimate analysis and ion-exchange chromatography can be seen in Table 4.2.

Table 4.2. The composition of BC 1 and BC 2.

Element (% dry basis)	BC 1	BC 2
Ash	7.8	5.6
Carbon	84.6	81.7
Hydrogen	1.1	2.1
Nitrogen	0.77	0.68
Oxygen	5.7	9.9
Chlorine	0.03	0.05
Sulfur	0.054	0.061

The results from the BET-analysis of non-agglomerated BC 1 and BC 2 can be seen in Table 4.3. Unfortunately, it was not possible to determine the specific surface area of the agglomerated samples. During the analysis of the agglomerated samples, the measurement in the BET equipment did not get stabilized, which means it was not possible to obtain a reliable value of the specific surface area.

Table 4.3. Results from BET-analysis on non-agglomerated samples.

Material	Specific surface area (m^2/kg)
Anthracite	1074
BC 1	8900
BC 2	14800

4.2 Pretreatment Results

BC 1 became ground in a BAC-mill and the result of the particle size distribution can be seen in Table 4.4.

Table 4.4. The particle size distribution of BC 1 after grinding. A comparison is also made with BC 2.

Sieve size (μm)	Amount of BC 1 on the sieve (wt.-%)	Amount of BC 2 on the sieve (wt.-%)
+800	38.1	20.0
+500	0.8	8.2
+425	3.1	1.6
+300	3.7	6.7
+212	3.2	7.5
+150	4.5	5.6
+106	4.5	5.7
+75	6.4	4.9
-75	35.7	39.8

In order to begin the agglomeration experiments with approximately the same moisture content in the two biomass chars, BC 2 became dried in a drying cabinet at 90°C. The material was dried on large plates. The result can be seen in Figure 4.1.

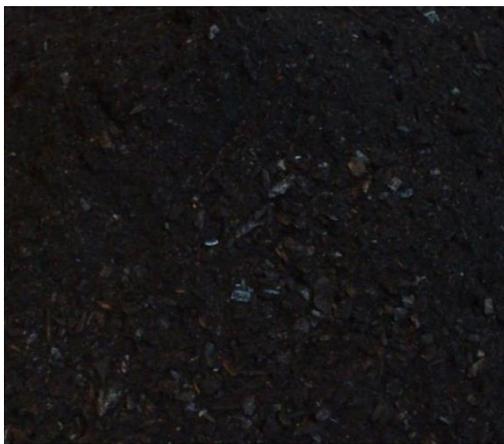


Figure 4.1. BC 2 after drying.

4.3 Binder Determination

In order to determine which binder that is suitable for each method and the amount of binder, agglomerates were made with each binder in the tumbling plate, kitchen machine and the hydraulic press.

After all agglomerates had been made with the various binders in each agglomeration method, the AD and the compression strength could be determined. The result of the measured compression strength of agglomerates made in each method, can be found in Appendix 2.

All AD measurements have been performed on the particle size fraction $-800\mu\text{m} +500\mu\text{m}$. The highest AD for each method is presented in Figure 4.2.

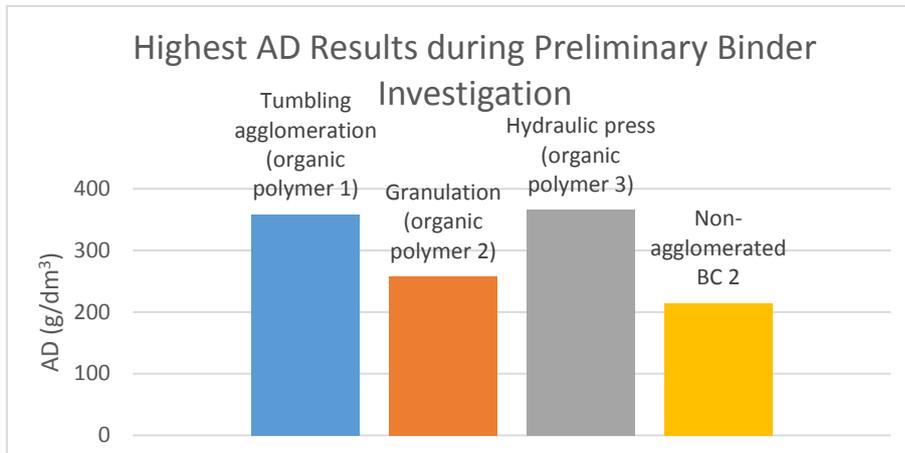


Figure 4.2. The highest AD of agglomerates from each method.

The amount of binder was determined by testing. The goal was to use the smallest amount of binder that was necessary to keep the agglomerates together. The water content was also determined by testing. The concentrations of binder and water in the three methods with the binder that gave the highest AD can be seen in Table 4.5.

Table 4.5. Concentration of water and binder during agglomeration in the binder investigation.

Binder	Amount of binder (wt.-%)	Amount of water (wt.-%)
Tumbling agglomeration (organic polymer 1)	3	63
Granulation (organic polymer 2)	4	56
Hydraulic press (organic polymer 3)	0.6	29.5

4.4 Agglomeration Results

4.4.1 Choice of Binder

The choice of binder for each agglomeration method was decided based on the AD results in Binder Determination, section 4.3. The AD results of the agglomerates made in the tumbling plate showed that organic polymer 1 as a binder gave the highest AD, which is why the organic polymer 1 is chosen for the large scale tumble agglomeration. Organic polymer 2 in the agglomerates made in the kitchen machine gave the highest AD, whereas organic polymer 3 in the pellets made in the hydraulic press gave the highest AD. A summary can be seen in Table 4.6.

Table 4.6. The binders that are going to be used in the large scale agglomeration.

Method	Binder solutions with water
Tumble agglomeration	Organic polymer 1 (50 wt.-%)
Granulation	Organic polymer 2 (8 wt.-%)
Extrusion	Organic polymer 3 (2 wt.-%)

4.4.2 Extrusion

Two batches with biomass char and binder were prepared for the experiments in the extruder, which can be seen in Table 4.7. The choice of the amount of binder and water were based on the results in Binder Determination, section 4.3.

Table 4.7. Concentration of binder and water of the two batches prepared for the extruder.

Batch	Organic polymer 3 (wt.-%)	Water (wt.-%)
1	0.6	29.5
2	0.2	9.6

For the first test run in the extruder, batch 1 was used. However, too much heat was produced so cooling with water was necessary. For the next run with cooling, the extruder got blocked by the material. To solve that problem, the end plate was exchange to another with larger holes, 2-3 mm for the third test run. Also for the third test run, more moisture was added to the feed, which resulted in 0.8 wt.-% binder and 39.4 wt.-% water. The frequency of the electric motor that operates the extruder was set to 40 Hz. The result from the third test run was a compacted material, which can be seen in Figure 4.3.

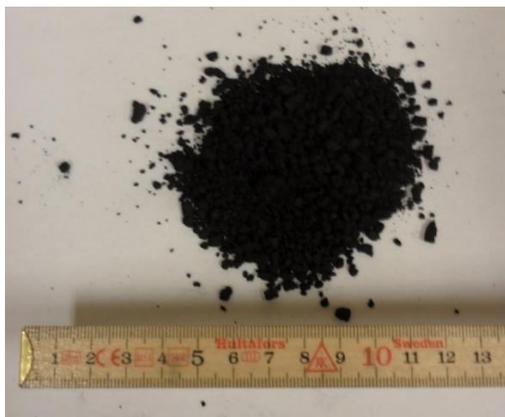


Figure 4.3. Agglomerates made in the extruder.

4.4.3 Tumble Agglomeration

The relative humidity and temperature were measured during the agglomeration in the tumbling plate, which can be found in Appendix 3. Agglomerates that were made in the tumbling plate can be seen in Figure 4.4.



Figure 4.4. Agglomerates produced in the tumbling plate.

The result from tumble agglomeration can be seen in Figure 4.5.

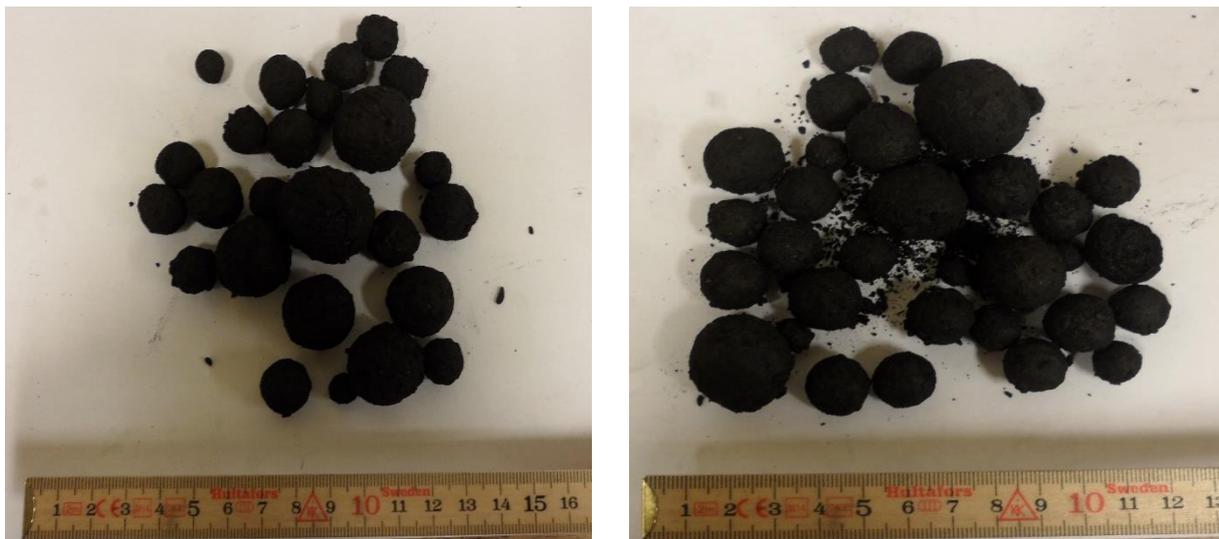


Figure 4.5. Pellets made in the tumbling plate. To the left: BC 1. To the right: BC 2.

During the agglomeration in the tumbling plate, the amount of water and binder were the same from the beginning for each biomass char, which was the same as in the Binder Determination, section 4.3. The concentration of binder and water can be seen in Table 4.8.

Table 4.8. The concentration of binder and water during tumbling agglomeration.

Material	Organic polymer 1 (wt.-%)	Water (wt.-%)
BC 1	3	50
BC 2	3	50

However, the added amount of water during the tumbling agglomerates varied a lot between the biomass chars, which can be seen in Figure 4.6.

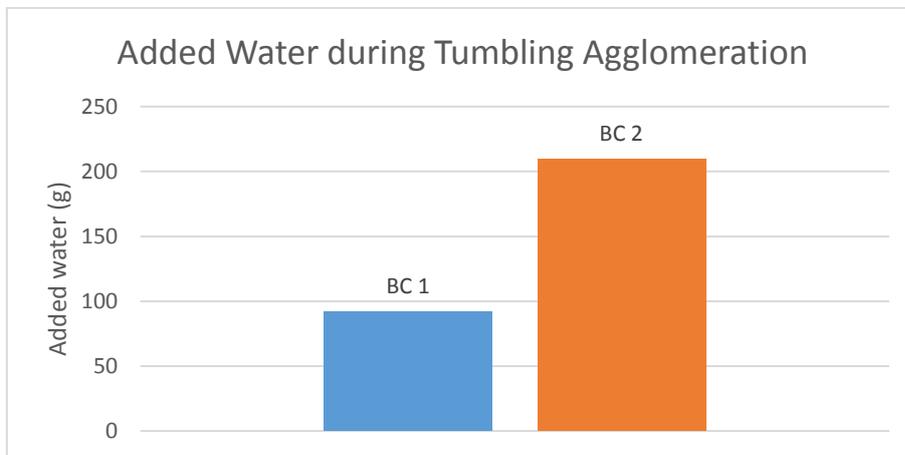


Figure 4.6. The different amount of water added to BC 1 and BC 2 during tumbling agglomeration.

The added amount of water in the Figure is an average based on ten runs in the tumbling plate.

4.4.4 Granulation

The granulation was performed in two batches per biomass char, since all material could not fit into the planetary mixer. The plan was to make the agglomerates in the same way as in the Binder Determination, section 4.3, with the same amount of binder and water and also the same granulation time. Unfortunately, less water and binder were used during granulation of BC 1 because it became too moist. BC 1 had not been investigated before either, which means it was necessary to determine the moisture content by testing.

Further, the planetary mixer had three different mixing speeds (1, 2 and 3) and the plan was to granulate at the highest speed. However, when the highest speed was set, the planetary mixer stopped working and that is the reason why speed 2 was used most of the time.

It was also difficult to see if any agglomerates had formed during the granulation, which means that it was necessary to stop the planetary mixer often. Another reason for stopping often was to avoid breaking any formed agglomerates, which could happen if the granulation time is too long.

Batch 1 with BC 1 had 3.0 wt.-% binder and 39.9 wt.-% water from the beginning, which can be seen in Table 4.9. The material became too moist and no agglomerates were formed when it was 3.7 wt.-% organic polymer 2 and 51.8 wt.-% water, which was the reason for adding more BC 1.

Table 4.9. A summary of granulation using BC 1 in batch 1.

Batch 1 (BC 1)	Organic polymer 2 (wt.-%)	Water (wt.-%)	Granulation time (s)	Speed
From start	3.0	39.9	60	1
Binder and water added	3.7	51.8	180	2
BC 1 added	3.6	49.6	60	2
BC 1 added	3.4	47.6	120	2

When it was 3.4 wt.-% binder and 47.6 wt.-% water, agglomerates were formed and it was therefore known how much water and binder that was necessary for batch 2. However, all the binder and water were not added at once to minimize the risk for making it too moist again. Approximately half of the amount of the binder and water were added at first. A summary of the procedure can be seen in Table 4.10.

Table 4.10. A summary of granulation using BC 1 in batch 2.

Batch 2 (BC 1)	Organic polymer 2 (wt.-%)	Water (wt.-%)	Granulation time (s)	Speed
From start	2.2	30.5	30	1
Binder added	3.4	43.7	30	2
Water added	3.3	46.0	180	2

Batch 1 and 2 made with BC 1 will be mixed before the evaluation of the agglomerates and the tests in pilot scale.

Although BC 2 was granulated in the binder investigation, it can be seen in Table 4.11 that the approach of how the granulation of BC 2 in batch 1 was made resulted in a lot of testing before agglomerates were made.

Table 4.11. A summary of granulation of BC 2 in batch 1.

Batch 1 (BC 2)	Organic polymer 2 (wt.-%)	Water (wt.-%)	Granulation time (s)	Speed
From start	3.4	44.0	30	1
Binder added	4.0	50.5	60	2
Binder added	4.3	54.0	60	2
Only granulation	4.3	54.0	30	2
Water added	4.3	54.4	10	2
Water added	4.3	54.8	10	2
Water added	4.2	55.5	10	2
BC 2 added	4.0	53.3	30	2
BC 2 added	3.9	51.3	30	2
Only granulation	3.9	51.3	30	2
BC 2 added	3.8	50.6	30	2

The procedure of batch 2 with BC 2 can be seen in Table 4.12.

Table 4.12. A summary of granulation of BC 2 in batch 2.

Batch 2 (BC 2)	Organic polymer 2 (wt.-%)	Water (wt.-%)	Granulation time (s)	Speed
Start	2.7	36.0	30	1
Binder and water added	3.8	51.5	30	2
Only granulation	3.8	51.5	60	3

It can be seen in the Table that speed 3 was set and it worked. For this batch, a smaller amount of material was used, which was probably the reason why speed 3 worked.

Batch 1 and 2 made with BC 2 were also mixed and the result can be seen in Figure 4.7.

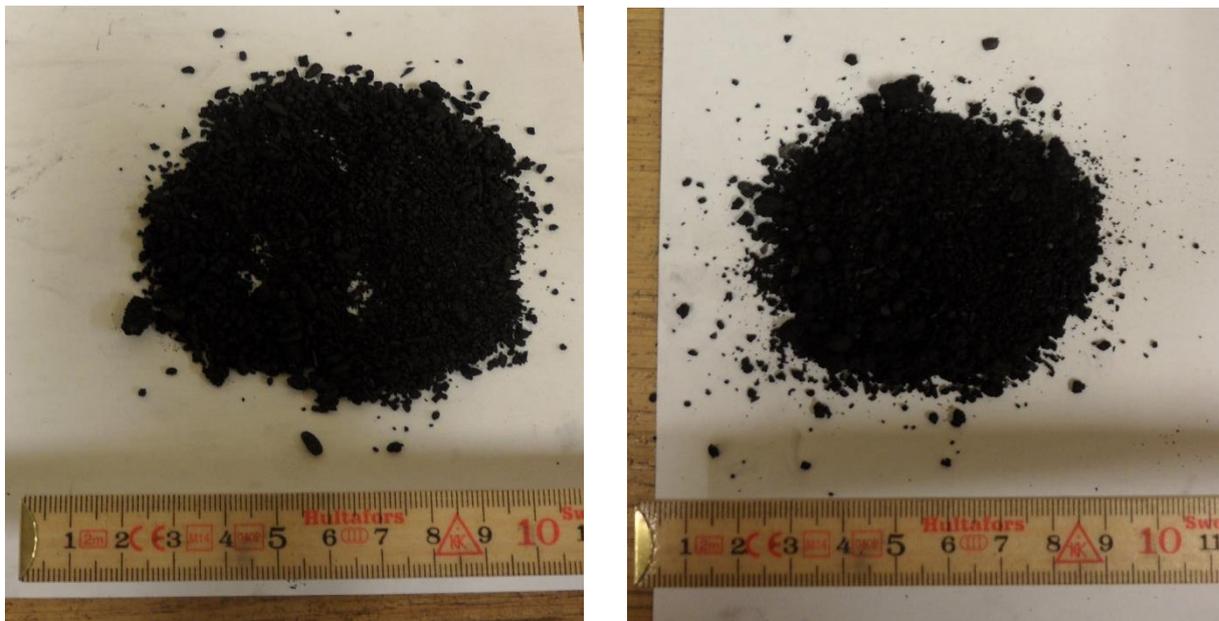


Figure 4.7. Agglomerates made in the planetary mixer. To the left: BC 1. To the right: BC 2.

4.5 Results from the Agglomeration Evaluation

Result from the AD measurements can be seen in Table 4.13. The measurements have been performed based on the entire particle size distribution. The increase or decrease of BC 1 agglomerates compared to non-agglomerated BC 1 and BC 2 agglomerates compared to non-agglomerated BC 2, are presented in the parenthesis in the Table.

Table 4.13. AD results. The percentage change is presented in the parenthesis.

Material	Method	AD (g/dm ³)
Anthracite	Non-agglomerated	810 [1]
BC 1	Non-agglomerated	191 [1]
BC 2	Non-agglomerated	253 [1]
BC 1	Tumbling Plate	225 (+18 %)
BC 1	Planetary Mixer	282 (+48 %)
BC 2	Extruder	374 (+48 %)
BC 2	Tumbling Plate	241 (-5 %)
BC 2	Planetary Mixer	314 (+24 %)

The reduction value was calculated by using Eq. 3.1 in Reduction Value, section 3.4.2. The result can be seen in Table 4.14.

Table 4.14. Calculated reduction values.

Material	Method	Reduction value (kcal/dm ³)
Anthracite	Non-agglomerated	5859 [1]
BC 1	Non-agglomerated	1371
BC 2	Non-agglomerated	1808
BC 1	Tumbling Plate	1615
BC 1	Planetary Mixer	2024
BC 2	Extruder	2673
BC 2	Tumbling Plate	1723
BC 2	Planetary Mixer	2244

The reduction value of non-agglomerated BC 1 and BC 2 are calculated based on the AD measured in the previous study [1].

The agglomerates made in the tumbling plate were ground in a disc-mill since those agglomerates became too large for the pilot tests. The extruded and granulated agglomerates did not need to be ground because the size of the agglomerates were suitable for the pilot tests. The particle size distribution for all agglomerated samples can be seen in Figure 4.8 and Figure 4.9.

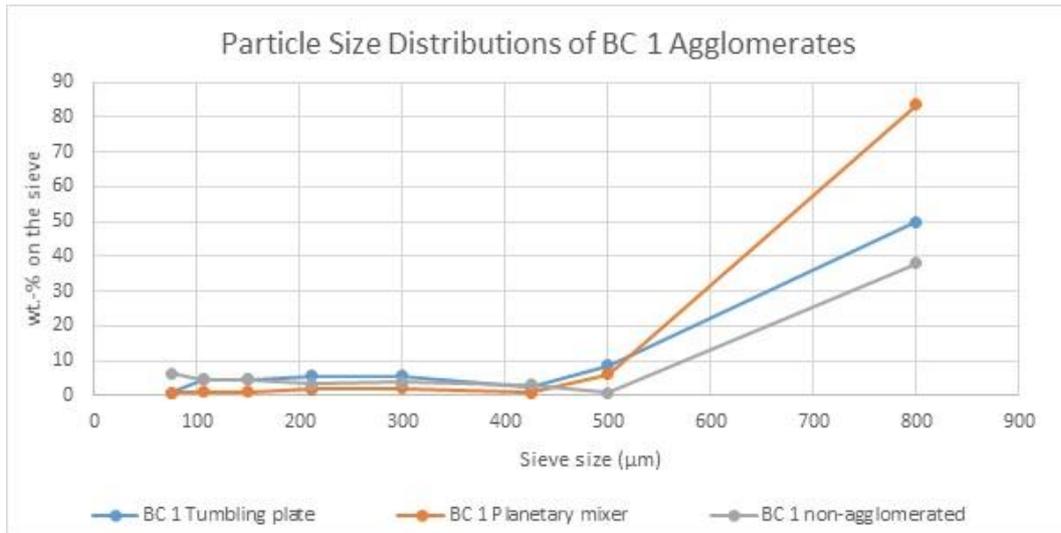


Figure 4.8. Particle size distribution of both agglomerated and non-agglomerated BC 1.

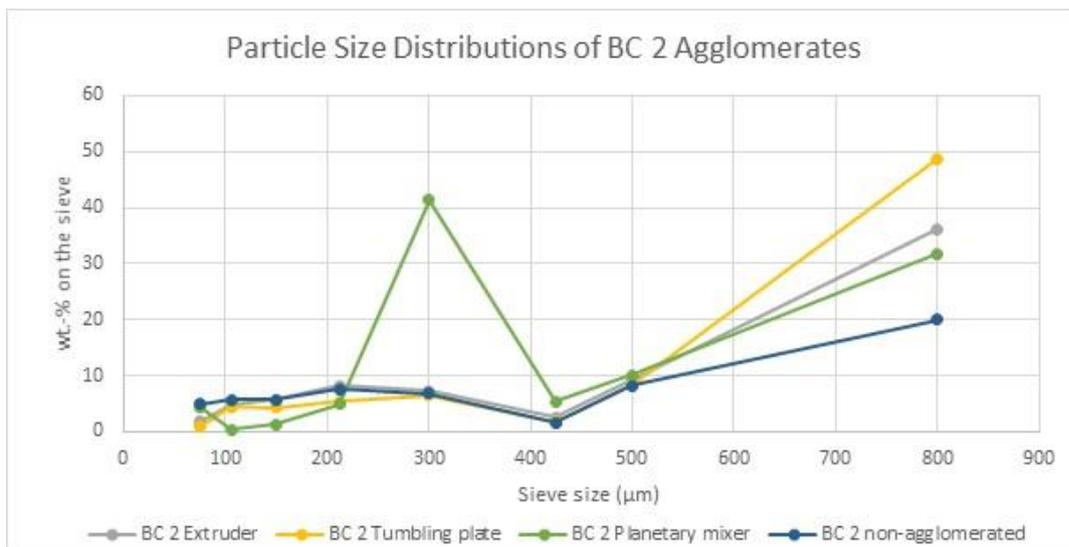


Figure 4.9. Particle size distribution of both agglomerated and non-agglomerated BC 2.

The compression strength results can be seen in Figure 4.10. Unfortunately, the agglomerates made in the extruder and planetary mixer became too small in order to investigate the compression strength.

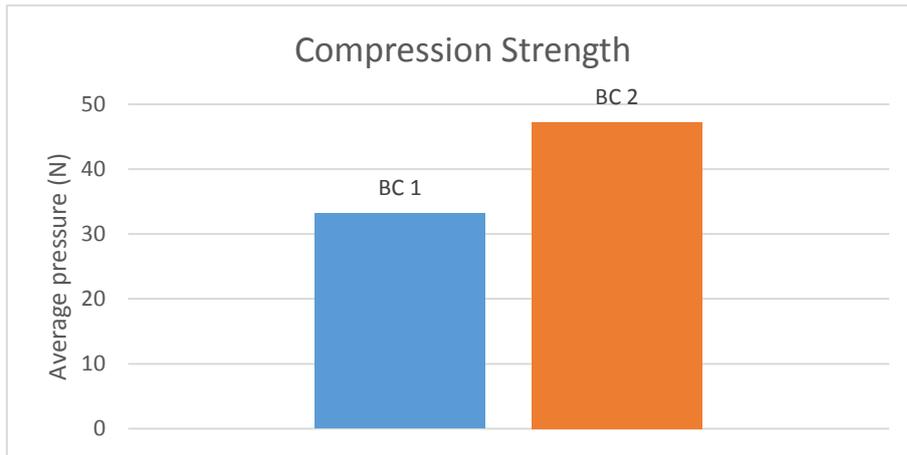


Figure 4.10. The compression strength of pellets made in the tumbling plate.

All agglomerates were dried in a drying cabinet over night at 90°C. The moisture content was determined afterwards, which can be seen in Table 4.15.

Table 4.15. The moisture content of the samples.

Material	Method	Moisture content (wt.-%)
Anthracite	Non-agglomerated	6 [1]
BC 1	Non-agglomerated	4 [1]
BC 2	Non-agglomerated	25 [1]
BC 1	Tumbling Plate	2.14
BC 1	Planetary Mixer	9.05
BC 2	Extruder	7.85
BC 2	Tumbling Plate	3.49
BC 2	Planetary Mixer	14.52

In order to see how much the moisture content affects the AD, the moisture content was removed and new AD was calculated. The result can be seen in Table 4.16.

Table 4.16. The AD after the moisture content have been removed. The percentage change is presented in the parenthesis.

Material	Method	AD (g/dm ³)
BC 1	Tumbling plate	219 (+13 %)
BC 1	Planetary mixer	220 (+32 %)
BC 2	Extruder	345 (+36 %)
BC 2	Tumbling plate	219 (-13 %)
BC 2	Planetary mixer	268 (+6 %)

In order to be able to compare the reactivity of the agglomerated materials, reactivity tests were performed in a TG oven. All samples had the particle size -800 μm +500 μm. The results, TG (%), from the reactivity tests can be seen in Appendix 4. The slope of the TG (%) curve, DTG

(%/min), was calculated when the temperature was <199°C, 200-399°C, 400-599°C, 600-799°C, 800-999°C and at 1000°C. The result of DTG (%/min) for the references can be seen in Table 4.17 and the result from the agglomerated samples can be seen in Table 4.18.

Table 4.17. The DTG (%/min) of anthracite and non-agglomerated BC 1 and BC 2.

Temperature range (°C)	Anthracite DTG (wt.-%/min)	BC 1 DTG (wt.-%/min)	BC 2 DTG (wt.-%/min)
<199	0.07	-0.03	0.05
200-399	-0.21	0.47	1.32
400-599	-0.07	0.23	-0.01
600-799	-0.19	0.18	0.40
800-999	0.32	0.83	0.68
1000	0.10	1.31	0.80

Table 4.18. The DTG (%/min) of the agglomerated samples during reactivity tests.

Temperature range (°C)	BC 1 Tumbling plate DTG (wt.-%/min)	BC 1 Planetary mixer DTG (wt.-%/min)	BC 2 Extruder DTG (wt.-%/min)	BC 2 Tumbling plate DTG (wt.-%/min)	BC 2 Planetary mixer DTG (wt.-%/min)
<199	0.10	0.22	0.07	-0.05	0.27
200-399	0.28	0.91	0.91	0.63	0.71
400-599	0.71	0.22	0.30	0.91	1.20
600-799	0.27	0.22	0.52	0.37	0.51
800-999	1.12	0.90	1.01	1.16	1.25
1000	1.16	1.11	0.82	0.79	0.65

4.6 Pilot Tests Results

One reference, with anthracite, and three of the agglomerated biomass chars in the reduction mixture were investigated in the single sagger furnace. The chosen agglomerates were BC 2 agglomerates made in the extruder, ground BC 1 agglomerates made in the tumbling plate and BC 1 agglomerates made in the planetary mixer. These agglomerates got the highest AD after the moisture content had been removed, which was the reason for choosing them in the pilot tests.

All anthracite was exchanged to the agglomerated samples in the reduction mixture. The amount of reduction mixture that fitted into the capsule can be seen in Table 4.19.

Table 4.19. Amount of reduction mixture in the capsule during the experiments in the single sagger furnace.

Material used in the reduction mixture	Reduction mixture that would fit in the capsule (%) (Max 30 kg)
Anthracite (Reference)	100
BC 2 (Extruder)	91
BC 1 (Tumbling plate)	85
BC 1 (Planetary mixer)	89

Figure 4.10 shows the capsule from above after the reduction.



Figure 4.10. The capsule from above after the experiment.

The result from the trials in the single sagger furnace can be seen in Figure 4.11.

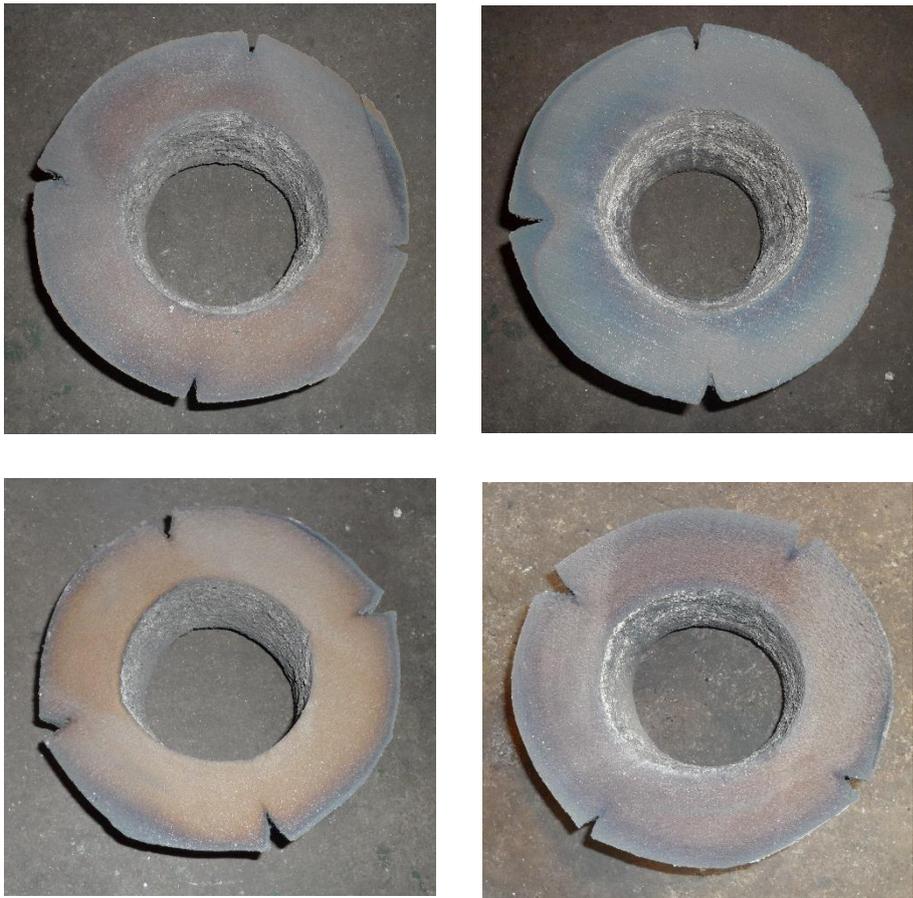


Figure 4.11. Upper left corner: reference (trial 1). Upper right corner: trial 2 with BC 2 pellets made in the extruder. Lower left corner: trial 3 with BC 1 pellets made in the tumbling plate. Lower right corner: trial 4 with BC 1 pellets made in the planetary mixer.

There was no visible sight of magnetite ore concentrate in the produced sponge iron tube with anthracite or with BC 2 agglomerates made in the extruder in the reduction mixture. However, it could be seen in the third trial, with BC 1 agglomerates made in the tumbling plate and in the fourth trial with BC 1 agglomerates made in the planetary mixer.

Table 4.20 below shows the remaining reduction mixture in the capsule after the reduction was finished. Unfortunately, there is no measuring of the remaining reduction mixture after the third trial.

Table 4.20. The remaining reduction mixture in the capsule after reduction.

Material in the reduction mixture	Remaining reduction mixture in the capsule after reduction (%)
Anthracite	48
BC 2 (extruder)	47
BC 1 (tumbling plate)	-
BC 1 (planetary mixer)	43

Results from the analysis of the sponge iron can be seen in Table 4.21.

Table 4.21. The analysis results of the sponge iron made in the single sagger furnace.

Material in the reduction mixture	Fe (total) (%)	Fe (metal) (%)	O (total) (%)	H₂-loss (O bound to Fe) (%)	C (%)	N (%)	S (%)
Trial 1 (Anthracite)	97.5	94.9	1.620	1.302	0.055	0.015	0.016
Trial 2 (BC 2 extruder)	97.2	94.8	1.479	1.189	0.108	0.018	0.005
Trial 3 (BC 1 tumbling plate)	98.2	96.9	0.98	0.697	0.055	0.016	0.006
Trial 4 (BC 1 planetary mixer)	98.0	98.0	1.154	0.76	0.008	0.010	0.004

Unfortunately, when the third trial with BC 1 pellets made in the tumbling plate were added to the reduction mixture, the bottom plate of the capsule had got a crack. The bottom plate was exchange to another for the fourth trial.

The results from the registering of temperature and gases during the experiments can be seen in Appendix 5.

5 Discussion

Unfortunately, the BET-analysis was not possible to achieve on the agglomerated samples. It was probably due to a lot of reasons and it would need further investigations to measure the specific surface area of agglomerated biomass chars and get a reliable result. One reason could be the high moisture content in the samples, which is probably due to the binders since it was possible to make the BET-analysis on the non-agglomerated samples.

If the particle size distributions of non-agglomerated BC 1 and BC 2 are compared with the suggested particle size distribution in the Agglomeration Mechanism, section 2.2.1, it can be seen that there are more particles that are smaller than 212 μm used in the agglomeration experiments compared to the suggested particle size distribution. For the agglomeration experiments in this master thesis, it seemed more important that the particle size distribution of BC 1 and BC 2 was alike than one of them was more alike the suggested particle size distribution. From the beginning, BC 2 had a larger amount of smaller particles than the suggested particle size distribution.

The agglomerates made in the extruder were expected to get the highest AD since extrusion is a high pressure method. The expectations were confirmed in the results since the agglomerates made in the extruder gave the highest AD. Corresponding results from the Preliminary Binder Investigation with the hydraulic press, section 4.3, also gave the highest AD. However, the AD result from the large scale agglomeration and the result from the Preliminary Binder Investigation are not completely comparable, since a specific particle size fraction was used during the measurement in the Preliminary Binder Investigation and the whole particle size distribution was used in the large scale evaluations.

The agglomerates made in the tumbling plate were not particularly compacted, which was quite surprising due to the result in the Preliminary Binder Investigation. One difference between the large scale agglomeration and the Preliminary Binder Investigation was the tumbling time and the rate of addition of material to the tumbling plate.

Interesting is that the AD became lower for BC 2 agglomerates made in the tumbling plate compared to the non-agglomerated BC 2. The reason could be how well the particles get packed in the beaker during the AD measurements, which means that the AD measurements are not precise. The human factor also plays a large role during the measurement. The fact that the agglomerates made in the tumbling plate became ground could also have affected the AD. Small particles were perhaps not able to fit into the voids between larger particles in the same way as in the non-agglomerated BC 2.

During the agglomeration in the tumbling plate, different amount of water was necessary for the biomass chars. One reason could be that the humidity in the room, where the tumbling plate was placed, varied over time when the agglomeration experiments were performed. However, the main reason is probably the specific surface area, or porosity, of the biomass chars. It is necessary to nearly saturate the starting material with water before agglomeration in the tumbling plate. Otherwise, it is not possible to make any agglomerates. The moisture content of BC 2 agglomerates made in the tumbling plate was approximately 40 % higher than the moisture content of BC 1 agglomerates made in the tumbling plate. The same is true for the moisture content of the agglomerates made in the planetary mixer. The moisture content of BC 2 agglomerates made in the planetary mixer was also approximately 40 % higher than the

moisture content of BC 1 agglomerates made in the planetary mixer. This can be compared with the specific surface area of the two biomass chars. The specific surface area of non-agglomerated BC 2 is 40 % larger than the specific surface area of non-agglomerated BC 1. A larger specific surface area means that the material is more porous. Consequently, BC 2 have a larger specific surface area compared to BC 1, which is the reason why BC 2 needed more water than BC 1.

The moisture content in the agglomerates also affected the AD, which could be seen in Results from the Agglomeration Evaluation, section 4.5. The moisture content also had an impact on the particle size distributions on the agglomerated samples. Agglomerates made in the planetary mixer contained a lot moisture, even though they had been dried at 90°C during one night. The high moisture content affected the sieving when determining the particle size distribution. Therefore, the particle size distribution of agglomerates of BC 2 made in the planetary mixer is not reliable.

A comparison have been made in Table 5.1 of the water added to the tumbling plate, planetary mixer and extruder and the moisture content of the agglomerates.

Table 5.1. A comparison between the water added during the various methods and the moisture content in the agglomerates.

Material and method	Binder	Water added to the material (wt.-%)	Moisture content in agglomerates (wt.-%)
BC 1 Tumbling plate	Organic polymer 1	51.0	2.14
BC 1 Planetary mixer	Organic polymer 2	46.8	9.05
BC 2 Extruder	Organic polymer 3	39.4	7.85
BC 2 Tumbling plate	Organic polymer 1	55.3	3.49
BC 2 Planetary mixer	Organic polymer 2	51.0	14.52

Based on the comparison in the Table, it is the binders that have the main effect on the moisture content in the agglomerates and not the added water. The water in the organic polymer 1 probably evaporates more easily than the water in the organic polymer 2 and organic polymer 3.

The agglomerates made in the planetary mixer seemed to have been compacted, although not as much as in the extruder. If speed 3 in the planetary mixer was used all the time, the AD would probably have become higher.

According to the Biomass Char as a Reducing Agent, section 2.1.5, biomass chars are more reactive than fossil materials, which is consisted with the reactivity tests made in this master thesis. However, the results from the reactivity tests are a bit uncertain, since the accuracy of the scale is ± 1 g, which means that the scale is not so stable and it is difficult set the scale to 0 g from start.

Interesting to see is if the reactivity is dependent on the AD. Figure 5.1 shows the DTG (wt.-%/min) at 1000°C versus the AD of the agglomerated samples and non-agglomerated BC 1 and BC 2.

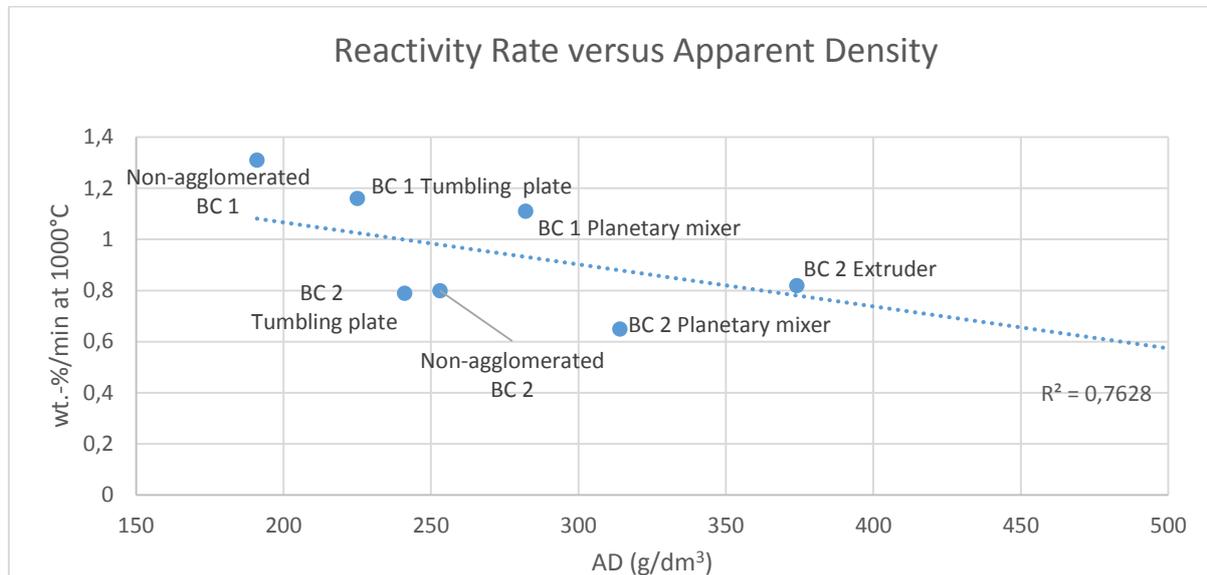


Figure 5.1. The reactivity (wt.-%/min at 1000°C) versus AD of both the agglomerated samples and non-agglomerated BC 1 and BC 2.

According to the Figure, increasing AD leads to a decrease in reactivity rate, which is preferable if it would be used in the sponge iron process. If the reactivity of the biomass chars is too high, the carbon in the material will react too fast, which could lead to oxidizing of iron to wüstite during the cooling stage in the end of the process. It is not preferable if the reactivity is too low either, since it could affect the Boudouard reaction, which would start too late in the process and the reduction time would increase. However, the reactivity rate of BC 2 agglomerates made in the extruder have increased when compared to non-agglomerated BC 2. The reason could be that all material have not been compacted during the extrusion. Most of the compacted material have probably a particle size that is $+800 \mu\text{m}$. During reactivity tests, the particle size fraction $-800 \mu\text{m} +500 \mu\text{m}$ was used for all samples. Moreover, some fraction of the material might have been ground instead of compacted, which could have led to broken particles or cracks. There is a possibility that, due to the high pressure in the extruder, more particles are closer in size to $500 \mu\text{m}$ than to $800 \mu\text{m}$. Smaller particles means higher specific surface area, which in turn means higher reactivity. Consequently, the result could indicate that the specific surface area have increased, leading to higher reactivity rate.

There was less reduction mixture left after reduction in the trials with agglomerated biomass chars in the single sagger furnace compared to the trial with anthracite. This also indicates that biomass char is more reactive than anthracite.

According to the Previous Study [1], an AD of 300 g/dm^3 would be enough to fit all reduction mixture in the capsule. However, the AD of the agglomerates made in the extruder became 374 g/dm^3 and all reduction mixture did not fit into the capsule. The amount of reduction mixture

that could fit into the capsule is surely dependent on the AD, which could be seen in Pilot Tests Results, section 4.6.

During the trial with anthracite in the single sagger furnace, the cooling time became too long, which could have affected the results. The high amount of carbon dioxide at the end of the trial in the single sagger furnace indicates oxidation of iron back to wüstite. Moreover, the high oxygen content in the sponge iron and the fact that approximately 2.5 % is not metallic iron is probably also an effect of oxidation.

Approximately 2.5 % is not metallic iron in the sponge iron produced in trial 2 either. All magnetite ore concentrate has not been reduced or oxidation of iron has occurred. There was no visible sight of it in the sponge iron tube, which means that the value is probably a result of oxidation of iron to back wüstite. It can be seen in Appendix 5 that the volume-% of carbon monoxide, during trial 2, is decreasing more during the reduction compared to the other trials. This is clearly a sign that the agglomerates made in the extruder have become more reactive. The increased reactivity of the agglomerates made in the extruder could also be seen in the reactivity tests.

The high reactivity of the agglomerates made in the extruder also resulted in a lower start temperature for the Boudouard reaction in the capsule, which can be seen in Table 5.2.

Table 5.2. An indication at which temperature when the Boudouard reaction began in the capsule during the trials.

Material in the reduction mixture	Approximate temperature when the Boudouard reaction start
Anthracite	810°C
BC 2 Extruder	600°C
BC 1 Tumbling plate	800°C
BC 1 Planetary mixer	700°C

The sponge iron tube in trial 3 showed a stripe of magnetite ore concentrate, which have not been reduced. The sponge iron tube had also collapsed a bit during the third trial, which could be due the lower AD of BC 1 agglomerates made in the planetary mixer compared to the agglomerates made in the extruder. The fact that a crack had been formed in the bottom plate after the third trial could also have affected the results. Due to the crack, the results from the analysis is not reliable. The result from the analysis of the sponge iron, produced in trial 4, is not reliable either and another analysis of the same material is necessary in order to draw any conclusions.

6 Conclusion

The AD of almost all samples increased compared to non-agglomerated BC 1 and BC 2. There were no compacted sample that reached the AD of anthracite either, which was the goal. However, in order to fit all necessary reduction mixture, with biomass char in the capsule, the AD need to be increased even more. One conclusion is that an AD of 300 g/dm^3 is unfortunately not enough. Another conclusion that can be drawn is that the AD is dependent on the moisture content. The moisture content in turn depends on the specific surface area or porosity of the material.

The high moisture content in some of the agglomerates affected the determination of particle size distribution, BET-analysis and AD. The materials need to be dried for a longer time and at a higher temperature. A binder, such as organic polymer 2, might not be the most suitable either.

The BET-analysis was not possible to perform on the agglomerated biomass chars. In order to determine the specific surface area, a new method or implementation need to be investigated.

The agglomerates made in the extruder resulted in the highest AD, which also means that it would be interesting to continue to investigate the extrusion method. It would for example be interesting to increase the pressure in the extruder by for example use even smaller holes in the end plate of the extruder. However, it might cause cracks or break the material while compacting it. The reactivity of the agglomerates increased compared to the non-agglomerated BC 2, which could be due to possible broken particles. One important conclusion is the fact that there is a correlation between the reactivity tests and the tests in the single sagger furnace. It can be useful knowledge for further investigations.

7 Future Work

It is necessary to increase the AD even more. One possibility is to increase the pressure in the extruder. If that will result in broken particles, agglomeration in the planetary mixer should be further examined, due to the AD results.

One opportunity is to exchange a part of anthracite, to the agglomerated biomass chars instead of all. Perhaps it is a too drastic replacement at the moment.

Interesting would be to look in a microscope at the agglomerates made in the extruder, in order to see if cracks have been formed. Also, a narrower particle size distribution could be used in the reactivity tests to see how much it affects the reactivity.

A new method for determining the specific surface area could probably give answer to some questions, such as the increasing reactivity of the agglomerates made in the extruder.

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Appendix 1

1.1 Results from Previous Study

Results from the previous study [1] are presented in Table 1.

Table 1. Results from the previous study [1].

	Anthracite	BC 1	BC 2	BC 3	BC 4
Moisture (%)	6	4	25	4	6
Volatile matter (% dry basis)	11	11	28	22	27
Fixed carbon (% dry basis)	81	85	64	76	58
Ash (% dry basis)	8	4	7	2	15
Sulfur content (% dry basis)	0.28	0.077	0.085	0.092	0.057
Apparent density (g/dm ³)	810	191	253	232	289
HHV (kcal/kg)	7233	7564	6478	7241	5913
Reduction value (kcal/dm ³)	5859	1447	1637	1677	1709
Surface area (BET) (m ² /kg)	8200	53000	103000	43000	3100
Reactivity in carbon dioxide (wt.-%/min)	0.51	2.72	1.75	2.22	1.83
Reduction mixture that could be placed in the capsule (max 30 kg) (kg)	30	25.3	29	27.8	29.2
Fixed carbon in the capsule (kg)	17.9	15.2	16.8	16.4	16.7
Reduction value in the capsule (kcal/dm ³)	4327	3286	3491	3459	3572
Remaining reduction mixture in the capsule after reduction (%)	54	45	48	46	44

The particle size distribution of anthracite was also determined in the previous study [1], which can be seen in Table 2.

Table 2. Particle size distribution of anthracite [1].

Sieve size (μm)	Amount of anthracite (%)
+4000	~10
+2000	~9
+1000	~16
+425	~28
+212	~22
-212	~15

Appendix 2

2.1 Details about the Preliminary Binder Investigation

2.1.1 Agglomeration in Tumbling Plate

Figure 1-6 shows the agglomerates made in the tumbling plate.



Figure 1. Agglomerates made with organic polymer 1.



Figure 2. Agglomerates made with organic polymer 2.



Figure 3. Agglomerates made with organic polymer 3.



Figure 4. Agglomerates made with organic polymer 4.



Figure 5. Agglomerates made with 3 % inorganic binder.



Figure 6. Agglomerates made with 5 % inorganic binder.

The size of the agglomerates were also measured on ten agglomerates with different sizes and an average was calculated, which can be seen in Table 1.

Table 1. Average particle size based on ten agglomerates made with each binder in the tumbling plate.

Binder used in the agglomerates	Average length (mm)	Average width (mm)
Organic polymer 1	14	8
Organic polymer 2	15	9
Organic polymer 3	12	5
Organic polymer 4	14	9
Inorganic binder (3 %)	11	7

The compression strength of ten agglomerates made in the tumbling plate was determined and an average was calculated. The results are presented in Figure 7.

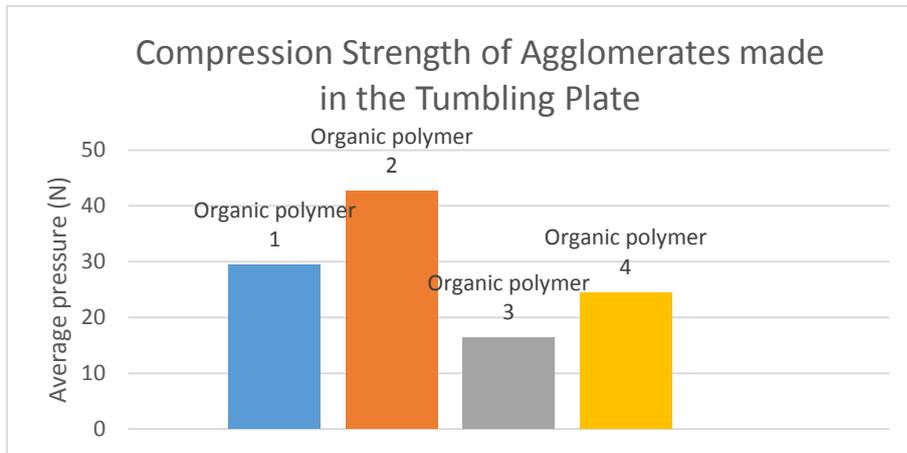


Figure 7. The compression strength of the agglomerates made in the tumbling plate, where an average pressure has been calculated based on ten agglomerates.

2.1.2 Granulation

Figure 8-12 shows the agglomerates made in the kitchen machine.



Figure 8. Agglomerates made in the kitchen machine with organic polymer 1.



Figure 9. Agglomerates made in the kitchen machine with organic polymer 2.



Figure 10. Agglomerates made in the kitchen machine with organic polymer 3.



Figure 11. Agglomerates made in the kitchen machine with organic polymer 4.



Figure 12. Agglomerates made in the kitchen machine with inorganic binder.

Table 2 present the result from size measurements and the compression strength.

Table 2. Average particle size and compression strength results based on ten agglomerates made with each binder in the kitchen machine.

Binder used in the agglomerates	Average length (mm)	Average width (mm)	Average pressure (N)
Organic polymer 1	12	8	29
Organic polymer 2	14	8	43
Organic polymer 3	10	6	16
Organic polymer 4	12	8	25

The compression strength of agglomerates made in the kitchen machine can be seen in Figure 13. It is an average pressure of ten agglomerates in the same way as for the agglomerates made in the tumbling plate.

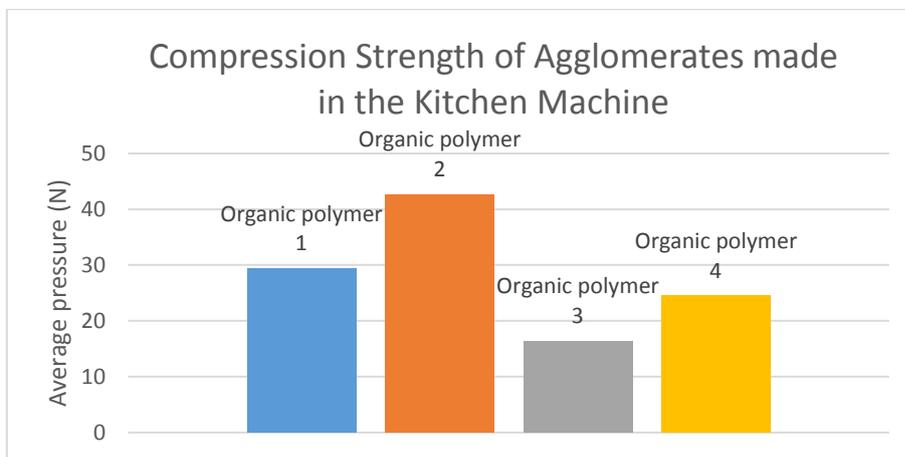


Figure 13. The compression strength of the agglomerates made in the kitchen machine, where an average pressure has been calculated based on ten agglomerates made in the kitchen machine.

2.1.3 Hydraulic Press

The pellets made in the hydraulic press can be seen in the Figures 14-17.



Figure 14. Pellet with organic polymer 1.



Figure 15. Pellet with organic polymer 2.



Figure 16. Pellet with organic polymer 3.



Figure 17. Pellet with organic polymer 4.

The height of the pellets is approximately 1.5 cm and the diameter is 2.5 cm.

The sustainability of the pellets made in the hydraulic press was also investigated by doing the compression strength. The pellet was placed on its edge and the results are presented in Table 3. Pellets made with organic polymer 3 and organic polymer 4 did not break during the compression strength and the highest pressure possible to reach with the compression strength equipment was 189 N.

Table 3. Compression strength of the pellets made in the hydraulic press.

Binder in the pellet	Pressure (N)
Organic polymer 1	85.20
Organic polymer 2	69.10
Organic polymer 3	>189
Organic polymer 4	>189

Appendix 3

3.1 Temperature and Relative Humidity during Tumbling Agglomeration

During tumbling agglomeration, the dew point (T_d , °C) temperature (T , °C) and relative humidity (RH, %) were measured. Figure 1 and 2 shows the measurements from two runs.

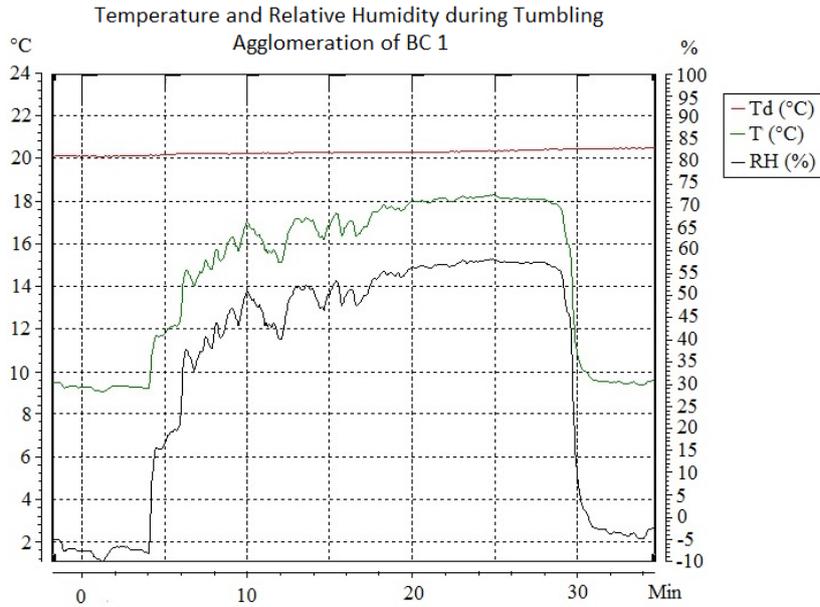


Figure 1. Measured T_d , T and RH during tumbling agglomeration of BC 1.

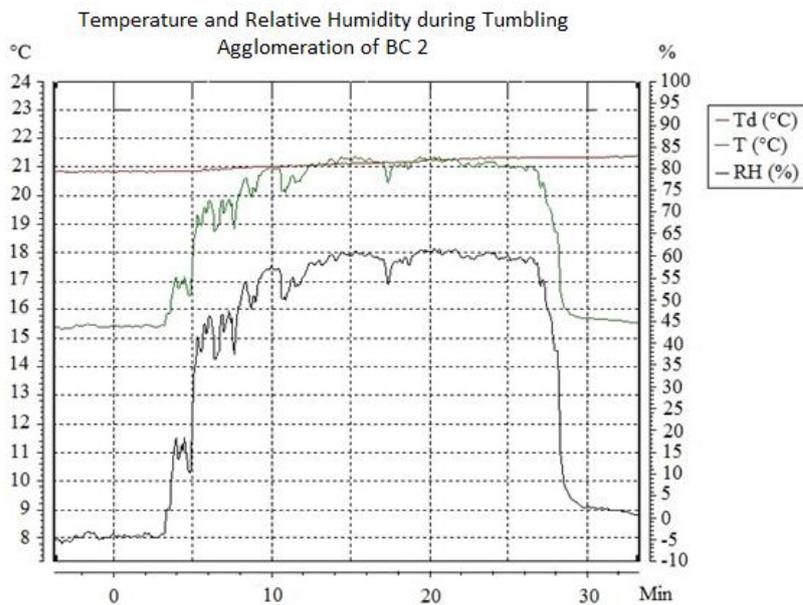


Figure 2. Measured T_d , T and RH during tumbling agglomeration of BC 2.

Appendix 4

4.1 TG (%) during Reactivity Tests

The results from the reactivity tests, TG (%), can be seen in Figure 1 and Figure 2.

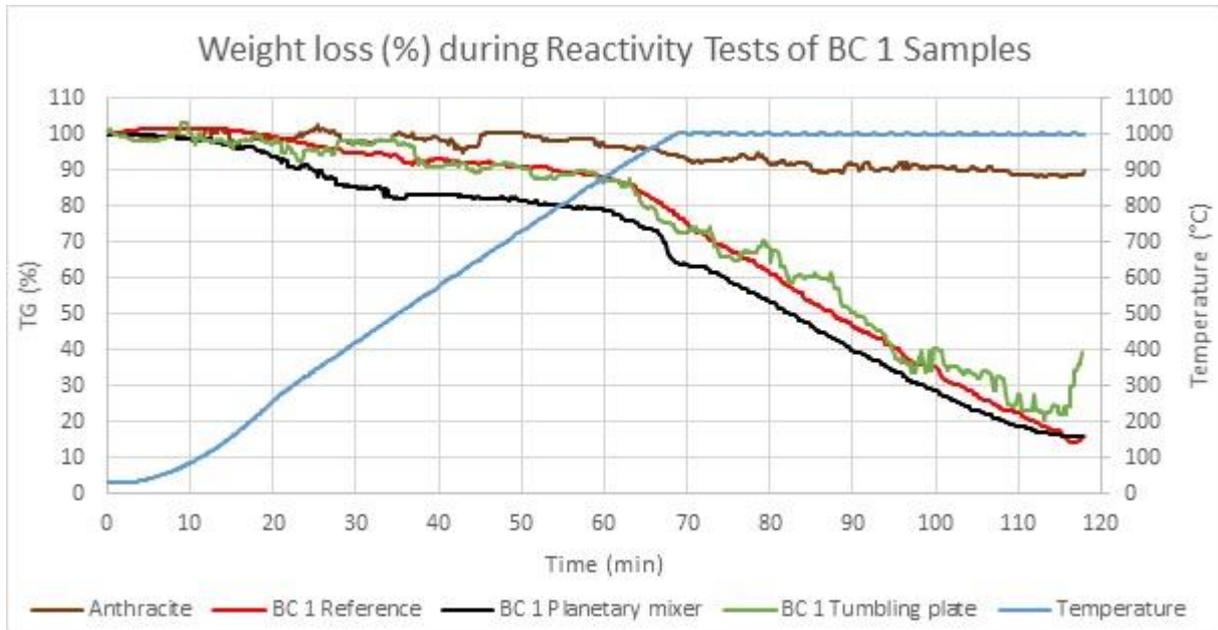


Figure 1. Weight loss (TG, %) of BC 1 samples and anthracite during reactivity tests.

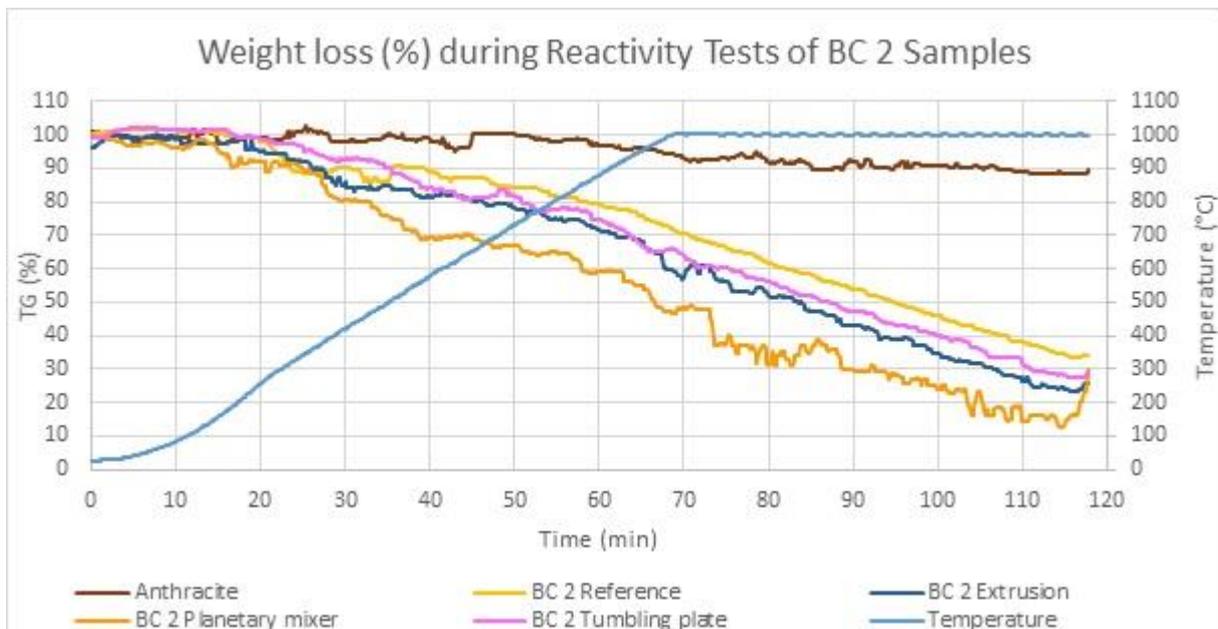


Figure 2. Weight loss (TG, %) of BC 2 samples and anthracite during reactivity test.

Appendix 5

5.1 Registered Temperatures and Gases during Tests in Pilot Scale

The results from the registering of carbon monoxide, carbon dioxide and temperature during the reactivity tests can be seen in the Figures 1-4. The measuring of the temperature and the amount of carbon monoxide during the test with the reference was unstable, a median was therefore calculated.

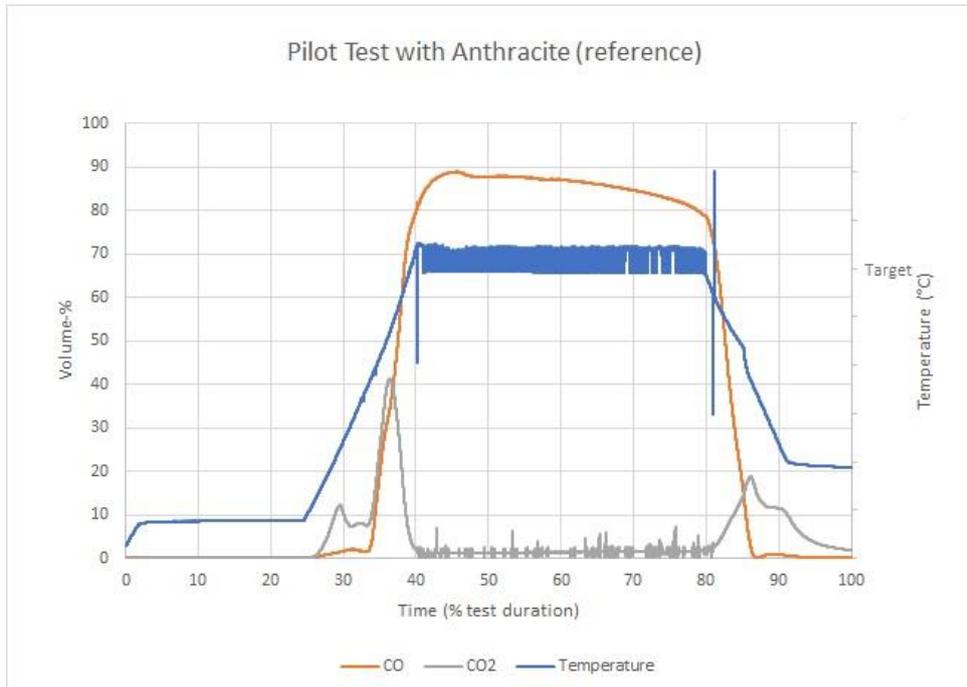


Figure 1. The registered amount of carbon dioxide, carbon monoxide and temperature during the trial 1 with the anthracite in the reduction mixture.

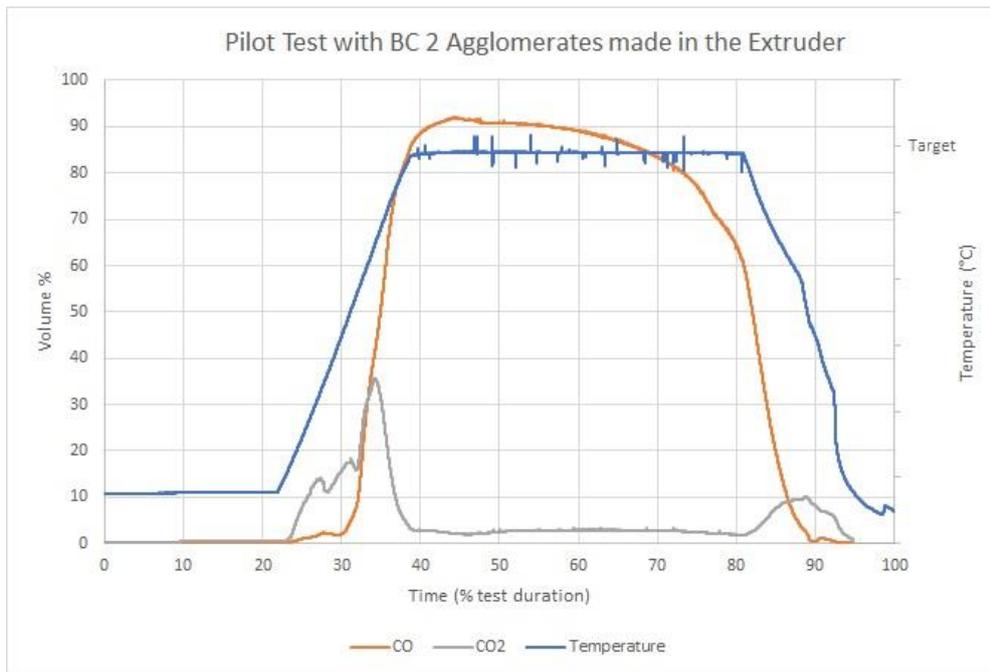


Figure 2. The amount of carbon dioxide, carbon monoxide and temperature during the trial 2 with BC 2 agglomerates, made in the extruder, in the reduction mixture.

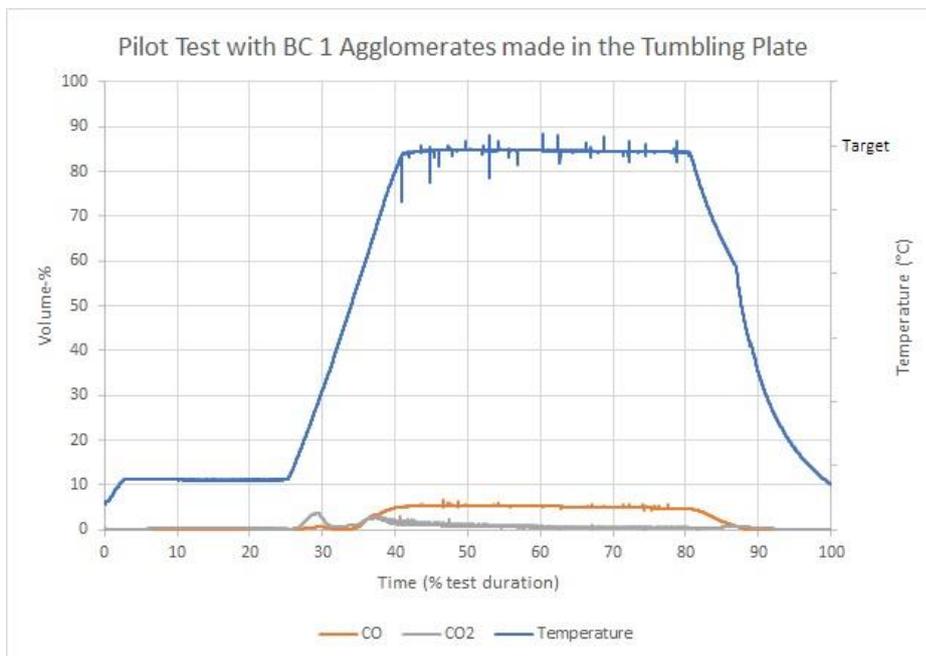


Figure 3. The amount of carbon dioxide, carbon monoxide and temperature during the trial 3 with BC 1 agglomerates, made in the tumbling plate, in the reduction mixture.

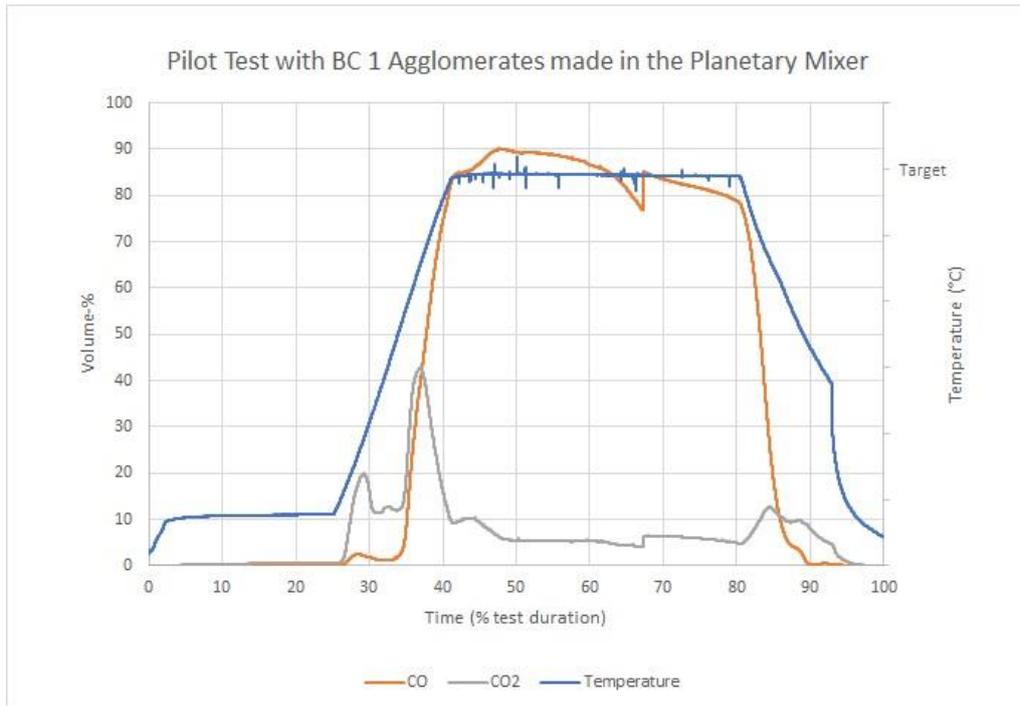


Figure 4. The amount of carbon dioxide, carbon monoxide and temperature during the trial 4 with BC 1 agglomerates, made in the planetary mixer, in the reduction mixture.