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Biochar-pellets as substitute for fossil coal in metallurgical processes

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Abstract

This thesis serves as a base for later research on substituting fossil coal and coke with biochar in the Norwegian metallurgical industry. Because Norwegian electricity production is almost entirely based on carbon dioxide - neutral hydropower, the nation's main pollutant is fossil coal. Biochar serves as an alternative to coal but can currently only partially satisfy the quality requirements for use in top-loaded smelting facilities. With comparison to fossil coal, biochar has a higher price and a lower mechanical strength. A coupling of pyrolysis and pelletising is therefore investigated to obtain a sustainable product with improved characteristics and without compromising the other requirements. Different compositions of feedstock for pelletising were investigated in a single pellet press. Good results were achieved with two binding agents, lignin and oil from a flash pyrolysis process. The materials were waste products from other processes to increase economic feasibility. Problems were discovered with the sticky characteristics of both materials during the process. Water was then applied as a lubricant to improve homogenising and extraction. Further experiments with more replicates and statistical analyses should be done to broaden the observations and extend the scientific value.

Abstract

Diese Thesis dient als Grundlage für eine spätere Erforschung der Substituierung von fossiler Kohle und Koks durch Bio-Kohle in der norwegischen Metallindustrie. Der größte Verursacher von Luftverschmutzung im Land ist die fossile Kohle, da die Stromversorgung nahezu vollkommen durch Kohlenstoffdioxid-neutrale Wasserkraft gedeckt wird. Bio-Kohle dient zwar als eine Alternative zu Kohle, kann jedoch die Anforderungen von top-geladenen Verhüttungsanlagen bisher nur teilweise erfüllen. Bio-Kohle hat im Vergleich zu fossiler Kohle einen höheren Preis und geringere Druck- und Abriebfestigkeit. Deswegen wird die Verbindung aus Pyrolyse und Pelletieren untersucht, um ein beständiges Produkt mit verbesserten Eigenschaften und ohne Einbußen zu erzielen. Verschiedene Materialzusammensetzungen wurden in einer Einzelpelletierpresse untersucht. Gute Ergebnisse wurden mit den zwei Bindemitteln Lignin und Öl einer Schnell-Pyrolyse erreicht. Diese Bindemittel sind Abfallprodukte aus anderen Prozessen und damit wirtschaftlich realisierbar. Die klebrigen Eigenschaften der in Wasser gelösten bzw. ausgehärteten Bindemittel riefen Probleme bei der Handhabung hervor. Wasser wurde als Schmiermittel hinzugefügt, um das Mischverhalten der Materialien und die Entnahme der Pellets aus dem Prägestempel zu erleichtern. Weitere Experimente und statistische Analysen sollten in der Zukunft durchgeführt werden, um die Erfahrungen zu erweitern und den wissenschaftlichen Wert zu steigern.

Preface

This thesis was written to finish my studies as a Master of Engineering at the FH Münster.

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1 INTRODUCTION

Growing concerns over the global climate change increased significantly in recent years and global greenhouse gas emissions need to be reduced to avoid critical effects. A majority of the scientific world agrees that one of the main causes is the use of fossil fuels, and the resulting carbon dioxide (CO_2) emissions. Renewable energy sources are a possible way to reduce said emissions. The usable energy originates from three different primary energy sources: The planets gravity and its motion, geothermal heat and solar energy (Kaltschmitt et al., 2009, pp. 1-2).

In terms of annual energy per square kilometre, the sun is by far the largest source of energy, followed by geothermal energy. Tidal forces are the lowest transformed sort of energy. Natural transformations cause different energy flows, e.g. solar energy in wind energy, hydro energy, or biomass. Climatic regulations limit the available energy forms for central and northern Europe to solar radiation, wind energy, hydro power, geothermal heat, and biomass (Kaltschmitt et al., 2009, p. 2).

Biomass is solar radiation transformed by the process of photosynthesis in plants and organic matter. Thus, biomass is stored solar energy and can be used upon request for power generation to provide base load energy. This is a major difference compared to other forms of solar energy devices such as solar cells and wind turbines. Their production depends on weather conditions and are subject to short term fluctuations (Kaltschmitt et al., 2009, p. 2).

Metal production is responsible for five percent of the total world greenhouse gas emissions, producing about two tons of CO_2 for each ton steel manufactured (Chandler, 2013), which suggests that metal production is a worthwhile point to research possibilities to reduce CO_2 emissions. Substituting fossil fuels is an affordable alternative to generate power and heat. Carbonised biomass can be further used to substitute fossil coke and coal as reducing agent in metal production.

Several companies operate in the metallurgical sector in Norway, making it the largest Aluminium producer in Western Europe with seven works in the country, and one of the largest ferro-silicon and silicon producers in the world (Ministry of Trade, Industry and Fisheries, 2001). The silicon produced by Elkem in Kristiansand, southern Norway, for example is used in aluminium alloys or solar cells (J. Thompson, Elkem, 2018).

The initiative “Climate Cure 2020” by Norway’s Climate and Pollution Agency estimates the national CO_2-emissions to reach 59 million tons for the year 2020. The goal is to limit this amount to 45 – 47 million tons. The initiative calculated a reduction potential of 4.3 million tons for the industry sector, which is about 30 – 36 % of the total reduction potential. Relevant for the metallurgical industry are the replacement of fossil consumables and fuel with biochar- and biomass-based solutions (Climate and Pollution Agency, 2010, p. 15).

The EYDE-Cluster is a group of companies located in the south of Norway, with the main task of planning a sustainable future in the regional process industry (e.g. Glencore in Kristiansand, Saint Gobain in Lillesand, Elkem and Elkem Solar in Kristiansand). It ranges from multinational companies to regional suppliers to educational institutes, including the Department of Engineering Sciences at the University of Agder (UiA). Their sub-organisation “EYDE Biocarbon” aims to establish a production of sustainable, high-quality, bio-carbon based woody biomass from Norway. To overcome the drawbacks of biochar over fossil coal, pelletising the materials under use of binding agents is an interesting idea, because biochar can substitute fossil coal and coke.

This thesis focusses on the applicability of biochar to the metallurgical industry, namely the good conditions for transport, handling and mechanical stress. Possibilities of optimising the biomass were investigated in laboratory conditions by processing and changing production parameters. The Department of Engineering Sciences at UiA offered support and equipment to reach a representable conclusion.

2 THEORY: BIOENERGY AND WOODY BIOMASS

This section supplies background information for the practical research of this thesis. It gives definitions for essential terms and further considers supply chain structures, the thermochemical conversion of woody biomass during heating processes and the composition of the fuel and special characteristics. Furthermore, all processes necessary for the research are described here, before the planned process is elaborated in chapter 5.

2.1 Definition

“Biomass includes all kinds of materials that were [...] derived [...] from contemporary photosynthesis reactions” (Koppejan & van Loo, 2012, p. 1).

Kaltschmitt et al. further describes biomass as substances belonging to the following fields (Kaltschmitt et al., 2009, pp. 2):

- natural phyto- and zoomass (plants and animals)
- the resulting residues (e.g. manure)
- dead and non-fossil phyto- and zoomass (e.g. straw)
- all matters, which for example originate from technical transformation or material use or come up during processes (e.g. paper and pulp, butchery residues, organic domestic waste)

Biomass is divided into primary and secondary products. Primary products derive from the direct use of sunlight, e.g. the direct photosynthetic use of solar energy, cultivating crops for their energy, herbal residues and side products from agriculture and forestry. Furthermore, primary products are produced by subsequent processing industries such as straw, forest and industrial wood. Secondary products are products obtained indirectly from the sun and products from extraction and conversion of organic matter in higher organisms like animals. Examples are zoomass, manure, and sludge. Peat, which is a fossil secondary product of deterioration of biomass, can be regarded as the border from biomass towards fossil fuels (Kaltschmitt et al., 2009, pp. 2-3).

Biochar is biomass with an increased relative carbon content, produced by a pyrolytic or hypothermal process. The natural carbonising process is accelerated, leading to similar characteristics as fossil coal, and enables the use of biomass for the same field of applications (Quicker & Weber, 2016, p. 3). Biochar is a carbon residue of pyrolysis or devolatilisation. It contains a certain number of volatile matter (VM) and ashes (AC) besides the fixed carbon

(FC). It is characterised by its high reactivity, porosity and disability to sinter, which makes it easy to handle (Basu, 2010, p. 55).

2.2 Thermochemical conversion

Providing useful energy from biogenic combustibles is possible by direct combustion or (previous) conversion into different secondary energy carriers respectively. To achieve this, thermochemical, physicochemical, or biochemical processes are used. The following chapter defines fundamental attributes of said combustibles and fuels. Furthermore, the physical and chemical fundamentals of chemical conversion processes are elucidated, as well as the comparable mechanisms they are based upon. Table 2-1 gives an overview of essential processing methods of biomass fuels, and the relevant secondary energies. The van Krevelen diagram in Figure 2-1 compares biomasses with other solid combustibles. It classifies solid fuels by their atomic ratio, hydrogen to carbon (H/C) and oxygen to carbon (O/C), and shows their ratios on a dry, ash-free basis. Carbon is primarily defining the calorific value. It visualises

that biomass has a much higher H/C and O/C ratio than fossil fuels, in parallel to a lower HHV (higher heating value, see chapter 2.3.5). However, fossil fuels show a higher combustion heat and a high CO_2-emission due to the lower H/C-ratios (Basu, 2010, p. 39).

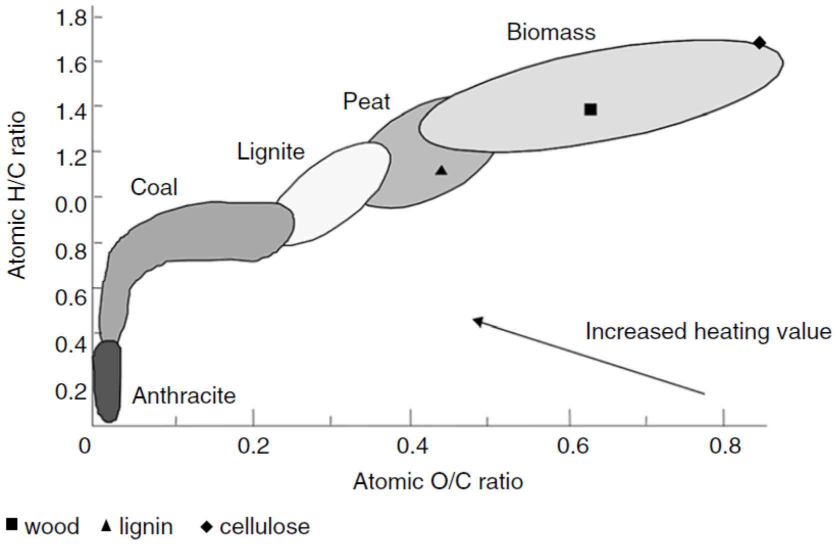


Figure 2-1: Classification of combustibles (Basu, 2010, p. 39)

Table 2-1: Processing of biomass fuels, according to Brenes, 2006, p. 95

Processing of biomass fuels	Thermal processing	Combustion	Heat Steam Electricity
		Gasification	Steam Heat Electricity Methane Hydrogen
		Pyrolysis	Biochar Biogas Bio-oil
		Liquefaction	Biofuels
	Biochemical Processing	Anaerobic digestion	Biogas
		Aerobic digestion	Compost
		Fermentation	Ethanol
	Physical Processing	Esterification	Biofuels

2.3 Feedstock composition and analysis

Thermochemical conversion of biogenic combustibles is mainly determined by their properties, especially for processes that are based on pollution. They produce CO_2-emissions when combusted which is compensated by the original plant during growth. Even though fossil fuel has its origins in plants and trees as well, it developed over millions of years and is therefore not part of the balance. The ability to thereby reduce CO_2-emissions puts them in focus for research and industry. Biogenic combustibles are defined by their qualitative attributes, their heritage and the sort of resource (Kaltschmitt et al., 2009, p. 333). The elementary composition, attributes for combustion and physical-mechanic properties influence the quality of the biomass as they determine the amount of volatile matter and residuals caused. Appendix 2 shows the chemical components, their meanings, effects on the thermochemical conversion, elaborating the processes regarding pyrolytic decomposition, gasification, and oxidation (see chapter 2.3.9, (Kaltschmitt et al., 2009, pp. 333-334).

The origin of the biomass gives many measurable attributes, which vary and therefore give an unique structure, and characterise the biomass. Describing and tracing its origins makes a remarkable part of an effective quality management of biogenic combustibles. The production chain of fuels and combustibles should be traceable over the whole process. Combustibles are divided into the following subcategories for classification. It is based on the unified identification system by the European Committee for Standardization CEN as EN 14961-1 (CEN, 2010):

- Woody biomass
- Herbaceous biomass
- Fruit biomass
- Blends and mixtures

Woody biomasses are trees, bushes and shrubs. Herbaceous biomasses originate from plants with non-woody stems and it dies towards the end of a growing season. They include grains and their by-products such as cereals. Fruit biomass are the parts of plants containing seeds. Blends and mixtures are materials of various origin. Blends are mixed intentionally, mixtures unintentionally (Alakangas, 2010). The actual species should be stated. The classification scheme for woody combustibles by their origin and the according subcategories are shown in Appendix 1. The product of carbonising woody biomass is biocarbon, an upgraded solid biomass fuel (combustible), which can serve as reductant in metallurgical processes. Table 2-2 presents advantages and characteristics of biocarbon. The biggest challenge is possibly to maintain the availability and quality for a reasonable price.

Table 2-2: Positive biocarbon characteristics (Skreiberg, 2017)

- High calorific value and energy density when compressed (pelletised)
- High reactivity
- No bacteriological degradation
- Low ash content
- Low NO_x and SO_x emissions
- Lower logistical costs than wood (dehydrated)
- Hydrophobic
- Facile processing, *e.g.* grinding for pelletising

2.3.1 Molecular structure

Biogenic combustibles mainly consist of the three biopolymers cellulose, hemicellulose, and lignin. These substances make up more than 95 % of the dry matter. Other substance groups appear in small amounts, such as fats, resin, and ashes. Annually plants contain proteins as well (Kaltschmitt et al., 2009, pp. 336-337). The weight distribution is displayed in Table 2-3.

Table 2-3: Composition of biomasses, according to (Kaltschmitt et al., 2009, p. 337)

Combustible	Cellulose	Hemicellulose	Lignin	Resin/fats	Proteins	Ashes
			Woody biomass [wt. $\%_{db}$]			
Fir	42.3	22.5	28.6	2.3	-	1.2
Pine	41.9	21.5	29.5	3.2	-	1.3
Spruce	41	24.3	30	n/a	-	n/a
Ash	40.2	25	26	2.2	-	1.3
Beech	45.4	22.2	22.7	0.7	-	1.6
Birch	40.9	27.1	27.3	2.2	-	1.8
Poplar	48.4	18.2	21.6	2.4	-	1.3
Willow	42.9	21.9	24.7	2	-	1.2

Cellulose ($C_6H_{10}O_5$) is the most prevalent organic matter in nature. It is the framework of non-woody cell walls and mainly responsible for tensile strength. Cellulose is a condensed polymer of glucose ($C_6H_{10}O_6$). It is the main component of the fibre walls and represents 40-45 % of the weight of dry wood (Koppejan & van Loo, 2012, p. 9). Hemicellulose consists of various sugars other than glucose and is the second most important group of biopolymers. It appears in diverse structures and functions as a support for the cell membrane and for gluing together cell walls. Hemicellulose represents 20 - 35 % of the weight of dry wood (Koppejan & van Loo, 2012, p. 9). Lignin ($C_{40}H_{44}O_{14}$) is a non-sugar polymer with high molecular mass. It accompanies cellulose and has a stiffening and luting effect (Koppejan & van Loo, 2012, p. 9). A high lignin content leads to high stability in the biogenic, even at low water content. Herbaceous biomass has up to 20 % of lignin, while woody biomass consists of 20 - 30 % of lignin. The biopolymer contains 64 % carbon, which is more than for cellulose at 42 %. This leads to differences in the energy content, as carbon is defining the calorific value primarily of the biogenic dry residue. Consequently, a high lignin content leads to a high calorific value (Kaltschmitt et al., 2009, pp. 336-337).

2.3.2 Elemental composition

The elemental composition of biomass can be divided into major and trace elements. Main elements are carbon, oxygen, and hydrogen, which originate from CO_2-assimilation and water intake (H_2O). Furthermore, there are seven other major components: Nitrogen, potassium, phosphor, calcium, magnesium, sulphur, and the non-nutrient chlorine. The nutrients are mostly part of the structure or play a role as fertilising escort substances (Kaltschmitt et al., 2009, pp. 338-339). The composition is displayed in Table 2-4.

Table 2-4: Contents of major elements in natural biomass combustibles, compared to hard and brown coal, according to (Kaltschmitt et al., 2009, p. 343)

Combustible	C	H	O	N	K	Ca	Mg	P	S	Cl
	[wt. $\%_{db}$]									
Stone coal	72.5	5.6	11.1	1.3					0.94	< 0.13
Brown coal	65.9	4.9	23	0.7					0.39	< 0.1
Spruce (with bark)	49.8	6.3	43.2	0.13	0.13	0.7	0.08	0.03	0.015	0.005
Beech (with bark)	47.9	6.2	45.2	0.22	0.15	0.29	0.04	0.04	0.015	0.006
Poplar	47.5	6.2	44.1	0.42	0.35	0.51	0.05	0.1	0.031	0.004
Willow	47.1	6.1	44.3	0.54	0.26	0.68	0.05	0.09	0.045	0.004
Miscanthus	47.5	6.2	41.7	0.73	0.72	0.16	0.06	0.07	0.15	0.22
Hay (landscaping)	45.5	6.1	41.5	1.14	1.49	0.5	0.16	0.19	0.16	0.31

From the three main components of dry biomass, carbon releases the largest amount of energy during oxidation, together with hydrogen. Oxygen only supports the process of oxidation. The amount of nitrogen correlates with the amount of protein, for example in grain. Fertilised biomass usually has a higher nitrogen value, as it is a common ingredient of fertilisers. It also increases the formation of nitrogen oxides (NO_x) during combustion, because it changes to gaseous phase almost completely during combustion. Fertilisation can also increase the amounts of potassium, sulphur, and chlorine. These elements can lead to corrosion in heat exchangers and exhaust systems (Kaltschmitt et al., 2009, pp. 339-345).

The occurring trace elements are silicon, sodium, iron, manganese, zinc, copper, molybdenum, cobalt, lead, aluminium, chrome, cadmium, nickel, mercury and arsenic. They count as essential micronutrients, even though some are also harmful (Kaltschmitt et al., 2009, p. 339). Trace elements, mainly heavy metals, influence the attributes and utilisation possibilities of the ashes, which form during the thermo-chemical transformation and from aerosols. The ashes influence particle emissions. Contamination with heavy metals is usually higher in woody biomass compared to annual plants. Bark could be particularly highly contaminated, since it has a longer time to take up elements and is subject to the surrounding atmosphere. Heavy metal residues are mostly concentrated in ashes and define their usability as fertiliser immensely (Kaltschmitt et al., 2009, pp. 345-348). The occurring amounts of trace elements in natural biogenic combustibles are shown in Table 2-5 on the next page.

Table 2-5: Trace elements in natural biogenic combustibles of dry matter, according to Kaltschmitt et al., 2009, p. 348

Sulphur	S	[wt. %]	< 0,08
Chlorine	Cl	[wt. %]	< 0,03
Nitrogen	N	[wt. %]	< 0,3
Arsenic	As	[mg/kg]	< 0,8
Cadmium	Cd	[mg/kg]	< 0,5
Chrome	Cr	[mg/kg]	< 8
Copper	Cu	[mg/kg]	< 5
Quicksilver	Hg	[mg/kg]	< 0,05
Lead	Pb	[mg/kg]	< 10
Zinc	Zn	[mg/kg]	< 100
EOX	Extractable organic halogens	[mg/kg]	< 3

2.3.3 Density

The density of biomass can be determined in different ways. Five relevant methods are described in the following.

The basic density is the ratio of the mass (dry basis) and the solid volume (as received). This incorporates the potential drying and therefore shrinkage of the material (Krajnc, 2015, p. 6).

The total weight divided by the actual volume of a solid content is the true density as the weight per volume. Measuring the solid constituent is complicated, as the material usually shows a complex structure. For wood, the typical true density of the cell walls, which hold the main solid content, is 1,530 kg/m³. It is measurable by a pycnometer, which calculates the volume by displacing gas, or it can be estimated by ultimate analysis (see chapter 2.3.11) (Basu, 2010, p. 42).

$$\rho_{true} = \frac{Total\ mass\ of\ biomass}{Solid\ volume\ in\ biomass} \tag{1}$$

The apparent density is based on the external volume of the biomass. This includes volumes of pores and cells, and it is most feasible for evenly shaped materials, as it gives the actual volume occupied, including possible inclusions. The volume is determined by either measurements or water displacement (Basu, 2010, p. 42).

$$\rho_{apparent} = \frac{Total\ mass\ of\ biomass}{Apparent\ volume\ of\ biomass\ including\ solids\ and\ internal\ pores} \tag{2}$$

The bulk density includes the overall occupied space and therefore might be influenced by material packing, as it includes the volume between particles. Thus, packing and rearranging the biomass may reduce the volume, which is the reason why the standardised bulk density determination requires a container to be dropped three times. For example, a container of five litres volume is being dropped from 15 cm height for a total of three times according to European Norm (EN) (ISO 17828, 2015). The mass also depends on the moisture content MC of the biomass and whether it has been dried. Therefore, the result is labelled either dry basis, or as received to express the uncertain drying state of the material (Basu, 2010, p. 43 ff.).

$$\rho_{bulk} = \frac{Total\ mass\ of\ biomass\ particles\ or\ stack}{Bulk\ volume\ occupied\ by\ biomass\ particles\ or\ stack} \tag{3}$$

The biomass growth density defines how much biomass is available per unit area of land. It includes the total amount of living organic matter above the ground. The value is related to an oven dry state and includes the entire plant (Basu, 2010, p. 44).

2.3.4 Thermodynamic properties

Temperature, density, and moisture of a biomass influence the thermal processes it is used in, such as pyrolysis. They determine how and how much heat is conducted. The specific heat of a material indicates its heat capacity, and it is affected by its moisture and temperature levels. Another critical thermodynamic property is the standard enthalpy of formation. $\Delta \mathrm{H}_{\mathrm{f}}^{0}$ being defined as the enthalpy released or required to form one mole of compound from the pure elements at 25 °C and one bar. When H_2O is formed as a product of combustion, 241.5 kJ/mol are released. It means that 241.5 kJ are removed from the system when hydrogen and oxygen leave their stable elemental form and combine to steam (Basu, 2010, p. 46).

$$\Delta H_f^0 = H_2(gas) + \frac{1}{2}O_2\ (gas) \rightarrow H_2O\ (gas) - 241.5\ kJ/mol \tag{4}$$

The heat of a combustion reaction $\Delta H_{r,comb.}^{0}$ can be calculated from the enthalpy of formation from equation (4) (Basu, 2010, p. 47).

$$\Delta H_{r,comb.}^{0} = \Delta H_{f,products}^{0} - \Delta H_{f,reactants}^{0} \tag{5}$$

The ignition temperature is essential for the combustion process, as the reaction becomes self-sustaining when it passed this point. Since it is higher for fuels which contain a high amount of volatile matter, the ignition temperature is about three times higher for coal than for wood. It further depends on the oxygen partial pressure, particle size, the heating rate, and thermal surroundings, giving it a unique value for different situations at hand (Basu, 2010, p. 48).

2.3.5 Heating value

The lower heating value (LHV), also called net calorific value q_{net} or net heating value, is the amount of heat released during the complete oxidation of a fuel or combustible. The heat of evaporation of the water formed by the hydrogen and the condensing moisture are not considered. The higher heating value (HHV), also called the gross calorific value q_{gr} or heat of combustion, is the amount of heat during a complete oxidation of a fuel or combustible, including the heat released from water vapour from hydrogen combustion and moisture by condensing in the exhaust fumes (ECN, 2018). One way to determine the heating values in a laboratory is to combust fuel in a bomb calorimeter. The higher heating value is the amount of heat released, until the products have returned to the starting temperature (usually 25 °C). For the lower heating value, only the heat energy of the combustion process is measured. Therefore, it is measured before the cooling process, to avoid the latent heat of vaporization to be recovered (Basu, 2010, p. 58). The HHV can be estimated by a calculation from the empirical Milne-equation (6) Milne et al., 1990).

$$HHV_{Milne} = 0.341 \cdot C + 1.322 \cdot H - 0.12 \cdot O - 0.12 \cdot N + 0.686 \cdot S - 0.0153 \cdot AC \qquad (6)$$

C, H, O, N, S, AC	mass and ash fraction	[wt. $\%_{db}$]
HHV	higher heating value dry	[MJ/kg]

2.3.6 Volatile components

The volatile matter of a combustible are its gaseous components, which are released during the pyrolytic process after water has evaporated. They appear in different compositions and concentrations and define how combustibles decay into inflammable, gaseous components. Woody combustibles contain an average of 82 % volatile components of the dry matter. Compared to this, common stone coal consists of 6 - 45 % volatiles of dry matter (Kaltschmitt et al., 2009, pp. 355-356).

2.3.7 Water and moisture contents

The common term used for water or moisture in biomass is moisture content (MC). Döring further defines the water content as the amount of water that can be extracted from the wet matter (usually referred to as “as received”), whereas the moisture content states the amount of moisture bound to the dry matter. The wood moisture is referred to the absolute dry weight of the wood, which is usually the mass after the material has been dried in an oven (oven-dry mass) (Döring, 2013, p. 99). It can be derived from the water content. For example, an amount of 100 % moisture correlates with a water content of 50 %. This leads to possible values for the moisture of above 100 % (Kaltschmitt et al., 2009, p. 356). For consistency, only the term moisture content will be used in this thesis, and to differentiate, the terms wet- and dry basis will be used. Parts one to three of EN ISO 18134 regulate drying methods for solid biomass to determine the MC. Part two elaborates the simplified process, which is applied in practical laboratory situations for the proximate analysis (see chapter 2.3.9). The material is placed in an oven at 105 °C for 24 hours. The weight is measured before, as “as received” and afterwards as “oven-dry”. The difference gives the MC (ISO 18134, 2015/17). MC influences the heating value of a combustible more than the type of wood, as a certain level makes the material unsuitable for combustion. A common value for wood pellets is a MC of 8 - 12 wt. $\%_{wb}$ (Döring, 2013, p. 41). The international standard for energetic applications of biomass is the MC referring to the total mass of wet matter. It can be calculated with the following equation (Koppejan & van Loo, 2012).

$$u = \frac{m_F - m_T}{m_T} \cdot 100 \quad [\%]\ dry\ basis \tag{7}$$

$$w = \frac{m_F - m_T}{m_F} \cdot 100 \quad [\%]\ wet\ basis \tag{8}$$

w	MC in [%] of total weight, wet basis
u	MC in [%] of dry weight, dry basis
m_F	Total mass before drying (as received)
m_T	Mass after drying (dry matter)

2.3.8 Ash residue

Ashes are inorganic compounds remaining after complete combustion. The ashes typically consist of silica, aluminium, iron and calcium, and small amounts of magnesium, titanium, sodium and possibly potassium (Basu, 2010, p. 52). They are present in biomass as salts, bound in the carbon structure as inherent ash or originating from processing the biomass, for example when a tree gets in contact with the soil during harvest (Koppejan & van Loo, 2008, p. 34). The ash content affects emissions and the technical design of combustion systems, as they increase dust formation in the process. Wood and bark are causing about 0.5 - 1.5 % ashes of the dry matter, except woods with a short rotation period (willow, poplar). For these, the ash content is up to several percent higher. An overview of heating values, ash, and volatile matter contents are listed in Table 2-6. A high ash content yields a low calorific value of a combustible (Kaltschmitt et al., 2009, pp. 352).

Table 2-6: Natural combustible characteristics (dry basis) of fossil coals and woody biomass, data acquired from Kaltschmitt et al., 2009, p. 360

	q_{net} [MJ/kg]	q_{gr} [MJ/kg]	Ash [%]	Volatile matter [%]
Stone Coal	29.7		8.3	34.7
Brown Coal	20.6		5.1	52.1
Spruce	18.8	20.2	0.6	82.9
Beech	18.4	19.7	0.5	84.0
Poplar	18.5	19.8	1.8	81.2
Willow	18.4	19.7	2.0	80.3

q_{net} net calorific value

q_{gr} gross calorific value

2.3.9 Proximate analysis

The composition of a combustible consists of moisture, volatile matter, ash content and fixed carbon. It is a simple and inexpensive process requiring an oven capable of reaching high temperatures. The process is standardised by norm. A test sample is heated in closed crucibles at 900 °C (950 °C for the American norm) for seven minutes following EN ISO 18123:2015. The sample cools down in a desiccator, and its weight is measured before and after to determine weight loss due to VM, which emerged during the process (ISO 18123, 2015).

The AC is measured following EN ISO 18122:2015. The dry matter is weighted and heated in a crucible. The process is required to pass in steps to 250 °C first and then 550 °C to avoid flaming. The processed sample is then cooled down in a desiccator and the residue is measured (ISO 18122, 2015). The result might deviate from the original inorganic mineral matter in the fuel, as parts can corrode during the thermal process. The AC is usually low but crucial for metallurgical process where ash can interfere with the smooth procedure.

Determining the MC is elaborated in chapter 2.3.7. Raw biomass is characterised by its high MC. Thus, a thermal drying process influences the biomasses attributes significantly, as a decreasing MC correlates directly with the deliverable energy being drained from a combustion process, because the energy from evaporation leaves the system. FC in biomasses originates from the photosynthetic fixation of CO_2. The FC is a variable value as it is depending on VM, which varies with different heating rates during the thermal process. Furthermore, a varying VM determines how a part of the organic carbon is transformed to pyrolytic carbon. Therefore, FC is measured following standards for all previous attributes. The amount of FC in biomass is the residue after subtracting MC, VM and AC, as shown in equation (9). It is the amount of carbon that remains after devolatising the biomass completely. It consists of carbon from the biomass and carbonaceous matter formed during the devolatilisation process (Basu, 2010, p. 55)

$$FC = 1 - MC - AC - VM \tag{9}$$

FC Fixed carbon

MC Moisture content

AC Ash content

VM Volatile matter

2.3.10 Thermogravimetric Analysis

Thermogravimetry (TG) and differential thermogravimetry (DTG) are processes that provide fast, comparable and stable results, and give information about the composition of a test probe like those of proximate analysis (Basu, 2010, p. 55). During thermogravimetry, a small test sample is inserted into a reactor filled with a selectable protective atmosphere. For this thesis, argon was chosen, as noble gases prevent reactions of the test material with the ambient surroundings (e.g. combustion). A thermal process commences; simulating a full pyrolytic reaction. The function of weight over temperature shows the weight loss for the full pre-set temperature range. The graph visualises emerging water, volatile matter and ash, while the value for fixed carbon is then calculated with equation (9). The temperatures, heating rates and duration can be programmed to suit the required standardised process. Differential thermogravimetry is the inverted curve of thermogravimetry, showing the rate of change in the weight loss of the test probe. The TGA further gives information about reaction mechanisms, kinetic parameters, thermal stability, and heat of reaction (Basu, 2010, p. 56).

2.3.11 Ultimate Analysis

An Ultimate Analysis (UA) is a complex system, which analyses weight percentages of basic elements in a test sample (Figure 2-2). If contained in the sample, these are usually carbon, hydrogen, oxygen, nitrogen, and sulphur. Sulphur is especially rather unlikely to be contained in biomass among other than traces. It is usually added from contamination during handling the biomass, e.g. forest soil. A technical feature is that the UA differentiates between moisture and hydrogen and oxygen respectively. Thus, results may show the water content, but in addition hydrogen and oxygen separately, which descended from the organic components of the test sample (Basu, 2010, p. 49); see equation (10).

MC and AC are the same values as determined by proximate analysis. Only the FC deviates, as the amount of FC is not included in the values for VM determined by ultimate analysis (Basu, 2010, p. 51),

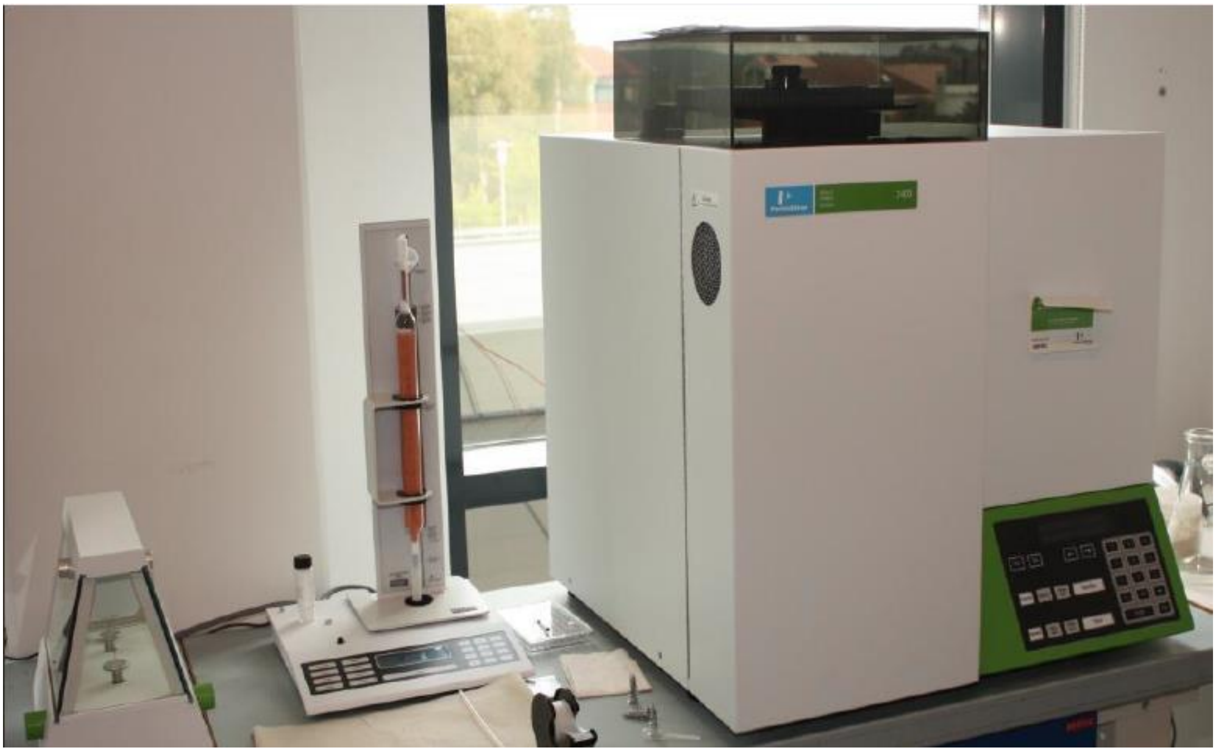


Figure 2-2: Elemental analysis with scale for ultimate analysis (Perkin Elmer 2400 CHNS/O Series II)

The first step of an UA is usually measuring the MC of the test sample in a separate process, following EN ISO 18134-3. This circumvents the above-mentioned speciality that hydrogen and oxygen are only considered from organic compounds, ignoring the MC of the test sample (ISO 18134, 2015/17). The system is then purged with a noble gas, e.g. Helium. After a warm-up phase, the measurement can commence. The probe is combusted completely, and the gases are led through a measuring column, determining the element composition. A software then computes the measurements correctly and shows the results on a computer screen. When calibrated correctly, the Ultimate Analysis (Perkin Elmer) gives precise and reliable results:

$$100\,\% = C + H + O + N + S + Ash + MC \tag{10}$$

2.3.12 Biomass conditions in terms

In many cases, the moisture content of biomass or a combustible is uncertain or at least fluctuating when delivered. The natural resource varies, and only processed materials can offer a controlled constitution. Therefore, the term “as received” is used, signalling uncertain MC that has yet to be determined by analysis or actual information from the vendor. Biomass in the condition “as received” contains all components before drying. By proximate analysis, the content of VM, FC, MC; and AC can be determined, forming 100 % of the weight, as described in chapter 2.3.9. Ultimate Analysis further determines the components carbon, hydrogen, oxygen, nitrogen, sulphur, ash, and moisture, forming 100 % of the weight as well, as described in chapter 2.3.11. Both analyses show the same amount for AC and MC (Basu, 2010, p. 56 ff.). The composition is displayed in Figure 2-3, which further shows, how other bases can be derived from “as received”.

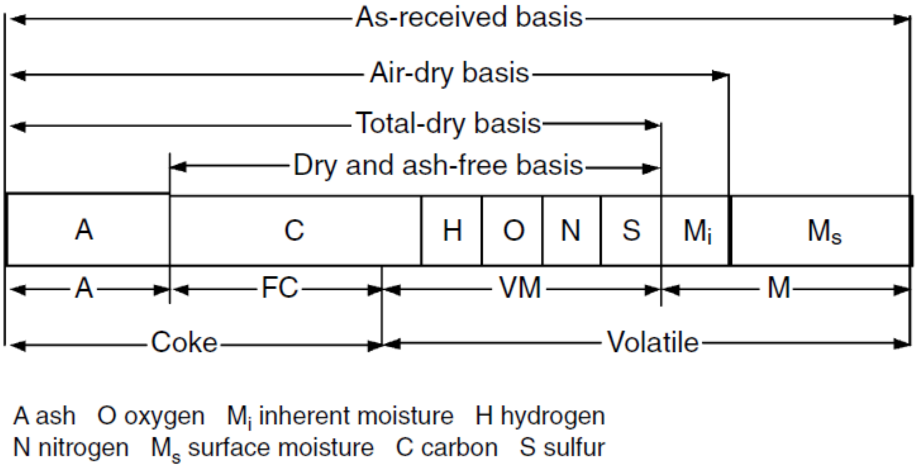


Figure 2-3: Bases of fuel composition and their denotaiton (Basu, 2010)

Drying the biomass in ambient air removes moisture on the surface. Following Figure 2-3, the mass of the “air-dry” biomass can be determined by subtracting the surface moisture M_S. Single components can be calculated by equation (11), using carbon as an example (Basu, 2010, p. 57):

$$C_{air-dry} = \frac{100\ C}{100 - MC_S}\ \% \tag{11}$$

Removing the inherent moisture as well gives the “total-dry” basis, which is achieved by the drying process. Using the example of Carbon, the content on a dry basis can be determined by equation (12):

$$C_{total-dry} = \frac{100\ C}{100 - MC}\ \% \tag{12}$$

For the “ash-free” basis, equation (12) can be extended by the ash content:

$$C_{total-dry} = \frac{100\ C}{100 - MC - AC}\ \% \tag{13}$$

2.4 Relevant thermal processes

Relevant thermal and thermochemical processes are displayed in Table 2-7. Slow pyrolysis is based on the ancient procedure of biochar production called carbonisation. The primary goal is normally to produce solid biochar. Side products are bio-tar/oil and gas. The process has a slow heating rate and a duration of several days for the carbonisation. The related process slow pyrolysis lasts several minutes. Process temperatures can vary but lie at around 400 °C for carbonisation and around 600 °C for slow pyrolysis. Both procedures are under exclusion of oxygen, to avoid combusting the material (Basu, 2010, p. 72).

Table 2-7: Thermochemical conversion processes, acquired from Basu, 2010, pp. 12, 72

Process	Temperature [°C]	Pressure [MPa]	Catalyst	Drying	Products
Slow pyrolysis	< 600				Char, bio-tar/oil, gas
Flash-pyrolysis	450 - 600 (oil) < 1,000 (gas)		Not required	Necessary	Bio-oil, chemicals, gas
Gasification	500 - 1,300	> 0.1	Not essential	Necessary	Gas, chemicals
Torrefaction	200 - 300	> 0.1		Essential	Conditioned biomass
Combustion	700 - 1,400	> 0.1	Not required	Not essential, but may help	
HTL	250 - 330	5-20	Essential	Not required	

Flash-pyrolysis is a process which is not relevant for the carbonisation of biomass directly, as its main product is bio-crude or -oil. The produced oil (flash pyrolysis oil, FPO) may be investigated as a binding agent for pelletising biomass. It is a relatively modern form of pyrolysis and can be based on a fluidized bed system. The process uses dried and shredded material, a pyrolysis reactor with an oil separator, and an integrated coke combustion unit to gain process energy. The goal is to maximise the gain of liquid pyrolysis products. Therefore, the biomass particles are heated fast with temperatures over 1,000 °C/s to 450 - 500 °C. The process lasts approximately a second and requires reactors with a good heat transfer, typically provided by a fluidised sand bed that leads to a fast and effective separation of fluid products (Kaltschmitt et al., 2009, p. 671). Besides pyrolysis, gasification is a de-volatilisation with an external oxidant, focussing on a maximised yield of gaseous matter. Process temperatures range from 800-1,100 °C. The product gas consists mainly of CO, CO_2, H_2O, H_2 and CH_4 (methane). Longer hydrocarbons are detectable in trace amounts. Typical oxidants are oxygen, steam or CO_2. Gasification with air leads to a gas with 4 - 7 MJ/Nm^3 dry, while oxygen leads to a higher GCV of 10 - 18 MJ/Nm^3 dry (Megajoule per norm-cubic metre). Condensed gases can be upgraded to methanol or used as a fuel for heat/power generation or in combustion engines. By removal of contaminants, for example tar, char particles, ash or alkali compounds, the product is suitable for gas turbines and in IGCC (integrated combined combustion cycle) (Koppejan & van Loo, 2008, pp. 9-11).

Figure 2-4 displays the relation between temperature and emerging pyrolysis products regarding their states solid, fluid, and gaseous. The dashed line gives the difference for high heating rates, which typically increase the percentage of gaseous and fluid products.

Hydrothermal processes use thermic reactions in the presence of liquid water above the vapour pressure curve. They offer the advantage that biomass can be utilized directly, without prior drying. Depending on the desired state of the product, the reaction medium is in a subcritical or supercritical state. The factors influencing the reaction are pressure, temperature, reaction time, and applied catalysts (Quicker & Weber, 2016, p. 38). The process can be divided into four different categories: Hydrothermal activation, carbonization, liquefaction and gasification. The processes and their products require different conditions, which are shown in Table 2-8 on the next page.

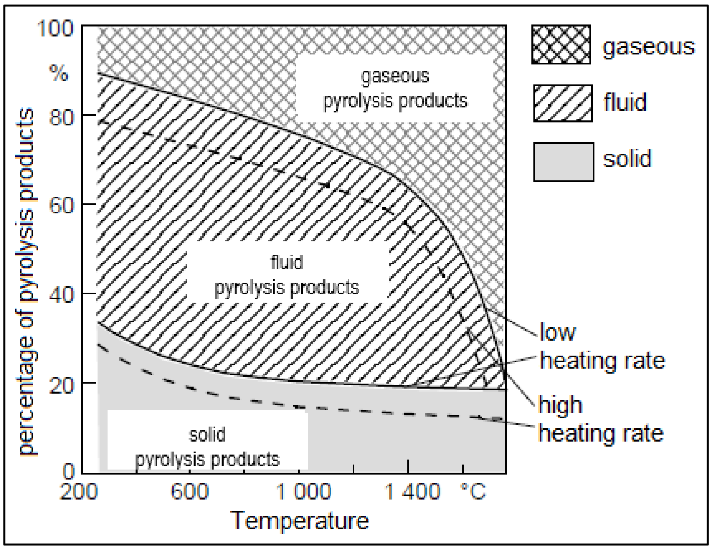


Figure 2-4: Products of thermo-chemical conversion of wood (Kaltschmitt, et al., 2009)

Table 2-8: Hydrothermal processes, from Quicker & Weber, 2016, p. 39

Process	HTA	HTC/VTC	HTL	HTG
Term	Hydrothermal activation	Hydrothermal/Vapothermal carbonisation	Hydrothermal liquefaction	Hydrothermal gasification
Primary product	Biochem. available biom.	Carbonised biomatter	Bio-crude	Syngas
Temperature in [°C]	120 - 200	180 - 260	250 - 350	350 - 700
Duration	1 - 60 min	2 - 16 h	10 - 15 min	1 - 5 min
Pressure in [bar]	2 - 90	15 - 60	150 - 240	250 - 500

The process duration determines whether the product is solid, liquid or gaseous. Liquid and gaseous products result from short process times, whereas carbonisation requires significantly more time at temperature levels like hydrothermal activation and liquefaction (see Table 2-8). The higher duration originates from the conversion reactions. The poly-reactions pass off slowly and require a longer reaction time. They are undesirable for activation, liquefaction and gasification of biomass, as the goal is not to achieve solid carbonaceous matter, which is the main product of slow process times (Quicker & Weber, 2016, pp. 39-40). HTL and HTC are the most relevant procedures for this thesis as they yield biochar and bio-crude. They are elaborated in the following.

Temperatures for HTL are close to the critical point, at 250 - 350 °C. The main product is an oily, liquid mix of bio-crude, water, and dissolved organic substances with a high energy content of about 30 - 37 MJ/kg (Quicker & Weber, 2016, p. 41). Other products are bio-carbon and a gaseous phase, which mostly consist of CO_2. The process is usually conducted with a basic catalyst to increase the oil yield. Other literature describes temperatures of 250 - 350 °C and pressures of 100 - 200 bar, a high hydrogen partial pressure, higher liquid yield than by pyrolysis, and a lower oxygen content being the essential characteristics for the HTL (Koppejan & van Loo, 2008, p. 11). Typical temperatures for HTC are between 180 - 260 °C, with a much longer duration of two to sixteen hours. The product is a hydrophobic, carbon rich solid suspension. The carbonisation increases the energy density and thus the HHV.

VTC is a variant of the HTC for which the biomass is treated with saturated steam compared to being submerged in water. VTC allows to have a higher content of solid biomass (dry basis) per total mass of feedstock in the reactor, but it also results in a lower carbon content in the solid product (Funke et al., 2013).

2.4.1 Gas phase and solid fuel kinetics

The gas phase interaction of biomass is essential for a combustion process, especially for processes sensitive to emerging volatile matter, e.g. a closed furnace (Koppejan & van Loo, 2008, p. 23). Thus, combusting and gasifying after pyrolysing biochar or pellets are an important factor influencing the suitability. The main ingredient, carbon, requires the delivery of the oxidant (O_2) to the carbon surface by diffusion or convection, where it is to be adsorbed. It reacts heterogeneously with the carbon, while the products, mainly CO_2 and CO, desorb and are carried away by further diffusion or convection. Heterogeneous reactions are rather slow, which results in a longer reaction time. A small particle size is therefore beneficial (Koppejan & van Loo, 2008, p. 23). Solid fuel combustion is a complex process, but mass balances and thermodynamic calculations can deliver important information for evaluating the fuel conversion and thermal performance. They allow to compute parameters such as air and gas flows, calorific value, combustion temperatures, and thermal as well as combustion efficiency. To keep a concise volume, this thesis focusses on the machines and systems used in practical environments to determine thermodynamic values. The theoretical background is elaborated extensively in relevant literature.

2.4.2 Chemical equations and calculations

When biomass or carbonaceous material is heated in restricted oxygen environment, it is pyrolysed or decomposed rather than combusted, resulting in solid carbon and condensable and non-condensable gases. Both the solid carbon and the condensed liquid, which evaporates as a gas from the pyrolysed biomass, react with CO_2, O_2 or steam to produce combustible or synthetic gas. The following equation shows the reaction for carbon (Basu, 2010, p. 23 ff.):

$$C_nH_mO_p + Heat \Rightarrow \sum_{liquid} C_aH_bO_c + \sum_{gas} C_xH_yO_z + \sum_{solid} C \tag{14}$$

During complete combustion on the other hand, 1 kmol of carbon produces 394 MJ heat and CO_2, as shown in the following equation (Basu, 2010, p. 30):

$$C + O_2 \rightarrow CO_2 - 393.770\ kJ/kmol \tag{15}$$

However, if the combustion process proceeds with limited air or oxygen supply, it is called gasification (see chapter 2.3.9). The carbon produces less heat than during combustion, and the reaction produces CO, which is a combustible gas, as shown in equation (16):

$$C + 0.5\ O_2 \rightarrow CO - 110.530\ kJ/kmol \tag{16}$$

The Fischer-Tropsch synthesis reaction involves a series of chemical reactions producing a mixture of hydrocarbons, ideally having the formula $C_nH_{(2n+2)}$. These hydrocarbons range from methane to gasoline and wax, usually featuring 10 - 20 carbon atoms. Most alkanes emerging from the reaction are linear and usable for diesel fuel. The catalyst, carbon, temperature, and the pressure of the reaction influence the composition of the resulting hydrocarbons, as shown in equation (17) (Basu, 2010, p. 24):

$$(2n+1)H_2 + nCO\ (catalyst) \rightarrow C_nH_{(2n+2)} + nH_2O \tag{17}$$

2.5 Practical applications of biochar

Compositions and binding agents for CO_2-efficient biochar are investigated as possible replacements for fossil coal or coke, as elaborated in chapter 5. Fossil coal and coke are reducing agents for the metallurgical industry (see chapter 2.5.2). This chapter summarises the main applications for biochar in the Norwegian and worldwide industry and gives an overview of the technologies and challenges. Metal oxide reduction giving carbon mono- and dioxide during the smelting process is shown in equations (18) and (19):

$$Me_xO_y + yC \rightarrow xMe + yCO \quad Me = alkaline\ earth\ metal \tag{18}$$

$$2Me_xO_y + yC \rightarrow 2xMe + yCO_2 \tag{19}$$

Equation (20) shows the calculation of the amount of carbon required to fully reduce one kilogram of hematite. In addition, Table 2-9 lists the carbon demand for relevant metallurgical processes, as determined via equation (20):

$$1{,}000\ g\ Fe_2O_3 \cdot \frac{1\ mol\ Fe_2O_3}{159.6\ g\ Fe_2O_3} \cdot \frac{3\ mol\ C}{2\ mol\ Fe_2O_3} \cdot \frac{12.01\ g\ C}{1\ mol\ C} = 113\ g \tag{20}$$

Table 2-9: Carbon demand for smelting metal oxides, from equation (20)

	Iron-oxide (hematite)	Iron-oxide (magnetite)	Aluminium	Silicon	Manganese
Formula	Fe_2O_3	Fe_3O_4	Al_2O_3	SiO_2	MnO
Carbon demand $[g_c/kg_{Me_xO_y}]$	113	104	177	200	85

Hematite = Iron oxide, rock mineral
Magnetite = Iron oxide, rock mineral

2.5.1 Industrial systems requiring carbonaceous reduction

The most common steel production method is the integrated process with a basic oxygen furnace (BOF). It combines (pig-) iron, steel scrap (less than 30 %), and a flux material to remove impurities. A lance blows oxygen into the furnace, raising the temperature up to 1,700 °C. Impurities are oxidised and the carbon content is reduced by 90 %. One ton of steel is produced from 600 kg of coke and 770 kg of coal. BOF are used in 74 % of the world's steel production (World Coal Association, 2018). The pig-iron used in BOFs can originate from blast furnaces, where iron oxide ore is reduced with iron ores, additives, as well as coke and other reducing agents. The latter are usually coal, oil or gas, for which biochar is a possible substitute (Stahlinstitut VDEh, 2018). A blast furnace is a shaft-shaped aggregate (Figure 2-5). The input of materials occurs from the top, while a reducing gas is blown in with a pressure higher than the ambient. To free the iron ores from the contained oxygen, they are reduced by a reducing agent such as carbon monoxide. For this, carbonaceous material, coke is usually introduced to gasify with the oxygen in the air blown into the bottom of the furnace, thus producing CO. The gas rises, binding the oxygen in iron ores and produces carbon dioxide. Other carbon carriers are also injected in the furnace to optimise the process and reduce the costs (Stahlinstitut VDEh, 2018). Biochar with a high mechanical strength and reactivity would reduce the environmental impact from produced carbon dioxide due to its climate neutral production.

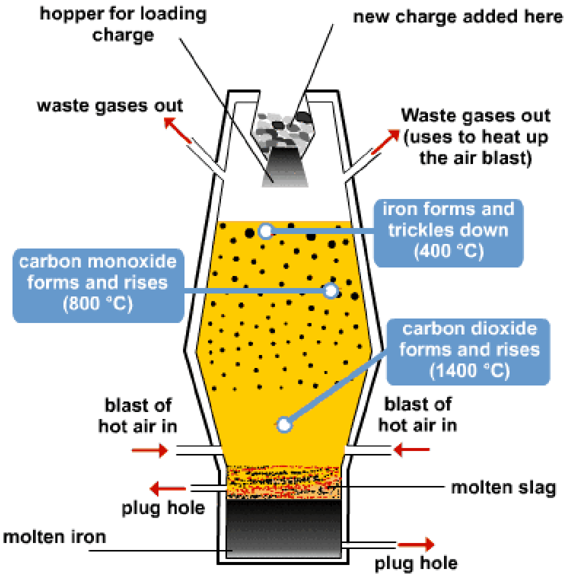


Figure 2-5: Blast Furnace (Dzoma, 2016)

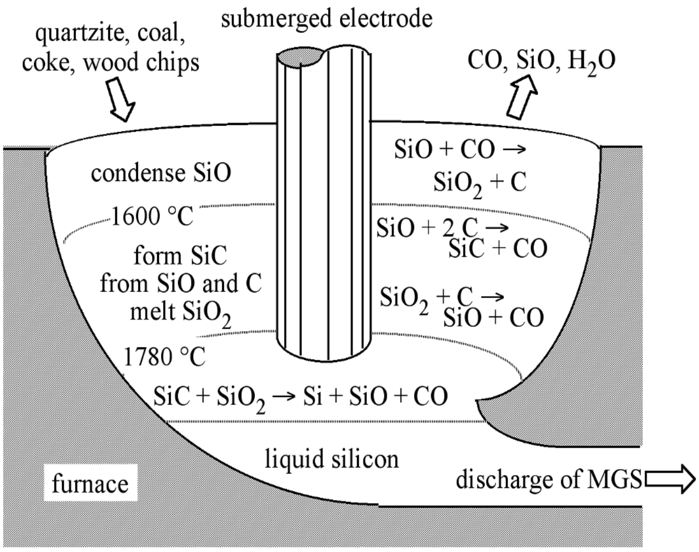


Figure 2-6: Electric Arc Furnace (Quizover, 2011)

The electric arc furnace (EAF), also known as mini-mill, recycles steel in combination with direct-reduced iron (DRI) or pig iron (see Figure 2-6 for an example with silicon production). An electric arc between two electrodes reaches through the scrap metal and raises the temperature to up to 1,800°C. Added flux is used to form slag by binding impurities. The slag is then easily removed from the mass. The electric arc furnace does not use coal directly but is often powered by electricity produced by coal combustion in the power grid. About 150 kilograms of coal are used to produce one ton of steel in electric arc furnaces. They make about 25 % of the worlds steel production (World Coal Association, 2018).

A submerged arc furnace is typically employed for producing semiconductors, and a simplified example process for a typical silicon-production is shown in Figure 2-7. The product is obtained by carbon-reducing silica at about 1,800 °C. Like steel production, silica can be reduced by biochar instead of pet coke. Additional reduction agents are coal and woodchips. The furnace consists of consumable graphite electrodes, a power supply system, and electric energy, gas removal-, heat recovery-, tapping-, casting- and crushing-devices. The material is charged, smouldered, and is led to an outflow located at the bottom. Resulting liquid silicon is freed from impurities and poured in predesigned moulds and then further processed (Chen at al., 2017). Equation (21) shows the reduction process of silicon:

$$SiO_2 + C \rightarrow Si + CO_2 \qquad (21)$$

For the above-mentioned furnaces, the quality of biochar pellets is important, especially regarding their behaviour at high temperature levels. The material is dropped in the furnace from the top and sinks. If the pellets dissolve in the beginning, the carbonaceous material would blow out or spread at the top. Therefore, a high durability is significant. If a blast furnace is used, where the carbonaceous material is blown in from the bottom, structural strength is of less importance.

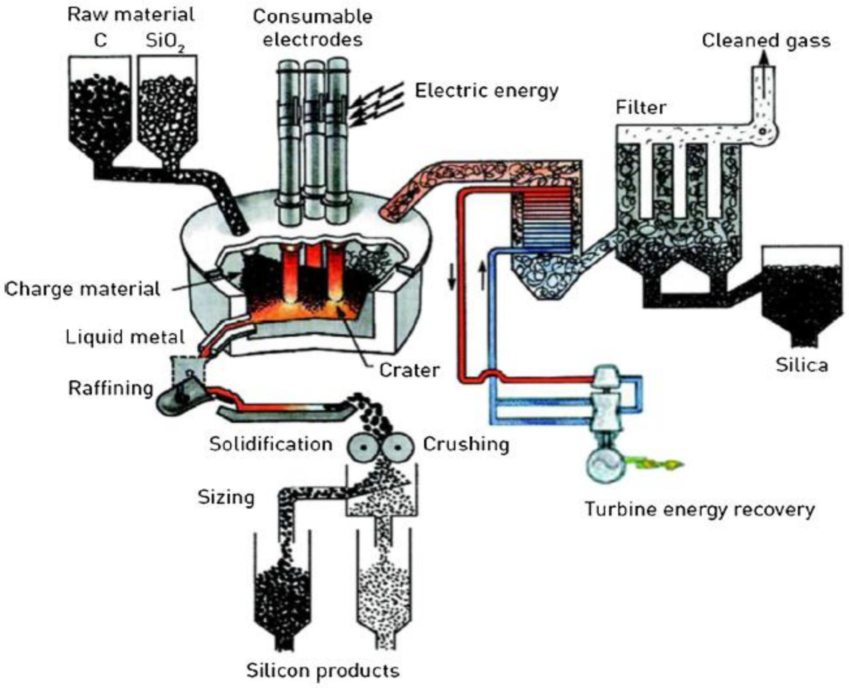


Figure 2-7: Submerged Arc Furnace, silicon production (Chen, et al., 2017)

2.5.2 Biochar for industrial carbonaceous reduction

For the use of biochar in metallurgical reduction processes, the carbon content is the main parameter. The calorific value however is negligible, as the reaction heat is mostly supplied by electricity in EAF and oxygen combustion in BOF respectively. The formation of VM should be kept to a minimum, as these are likely to throw material out of an open kiln or increase the pressure in closed systems. Excess pressure might possibly lead to a malfunction. Sulphur can cause corrosion in the system and thereby shorten the service intervals or lead to malfunctions. The energy consumption and emissions (gate to gate) of blast- and electric arc furnaces from different production methods were studied in recent publications (Anderson et al., 2002; Norgate et al., 2012). The results for CO_2 emissions in [kg/t_{steel}] suggest that *“sustainably grown biomass offers the greatest potential to reduce the fossil fuel and greenhouse gas footprint of* *steel production"* (Norgate et al., 2012, p. 1). Coke can be partially replaced as a reductant and fuel in the blast furnace, and pulverised coal can be fully replaced as a fuel in blast furnaces. For recarburising liquid steel, coal-based char can be fully replaced (Norgate et al., 2012, p. 5). It might be problematic to fuel large blast furnaces with biochar to greater amounts though, as it offers a lower crushing strength compared to coke. Rates of up to 20 % are suggested.

Recent publications analyse the characteristics, costs, and impact of implementing biochar in modern blast furnaces (Norgate et al., 2012; Babich et al., 2010; Feliciano-Bruzual, 2014) Babich (2010) compared the elemental composition of biochar, coal and coke. The requirements of biochar to compete with fossil coal or coke are displayed in Table 2-10. Exchanging fossil coal or coke with biochar is a feasible way to mitigate CO_2-emissions for metallurgical applications in blast furnaces. Babich states that by using biochar, the CO_2-input decreases by 37 - 45 % for replacing the partition of coke for analysed reactant-mixes, and the specific surface is 60 - 350 times higher than for pulverised coke leading to a higher reactivity (Babich et al., 2010, p. 88).

Table 2-10: Accumulated requirements for renewable reduction agents (Babich et al., 2010)

FC	fixed carbon	[wt.%]	Larger than	80
AC	ash content	[wt.%]	Smaller than	10
VM	volatile matter	[wt.%]	Smaller than	10

Feliciano-Bruzual states that for examined cases the injection of pulverised particles of biochar into a blast furnace can mitigate a quarter of CO_2-emissions (Feliciano-Bruzual, 2014, p. 241). Norgate et al. (2012) concluded that the estimated reduction of CO_2-emissions (gate-to-gate) from the use of biomass reaches 1,700 kg/t_{steel} for blast furnaces and 500 kg/t_{steel} for electric arc furnaces, when biomass is seen as CO_2-neutral (Norgate et al., 2012, p. 2).

3 SUPPLY CHAIN STRUCTURES AND PRE-TREATMENT

The main steps of the supply chain of woody and herbaceous biomass are growing, managing, and harvesting. The exact supply chain can vary though, depending on the material and local conditions. For example, the comminution of the matter before or after transporting it from the growing site to further processing (Koppejan & van Loo, 2008, p. 60).

Forest residue is mostly produced from clear felling or thinning out forests. It is possible to harvest energy components and timber simultaneously in an integrated harvesting system to decrease supply costs. The tree is harvested and handled, and the energy part is separated before the comminution at the edge of the forest. The integrated harvesting is the most promising system for a profitable, homogenous product. Thinning and clear felling contain of the following main categories (Koppejan & van Loo, 2008, p. 61):

- Felling
- Extraction (stump to roadside)
- Processing
- Comminution (chipping/hogging)

Short rotation woody crops are woody tree species, which have been bred and selected to have a high rate of juvenile growth. Willow is especially popular in northern Europe, mostly Sweden, as a feedstock for biomass supply chains. It can be harvested in about three to seven years (Jackson, 2017). To grow these crops, the proper resource management is required. It consists of managing fertilizers, which could include the utilisation of waste water, sewage sludge, biomass ash, and pest control. Cost efficient and economical harvesting technologies are still under development (Koppejan & van Loo, 2008, p. 62).

Producing a feedstock from wood for pelletising or pyrolysis for commercial use requires several steps. These are usually debarking and milling the trees, wet storage and transport, drying, dry storage, pelletising, pellet storage, packaging, and transporting the product (Döring, 2013, p. 71).

3.1 Pellet production and necessary pre-treatment of the feedstock

Untreated biomass has a low bulk density, which makes it challenging to transport and handle from a financial and organisational point of view. Chipped wood reaches from 250 - 450 kg w.b./m³, and straw and grass bales have about 120 kg w.b./m³ and 200 kg w.b./m³ respectively (Koppejan & van Loo, 2008, p. 40). Thermal treatment can facilitate the storage of biomass. By drying, the bulk density sinks while the energy density grows. The initial problem is not solved by this, though, as the product is more friable and dusty. Therefore, mass and energy density are increased by applying pressure, producing solid pellets. Pelletizing wood increases the bulk density to about 600 kg w.b./m³ and the energy density to roughly 10,000 MJ/m³, which is almost three times higher than from woodchips (Koppejan & van Loo, 2008, p. 40). Pelletising the wood leads to reduced costs for transport and improves handling and feeding. It reduces dust formation and gives the material a consistent shape. Seasonal products can be stored efficiently and thereby provided over the whole year, while they might be available for harvesting only in short periods (Nielsen et al., 2010).

The industrial process contains several automated steps, which usually run in a continuous flow. As some plants may have individual specifics, only the essential process is described. It is essential, that the material is free of any impurities such as stones or metal shards. A Fe/Ne separator (ferrous/nonferrous) removes ferrous particles from the biomass with a magnet. This avoids increased wear on the following process and fire hazards caused by sparks. An air sifter then removes heavy objects like stones from the wood. A hammer mill contains a rotor with movable strikers, powered by an electrical engine. The wood is broken up by the strikers by the sudden change of momentum and a milling and shearing effect at the exit screen. This screen works as a sieve and the hole size determines the desired width of the product, the throughput and energy consumption. An increasing water content further decreases the capacity and increases the specific energy consumption (Döring, 2013, pp. 81-82, 116).

Drying in mass production serves as preservation and increasing the heating value, and to reduce weight and increase quality of the product. (Kaltschmitt et al., 2009, p. 314). Reducing the water content of the biomass makes an expensive step during pellet production but has a great effect on the overall economic efficiency. Thus, it is a critical step for industrial applications and requires optimisation in construction and design to keep the process beneficial. In industrial applications belt and drum dryers are common (Döring, 2013, p. 99). The scientific environment of the experiments in this thesis requires precision and a smaller batch size, so that drying ovens are preferred. To determine the water and moisture content of the material, a test sample is weighted before and after the drying process. Döring describes an industrial drying process in an oven at 100-120 °C for several hours, until no further decrease in weight is determinable (Döring, 2013, p. 100).

The industrial pelletising process consists of the following steps until pelletising: Fe/Ne separator, air sifter, hammer mill, additive silo and proportioning, mixer, homogenising silo, mixer with addition of steam, pellet press, and a cooler (Döring, 2013, p. 116). For testing different additives and their attributes, a single pellet press can be used. Depending on the chip size after the milling and drying process, the material can be blended with additives such as starch, water, or experimental materials like different compositions of pyrolysis tar/oil. In common wood-pellet production, starch might be added as a binding agent, depending on the pellet quality regarding surface condition and wear. A mixing process with a duration of up to fifteen minutes ensures a homogenous spread of the additive and gives the starch time to start a swelling process. Water might be used here as well, depending on the water content, and it should be heated for easier processing. The pellets might also be preheated or mixed with steam to keep the moisture level constant. Steam further increases the binding characteristic of starch and improves the pellet quality, reduces the power necessary for pelletising and maximises the throughput (Döring, 2013, p. 118).The pellet press consists of a drawing die and rotary edge runners. The chips are forced through a gap into a moulding channel and cut off afterwards to the desired length. Afterwards, the pellets are guided into a cooler, as the pressure heats up the pellets to 70-95 °C (Döring, 2013, pp. 118-119).

3.2 Agglomeration

Carbonisation of woody biomass generally lowers the abrasion resistance and mechanical strength. Thus, less energy is required to mill or chip the matter. However, small particles are problematic to handle, process and store, if not furtherly processed immediately. Agglomeration is recommended to achieve attributes to improve logistic handling, grain size, and chemical or physical requirements from the industry. There are three basic agglomeration principles, from which two are impractical for the metallurgical industry (Quicker & Weber, 2016, pp. 148-149). Thermic agglomeration (sintering) is only useful for metallic or oxidic feedstock and thus not suitable for woody biomass. Wet agglomeration produces pellets with about a third of the density of pellets from press agglomeration, and requires, due to its sensitive process, a high effort in measurement and control systems (Quicker & Weber, 2016, p. 151).

Press agglomeration is practicable and usually contains three processes. Homogenizing the particle spread, deforming particles, and their size being reduced. A high degree of carbonization decreases the deformability, which is the essential attribute for a better material strength. Biomass from a pyrolysis process with high temperatures makes binding agents necessary to reach the required material strength, while biochar from HTC processes has a less intense grade of carbonization, thus a higher material strength even without binders (Quicker & Weber, 2016, p. 152). Practical procedures to apply press agglomeration are distinguished in closed and open methods. As a large surface area is one of the main goals to increase reactivity, the pellet size is to be kept small. The open pellet press is very efficient regarding this factor and offers a high throughput and a continuous production. Pellet presses are suitable for pelletising with or without small amounts of binding agents, and work with counter-pressure supplied by the biomass or the biochar (Quicker & Weber, 2016, pp. 156-158).

Regular wood pellets are treated with starch and water, if necessary, to acquire the desired mechanical strength and moisture content (see chapter 3.1). This brings up the question whether there are other additives, that can improve the quality and certain attributes required for practical applications. The technical complexity is one of the main influences on how economically efficient the fuel generation process is. Depending on, if there are more volatile matters, ashes or other side products emerging, an additional pyrolysis process might be required after pelletizing, as they might negatively influence the industrial application. There are two basic processes possible, depending on the starting material biochar or woody biomass, as shown in Figure 3-1. The second process contains a second pyrolytic process, which serves to enable heat-depending agglomeration, for example from lignin, and to lower VM.

The binding agent should be available in sufficient amounts at a reasonable price. The quality might be varied to find the balance between costs and efficiency. In one case there were the improvements and costs of commercial lignin preparation (Indulin AT), and technical lignin from a Kraft-process (black liquor) as a binder of wood pellets, compared. The commercial lignin led to better results in quality, but also increased the price per ton compared to black liquor. The cheaper material might lead to an insufficient quality though. *“Kraft black liquor pellets were soft and spongy and easily fell apart”* (Stevens & Gardner, 2010, p. 443).

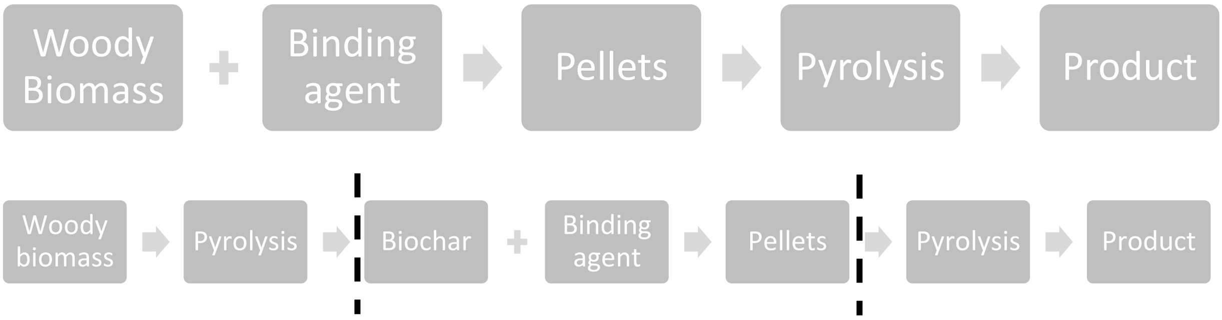


Figure 3-1: Principal processes, wood, and biochar as base material

The essential factors influencing the mechanical attributes of pellets are the quality of the biomass, the applied pressure and the binding agent. The latter also changes the final product regarding ash content, volatile matter and the calorific value. Thus, the sort and effects of the binder are important. Quicker & Weber states, that organic binders like molasses increase the mechanical strength directly after pelletising and take little influence on the calorific value and ash formation but are difficult to apply and homogenise with the biochar. The source further states, that inorganic binders like cement and alumina strengthen the product after the hardening process of the pellets, but they usually increase the ash content and influence the ash melting behaviour (Quicker & Weber, 2016, p. 158).

Research has shown good results with several types of binders: Starch is a common binder for wood pellets (Döring, 2013, p. 118). Heavy oil (Sharma AK, 2002) and hardeners such as several hydroxide compounds have been investigated as well (Hu et al., 2015). Lignin is a common binding agent for wood pellets (Stevens & Gardner, 2010). As an effort to improve the economical aspect regarding a possible industrial application for the metallurgical industry, cheaply available alternatives have been evaluated. These are mostly residues from other industrial processes such as alkaline lignin from manufacturing paper, and calcium hydroxide as hardener by hydration could develop mechanical strength (Mancera, 2011; Sun, 2011). As biochar is an already partly implemented resource for reduction processes in metallurgical processes (see chapter 2.5.2) and the binder and hardener might be taken from residue. This solution is suspected to be a feasible, economical, and physical improvement of regular biochar pellets.

Coal tar pitch is used as binding agent for carbon electrodes and for coal, biochar or coke breeze briquettes. Its characteristics such as softening point, specific gravity, and volatile matter make it an applicable binder for the metal industry (Benk & Coban, 2011)

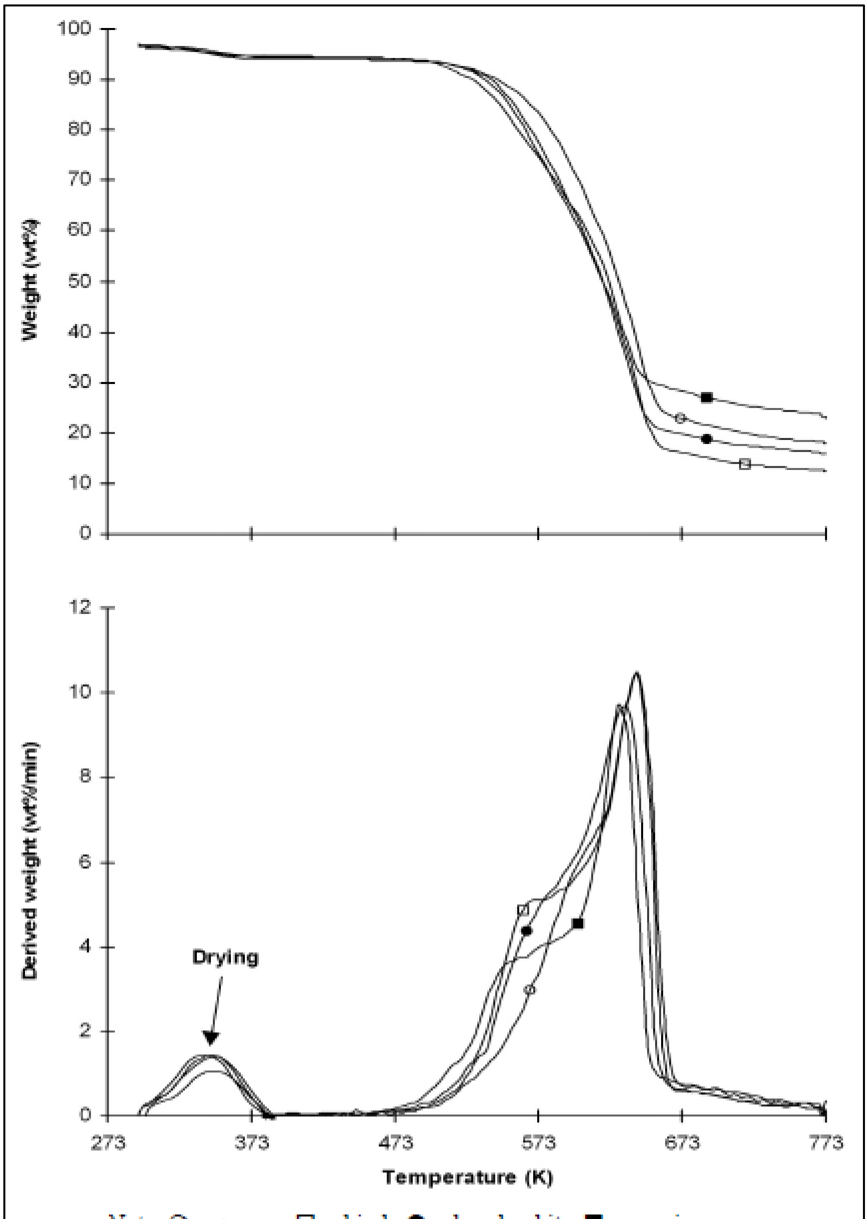
3.3 Pyrolysis

Pyrolysis is one of several thermal processes for transforming biomass in three different product streams: A fluid phase consisting of watery pyrolysis- or bio-oils/-tars, a solid phase in form of bio-matter like coke or char, and a gas phase consisting of condensable gasses. These then break down into non-condensable gases like CO, CO_2, H_2, and CH_4. Other side products are oxygen containing substances like acetic acid and methanol, which can be marketed for profits (Kaltschmitt et al., 2009, pp. 674, 686). The share ratio of all products depends on several factors, which lead to the related processes gasification, combustion, liquefaction, and torrefaction. The terms originate in the same field, but feature distinctive specialties like the fuel type, temperature, time, pressure, heating and reaction rate, and oxidation agents as well (Kaltschmitt et al., 2009, pp. 377). For this thesis relevant processes are described in the following, where the classical process of biochar production is elaborated.

After the drying process up to 150 °C, where mostly water evaporates, and the lignin-content softens up, the first conversion phase reaches up to 220 °C. Large amounts of water and traces of CO_2, acetic acid and formic acid evaporate in an endothermic reaction. Quicker & Weber states that between 120 °C and 220 °C fragments in the solid depolymerize and re-condensate (Quicker & Weber, 2016, p. 17). The pyrolytic decomposition begins during the second phase at up to 280 °C with larger amounts of CO_2, acetic and formic acid released. The third phase is the main degasification process with a strong exothermic reaction up to about 500 °C and an amount of 880 kJ/kg heat released. Inflammable gases like carbon monoxide (CO), methane (CH_4), formaldehyde (CH_3OH), acetic ($C_2H_4O_2$) and formic acid (CH_2O_2), methanol (CH_2O), hydrogen (H_2), and smoke containing small drops of condensable organic compounds (Kaltschmitt et al., 2009, p. 384). Quicker & Weber (2016) states that the temperature range for the main degasification process of a pyrolytic carbonization ends between 400 - 450 °C. Both Quicker and Kaltschmitt state that until 300 °C the fibrillary structure of the bio matter consists, and that above 400 °C the crystalline structures of graphite begin to form. In the fourth step above 500 °C most of the degasification process is finished. The endothermic reaction releases mostly carbon monoxide (CO) and hydrogen (H) (Quicker & Weber, 2016, p. 17 ff.).

3.3.1 Pyrolytic decomposition

Apart from the chemical compounds there is a specific thermal degradation process of the main biopolymers cellulose, hemicellulose, and lignin. Figure 3-2 shows the results of a thermogravimetric analysis of four wood species. Thermogravimetry is a common tool to assess the behaviour of biomass and its constituents during thermic processes. The temperature, mass loss, and mass rates are recorded during a time. As showed on the thermogram, a limited mass is lost is until 200 °C caused by evaporating free and bound water from the biomass. The devolatilisation process starts at about 200 °C with an increasing rate and reaches a shoulder point at roughly 300 °C, where hemicellulose decomposes and causes a temporary delay in increasing weight loss (Koppejan & van Loo, 2008, p. 8 ff.). According to Strezov et al. (2006), the decomposition of hemicellulose is occurring in the range from 190-320 °C. *“hemicellulose, as the least stable and highly reactive wood constituent, forms char yields of approximately 30 w.t. %”* (Strezov et al., 2006). Hard woods contain more hemicellulose, which is shown by a longer shoulder around 300 °C. The peak between 300-400 °C pictures the decomposition of



Note: ○ = spruce, □ = birch, ● = beech white, ■ = acacia.
5mg samples heated at a rate of 10°C/min.

Figure 3-2: Thermogravimetric analysis of four wood samples (Koppejan & van Loo, 2012) cellulose and the peak of absolute weight loss, before it falls rapidly until the process reaches 400 °C, where most of the volatiles are gone. According to Strezov et al. (2006), cellulose is the component with the highest decomposition rate due to thermal rupture of sugar units. Furthermore, it produces large amounts of VM and low char yields. Strezov et al. states a temperature for decomposing lignin from 320-450 °C, giving the highest char yields of between 45-50 w.t. %. According to Koppejan & van Loo (2012), Lignin decomposes throughout the whole process, peaking between 400 - 500 °C. Further, Figure 3-2 shows that birch has the lowest lignin and highest hemicellulose content. This results in the lowest char yield (Koppejan & van Loo, 2012, pp. 8-10). The deviating temperature zones for decomposing materials can be explained by using different materials and conditions.

4 OBJECTIVES

The thesis focusses on evaluating whether pelletising could be an interesting treatment in the production line of biochar for the metallurgical industry. Some materials, that have been proven to be useful binders in the past (e.g. starch and lignin as mentioned in Stevens & Gardner (2010) and Hu et al., (2015)), will be selected to investigate their behaviour during pelletising. Furthermore, whether the selected binding agents combined with base materials can improve quality and yield of a possible product and if it is feasible from an economic standpoint will be investigated. The product should reach physical strength like values of fossil coal and coke to be a feasible replacement (see chapter 2.5.2). The results may lead to more specific projects in the future at the Department of Engineering Sciences at the University of Agder in Grimstad.

4.1 Objective 1

The main objective is to investigate technically and financially feasible ways to pelletise biochar with binding agents for the use in metallurgical application. This proceeds in the form of an initial screening, on which future, extensive research work can be based upon. The assumptions made to estimate materials and compositions will be based on the thorough literature research of recent publications and essential books in chapters 2 and 3. Essential factors influencing the mechanical attributes of pellets are the quality of the biomass, the applied pressure and the binding agent. The quality was already proven suitable by recent publications (see chapter 2.5.2). Applicable pressures and binding agents will be investigated in this thesis. The practical part starts with a row of pre-experiments prior to the main pelletising run. The behaviour of base materials and binding agents will be studied in the pre-experiments, and the most promising compositions will be selected for the final run. An adequate process delivering reliable results needs to be developed.

For the main experiment, a base material, either wood or biochar, must be selected and prepared for pelletising. The experiments are designed to be statistically relevant. Biochar is produced by pyrolysis with adequate process variables like temperature, duration, and under exclusion of air. Binding agents need to be investigated for their attributes prior to the experiments, e.g. by thermogravimetric analysis. Lignin and starch require treatment like heating or thorough mixing to achieve the best binding properties. The literature research further reproduces how pellets can be made properly and with low failure rates. Previously determined parameters shall give a structured pelletising setup. By only changing one parameter at time, the results should give reliable information for further research.

4.2 Objective 2

In addition to the physical and technical aspect, the secondary objective is to investigate the economic feasibility of replacing fossil carbonaceous matter with biomass. Therefore, significant literature must be analysed, and more research about political and financial circumstances regarding pyrolysis, pelletising, and binding agents should be conducted. The current climate-plans of Norway and the European Union allowed estimates on how much biomass and reduction of CO_2-emissions will be supported in the future. As biochar is not as commonly pelletised as woody biomass, it requires investigating possible problems during the process. Observations from the experiments can give insight on possible problems emerging from the unusual materials. Possible impacts of biochar and binding agents on the standardised process of pelletising described in chapter 3.1 will be assessed in the economic consideration.

5 MATERIALS AND METHODS

After evaluating relevant literature and research papers, the following binders have been selected from a wide range of promising materials: Flash pyrolysis oil (FPO) (Biomass Technology Group BV, 2018), consumer grade starch, water, and lignin produced by Borregaard. This selection limited the volume of the experimental part to a feasible and efficient size. The materials cover both organic and inorganic components, and very specific, widely available and waste materials. This aims to gather a wide range of results, considering the grade of technical efficiency and the economical aspect as well. The laboratories at the University of Agder offered qualitative equipment to properly examine and pelletise the materials.

As preparation for the experimental part, a row of pre-experiments were conducted. They consisted of analysing the feedstock and binding agents to presume their behaviour during process conditions, e.g. high temperature, pressure, and pyrolysis. The feedstock of biochar and wood originated from industrial production and was delivered in various sizes. Therefore, the samples had to be conditioned, before the planned experiments could commence to provide a homogenous feedstock. The prepared biochar, wood and binding agents were analysed according to standard norms. Proximate (chapter 2.3.9), ultimate (chapter 2.3.11) and thermogravimetric analysis (chapter 2.3.10) gave all necessary information to determine the composition ratios for the main experiments.

The pre-experimental pelletising was conducted by a manual pellet press, because it simplified the process, as detailed measurements of pressure were not necessary for the elaboration of composition ratios. Pellets were produced in varying ways to investigate ideally a broad spectrum of possible outcomes.

The main experimental run was based on the previously made findings and additional information from the literature review. The TGA showed, how binding agents would behave at higher temperatures, and was therefore an important tool. It was conducted an analysed only for the materials, that have proven useful in the pre-experiments. This allowed to keep the process lean. The single unit hot pellet press was delivered in time to use for pelletising all compositions of the main experiment. It allowed to take detailed information about pressure levels and density and increased the value of the results.

The feasibility evaluation was based on findings of both experiments and literature review combined. It was a wide analysis to avoid the results from being too specific for one metallurgical facility, site or product.

6 PRE-EXPERIMENTS

A row of pre-experiments has been conducted to get familiar with the available equipment and laboratory conditions at UiA. The main goal was to identify promising combinations and ratios of biomasses, binders, and attributes, e.g. temperature and moisture content. This gave an insight on behavioural characteristics and lead to the final experimental setup, elaborated in chapter 7.

6.1 Experimental setup of the feedstock material analysis

Industrial grade charcoal (IC) produced in Poland and wood meal produced from customer grade wood pellets served as the first feedstock due to good availability. The charcoal consisted of different hardwoods species, specific to the forest and country of origin. The wood pellets were produced by Umas, Norway following CEN/TS 14961:2005 (ENplus, 2015; Ulf Mediaas AS, 2018). Both materials were milled in a hammer mill with a two-millimetre sieve, split three times as a statistical sample and sieved in a sieve tower. The sieve tower separates the sample in size ranges from < 0.125 - > 2 mm diameter, as shown in Figure 6-1. Only the smallest particles of < 0.125 mm have been used to determine the contents of moisture (MC), ash (AC), and volatile matter (VM) of a 1 g sample with proximate analysis (PA) in a muffle furnace shown in Figure 6-2. The VM has been tested according to ISO 562 and ASTM D 3175 standards (900 °C and 950 °C respectively), with a relative difference of about 1 %.

Figure 6-1: Left: Hammer mill with a 2 mm sieve. Right: Sieve analysis by sizes, (Gerrit Surup)

Furthermore, an ultimate analysis (UA), also known as elemental analysis, was conducted. The machine malfunctioned shortly after the experimental work began and analyses could not commence. For the pellet materials, PA, bulk density, durability, and fines were measured. For measuring AC, the material has been combusted in a crucible in a muffle furnace following ISO 18122 (ISO 18122, 2015).

For further experimental preparation, industrial grade wood pellets for heating stoves were analysed for bulk density, durability, and fines. For the pellets, the same preparation was applied as for the industrial biochar by milling and sieving.

Lignin was chosen due to its reputation as a binding agent for wood pellets (Borregaard LignoTech, 2018). Two lignin types were acquired: Lignobond DD (LB) and PellTech (PT) from Borregard, Sarpsborg, Norway. They were analysed in UA and used in different compositions, following results of previous publications (Ahn et al., 2014; Hu et al., 2015).

Figure 6-2: Left: Drying chamber (MC). Right: Muffle furnace (Henrik Kofoed Nielsen)

6.2 Experimental setup of the pellet screening

The pre-experimental pellets have been pelletised with a manual pellet press, which was designed for a bomb calorimeter, as shown in Figure 6-3. The die had a diameter of 14 mm. Pelletising material consisted of filling a sample in the pellet die and compressing by screwing the rod downwards. The applied pressure was not measurable. All compositions were produced three times to be statistically relevant. Several compositions of wood meal, starch, and water were pelletised. The products were treated at temperature levels between 300 – 800 °C. to investigate the behaviour of pelletised wood in a thermal process. Particle sizes of the industrial biochar (IC) have been separated in the sieve tower according to the following ranges: < 0.125 mm, 0.125 mm - 0.250 mm, 0.250 mm - 0.5 mm, 0.5 mm - 1 mm and < 2 mm. They have been pelletised without any binding agents first to illustrate that binding agents are necessary.


Figure 6-3: Manual pellet press (from bomb calorimetry)

In the next step, biochar meal was pelletised with water as binding agent in the steps 30, 50, 70, and 90 wt. % of total weight. Three samples of ~ 2 g each have been produced for each composition. The water was mixed with the help of a magnetic stirrer.

Starch was pelletised with IC and wood meal. All materials were mixed for five and fifteen minutes at room temperature and on a magnetic heating mixer at 80 °C. The wood meal was mixed with a solution of five percent starch and 20 wt. % water of total weight, based on industrial standards (Döring, 2013). For the IC, water percentages were 10, 20, and 30 wt. %. Experimental pyrolysis was conducted at 300/500 °C for wood meal and 500/800 °C for IC.

As coal tar pitch has already proven useful as a binding agent (chapter 3.2), it was presumed to deliver good results. A feedstock of flash pyrolysis oil (FPO) as available and chosen because of its similar characteristics. To evaluate the effects of FPO)as binding agent, a fixed amount of 40 wt. % was pelletised with IC. Four sets were produced and subject to following thermal treatments: Drying at 105 °C and pyrolysis at 500, 800, and 900 °C. Five weight percent of starch were added to a fifth set of pellets as a test.

A second pelletising cycle was carried out after the lignin was acquired from BorreGaard. Water and a magnetic heating stirrer were used to dissolve the lignin at 80 °C. Two solutions with parameters as shown in Table 6-1 were produced. The table contains the next compositions of LB, FPO and IC.

Table 6-1: Pelletising compositions with LignoBond (LB), flash pyrolysis oil (FPO), water, and industrial biochar (IC)

Composition LignoBond 1			Composition LignoBond 2		
Ind. biochar	[wt. %] of total weight	60	Ind. biochar	[wt. %] of total weight	50
H_2O		20	H_2O		25
LB		20	LB		30
Composition FPO 1			Composition FPO 2		
Ind. biochar	[wt. %] of total weight	65	Ind. biochar	[wt. %] of total weight	70
FPO		30	FPO		20
LB		5	LB		10
Composition FPO 3					
Ind. biochar	[wt. %] of total weight	50			
FPO		20			
LB		15			
H_2O		15			

Eventual durability tests were, depending on the available number of pellets, conducted in the machine shown in Figure 6-4 which can follow EN.

Figure 6-4: Durability test according to EN

6.3 Results of pre-experiments

Observations made during pelletising are described and interpreted in the following. It is notable that discoveries made during the process led to some variations. All materials were handled in the same manner, e.g. the binding agents starch and LB required to be dissolved in a fluid first to improve the effects. When dissolved in water, both binders formed a glue-like fluid. Drying and hardening were important factors. Especially starch-water mixes needed to be processed quick, as the moisture evaporates especially at higher temperatures. Thus, the moisture was exemplarily calculated before and measured after the pelletising for biochar and water (see Table 6-5). All compositions were saturated around 40 - 50 wt. % of total moisture. This led to wetting of the pelletising equipment from water or FPO emerging due to pressure. Both materials caused lubrication and easier extraction of pellets. If FPO dries, it led to clogged tools and required cleaning with acetone. This is an important factor, if FPO is considered for industrial application.

6.3.1 Discussion of the material examination

Table 6-3 shows the results of UA and PA of the base materials industrial biochar and wood pellet meal. As expected, the measured values were within the limits given by the producer. Results of the durability test of the wood pellets are shown in Table 6-2 and within standard values (ENplus, 2015). The wood pellets disintegrated completely after thermal processing and would therefore require another pelletising to reach relevance regarding mechanical stability. They are produced with starch and only the non-pyrolysed wood meal was used for pelletising. The biochar showed a high carbon content and low AC.

Table 6-2: Results industrial grade pellets

Fines	[%]	0.2
Abrasion	[%]	98.89
Bulk density	[kg/m^3]	642

Table 6-3: Results of proximate and ultimate analysis of the base materials, industrial biochar and industrial-grade wood pellet, both as received

Proximate Analysis	Moisture Content MC in [wt.$_{ac}$ %]	Volatile Matter VM in [wt.$_{ac}$ %]	Fixed Carbon FC in [wt.$_{ac}$ %]	Ash Content AC in [wt.$_{ac}$ %]
Biochar	2.26	11.90	83.93	1.8
Wood pellet	4.84	79.84	15	0.32
Wood pellet, pyrolysed			97.09	1
Ultimate Analysis	**Carbon in [wt.$_{ac}$ %]**	**Hydrogen in [wt.$_{ac}$ %]**	**Nitrogen in [wt.$_{ac}$ %]**	**Oxygen in [wt.$_{ac}$ %]**
Biochar	85.91	2.40	1.26	8.58

Both lignin types were analysed with PA and UA, as shown in Table 6-4. LB contains less ash, but more VM than PT. As a secondary thermal treatment was planned after pelletising, LB was chosen as the binding agent for the main experiment, because the ash residue was considered critical. LB also contains more carbon, suggesting an increased reactivity.

LB and starch showed excellent results when solved in water, and LB when solved in FPO, at a temperature of 80 °C. The temperature was chosen to avoid evaporating water, while an increased solution rate was already noticeable from 50 °C. Depending on the mixing ratio, the materials formed a sticky fluid with low viscosity. At a mixing ratio of 30 wt. % binding agents and less than 70 wt. % of the total weight or more, the compound started to harden and was hard to handle.

Table 6-4: Results of proximate and ultimate analysis for lignin types LignoBond and PellTech (Borregaard)

LignoBond Averages out of three samples			
		Proximate	Ultimate
MC	[wt. $\%_{dry}$]	6.44	
VM	[wt. $\%_{dry}$]	74.02	
FC	[wt. $\%_{dry}$]	0	
Ash	[wt. $\%_{dry}$]	22.44	
C	[wt. $\%_{dry}$]		39.89
H_2	[wt. $\%_{dry}$]		4.85
O_2	[wt. $\%_{dry}$]		26.24

PellTech Averages out of three samples			
		Proximate	Ultimate
MC	[wt. $\%_{dry}$]	5.89	
VM	[wt. $\%_{dry}$]	34.26	
FC	[wt. $\%_{dry}$]	21.06	
Ash	[wt. $\%_{dry}$]	38.79	
C	[wt. $\%_{dry}$]		33.98
H_2	[wt. $\%_{dry}$]		3.97
O_2	[wt. $\%_{dry}$]		17.37

6.3.2 Discussion Pelletising

All pellets from wood meal, starch, and water were instable and became brittle from slight pressure or during drying at ambient atmosphere, as shown in Figure 6-5. Furthermore, the pellets disintegrated during thermal treatment at 300/500 °C. The pyrolysed pellets offered the highest amount of fixed carbon. However, the value for AC exceeded the requirements by European norm of 1 % (ENplus, 2015). The thermal process destroys structures within the wood from cellulose, which stabilised the structure. The test with wood meal as basis was discontinued due to the high content of VM and moisture, leading to a loss in stability at increased temperatures. Thus, the assumption in chapter 3.2 was verified. Wood pellets do not offer mechanical stability during thermal treatment, as the volatiles emerge from the material and influence the stability.

Figure 6-5: Unstable wood pellets, 20-30 $\%_{dry}$ moisture content

Different particle sizes of IC led to acceptable pellets, which are shown in Appendix 3. The results show that the pellet quality and abrasive resistance decrease with increasing particle size. However, the mixed, unsorted particle size led to similar results as the smallest particle size. This can be explained by the effect from smaller particle sizes filling gaps between larger ones (see agglomeration, chapter 3.2). Thus, all further experiments were conducted with a mix of particle sizes regarding the economical aspect, as it saves the process of sieving the biochar meal. The pellets from pure IC broke partly and showed a lot abrasion during extraction and handling. The reason is the lack of binding agent and a very brittle material, which is hard to agglomerate just by plastic deformation. Therefore, water or other binding agents are necessary to lubricate the pellets during extraction from the press and to increase the stability.

The pellets from IC and water supported this hypothesis. At 90 wt. % of the mix, water was expelled during the pelletising. It was assumed that the material mix reached a form of saturation. Increasing the MC was therefore not necessary, and pellet size and quality seemed to be depending on the MC. Samples with more than 25 wt. $\%_{wb}$ MC (after pelletising) led to condensation in the sealed storing container. The samples have been dried and weighted for the final MC, and to observe their behaviour during drying Table 6-5 shows the results.

Table 6-5: Biochar pellets with water as binding agent (MC of biochar: 2 wt. $\%_{ar}$)

Water in [%] of total weight	MC before pelletising in [%]	MC after pelletising in [%]
30	24	27
50	34	30
70	42	42
90	48	43

It seemed that water was expelled during pelletising, when the MC before exceeds 40 %. Furthermore, expulsion of the pellet was related to the quality and length of the pellet. The pre-experiment with water as the sole binding agent was concluded after this process, as the pellets failed to reach satisfactory stability after storing and drying. The overall abrasive resistance after storing and drying was unsatisfactory as well. Appendix 4 shows the qualitative results.

Figure 6-6 shows pellets with IC, starch, and water. The visual results of pelletising with binding agents indicate that a proper mixing process is essential for qualitative results. The figure shows that the starch had to be dissolved properly in water prior to pelletising. Thus, the mixture was prepared on a magnetic stirrer with increased temperature at 80 °C. Further tests at 10/20/30 wt. $\%_{db}$ were conducted, and the results are shown in Appendix 5. All pellets showed small fractions on the side, and low abrasion from handling. Pellets pyrolysed at 500/800 °C were stable but showed high abrasion from a durability test. A TGA of starch displayed that complete combustion is reached around 550 °C. This signalised that starch is not suitable for high temperature treatments, as it would become instable too early. The brittle structure after a resting period can be explained by the surplus moisture evaporating at ambient conditions, which could be expected in an industrial production as well. Resting at 18 °C room temperature and 20-30 % MC_{wb} displayed that the starch's binding ability was not sufficient for biochar. Pellets broke from slight pressure. At increased moisture levels, the pellets became more stable, but were easily deformable. The increased stability is a result from water functioning as lubricant while extracting the pellet from the pellet die.

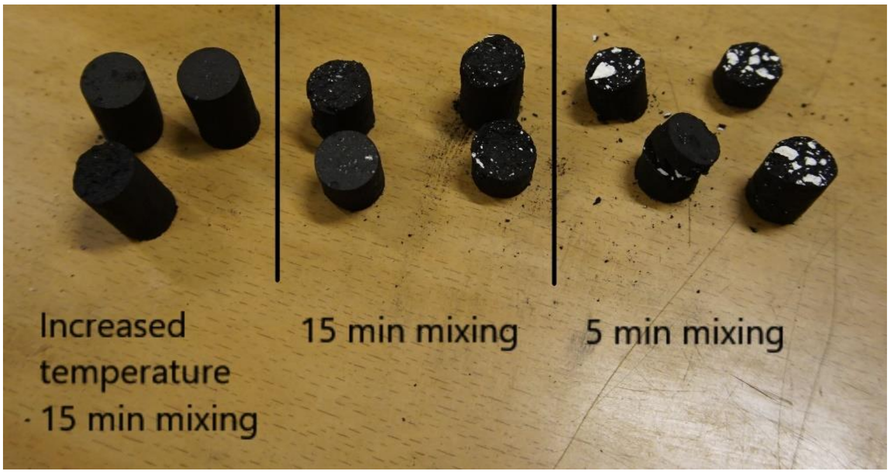


Figure 6-6: Pelletising industrial biochar - meal, water and starch. Decreasing mixing temperature and duration

Pellets from IC and FPO gave good results throughout the experiment, as shown in Appendix 5. At 40 wt. $\%_{wb}$ FPO, a continuous excess showed during the pelletising. This indicates, that the maximum amount of oil lies slightly below that level to avoid clogging from old oil residues in industrial pelletisers. The results of different thermal treatments are shown in Table 6-6. They visualise how the pellets improved from thermal treatment regarding the abrasion until 800 °C and give a good basis for the main experiment in chapter 7. The tested combination of IC, FPO and starch led to pellets with higher abrasive properties as the combination of IC and FPO and was therefore not further investigated.

For pelletising LB, the same mixing durations and temperatures as for starch and biochar were applied. The final composition was stirred for fifteen minutes to ensure a homogenous mix. The results are shown in Appendix 5. The composition of 60 wt. %$_{wb}$ IC, 20 wt. %$_{wb}$ LB and 20 wt. % water gave good results. Almost no abrasion or instability was detectable. The mix with 70 wt. %$_{wb}$ IC gave similar results and led to the conclusion that lignin is a promising binding agent for the main experimental setup. The lignin solved in water and formed an excellent glue with water and a temperature of 80 °C.

The last composition of IC, LB, FPO, and water led to varying results. The pellets are shown in Appendix 6. They visualise how both groups with 10/15 wt. %$_{wb}$ became brittle, with parts breaking off and abrasion. The best result was achieved with 5 wt. %$_{wb}$ LB, dissolved in 30 wt. %$_{wb}$ FPO at 80 °C and pelletised with 65 wt. %$_{wb}$ IC. The result suggests that the lignin content can be lowered in future experiments.

Table 6-6: IC with 40 wt. %wet FPO, different thermal treatment

Thermal treatment	Process temperature	Weight loss from durability test
	[°C]	[wt. %$_{dry}$]
Drying	105	< 5
Pyrolysis	500	< 2
Pyrolysis	800	< 2
Pyrolysis	900	< 5

7 EXPERIMENTAL SETUP

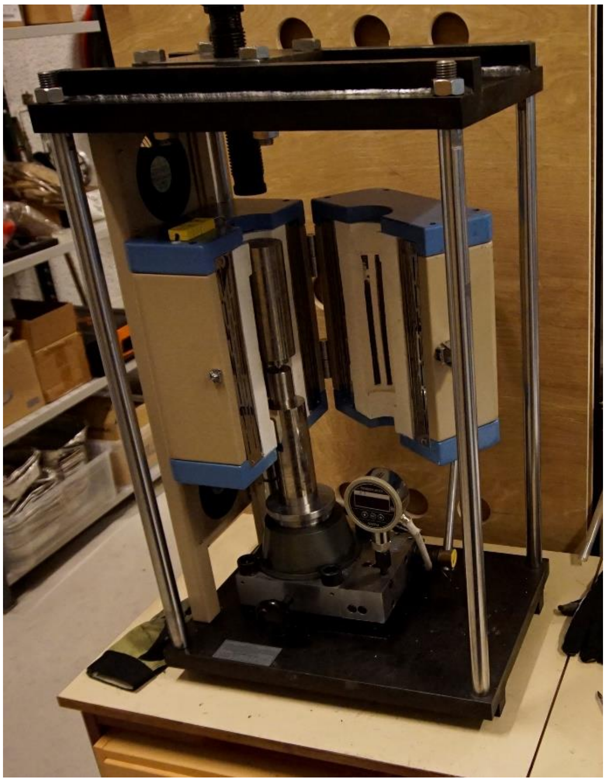


Figure 7-1: Single unit hot pellet press at UiA, by MTI corp. USA

The final compositions were based on the findings from the pre-experiments and were limited according to the best results to achieve a relevant and structured process. For the carbonaceous feedstock, several materials were analysed and compared. The best result was chosen for the pelletising. It was chipped, milled through the hammermill shown in Figure 6-1, thus sieved to particle width of less than two millimetres, and pyrolysed at 800 °C. No further sieving was applied based on the findings before that a mix of particle sizes below two millimetres had similar binding abilities as biochar sieved to < 125 mm. Two available lignin types, Lignobond DD and PellTech (further referred to as LB and PT), and flash-pyrolysis-oil from BTG Enschede (FPO) and water served as binding agents. The focus was on LB and FPO due to the lignin analysis in Table 6-4 and TGA (shown in chapter 8).

While the depolymerisation of biochar during a pyrolytic process was already elaborated in chapter 3.3, the behaviour of binding agents is uncertain. With a thermogravimetric analyser (TGA, Mettler-Toledo TGA/DSC) the behaviour of a combustible can be analysed in relation to its weight over time during a thermal process. The two most promising binding agents, FPO and LB, were analysed. The heating cycle began with holding the temperature for five minutes at 30 °C, then heating up to 800 °C at 10 K/min. After 90 min, air is guided into the system for complete combustion. The process is ended after 105 min. 50 ml/min of argon was used to purge the system during the pyrolysis and 50 ml/min air in the end to combust the sample. Three statistic samples of FPO and LB were prepared by filling between 5 – 15 mg each in a crucible.

The manual pellet press used in the previous experiments was not further required. It was replaced by a laboratory-grade single unit hot pellet press by MTI corporation, USA, as shown in Figure 7-1. The figure does not show the included control unit, which controls the heating program. It can conduct complex heating cycles up to 1000 °C with predetermined time-temperature curves. Though, this function was not used in the experiments, as the sufficient temperature for optimal binding abilities of the materials lies below 100 °C, as determined in the pre-experiments. The composition was heated with a magnetic heating stirrer instead. The press can produce pressure of 24 tons between the cylinders. The metal-die is designed for pressures of up to three tons and 400 °C and has an inner diameter of quarter of an inch due to the imperial system used in the USA. This diameter came closest to the common pellet diameter of six millimetres for commercial pellets (ENplus, 2015). The pellet-materials were composed before insertion into the pellet die.

Lignin was then added to water on a magnetic stirrer plate until it reached the required temperatures ensuring properly dissolved binding agents around 80 °C. The dry materials (biochar) were then added and the mix was stirred for fifteen minutes to ensure a homogenous blend. For each pellet, about two grams were given in the steel die and pelletised. Each composition contains a certain amount of biochar and water.

The experimental runs were divided into seven compositions based on results of the pre-experiments. The exact compositions are shown in Table 7-1. All compositions were produced three times to serve as statistic example.

Table 7-1: Compositions in % of total weight of pyrolysed spruce (800 °C), pyrolysis oil (FPO), LignoBond lignin (LB), Pelltech lignin (PT) and water, [wt. $\%_{wb}$]

Composition 1		Composition 2		Composition 3		Composition 4	
Spruce	50	Spruce	55	Spruce	55	Spruce	55
FPO	30	FPO	20	FPO	15	FPO	15
H_2O	20	H_2O	0.25	H_2O	25	H_2O	25
LB	0	LB	0	LB	5	PT	5

Composition 5		Composition 6		Composition 7	
Spruce	60	Spruce	65	Spruce	67
FPO	30	FPO	28	FPO	28
H_2O	10	H_2O	7	H_2O	5
LB	0	LB	0	LB	0

8 RESULTS OF THE MAIN EXPERIMENTS

Norway spruce was chosen as the carbonaceous feedstock. Table 8-1 shows the results of literature research and proximate analysis, comparing different materials, and showing the merits of Norway spruce.

Table 8-1: Comparison of Norway spruce, fossil coke and coal, and pyrolysed spruce

	Unit	Test standard	Norway spruce	Oak	Coke (Babich et. al)	Fossil coal (Babich et. al)	Norway Spruce pyrol. (800 °C)
MC	$\%_{ar}$		8.6	7.6	4.94	2.30	0/1.95 (amb)
Proximate analysis							
AC	[wt. $\%_{dry}$]	EN 14775:2009	0.8	1.6	9.63	10.27	1.48
VM	[wt. $\%_{dry}$]	EN 15148:2009	80.6	82.6	3.00	8.60	4.41
Ultimate analysis							
Carbon	[wt. $\%_{dry}$]	EN 15104:2011	53.2	50.6	88.00	82.80	94.11
Hydrogen	[wt. $\%_{dry}$]	15104:2011	6.1	6.1	0.35	2.31	0.8
Oxygen	[wt. $\%_{dry}$]	EN 14918:2010	39.6	41.4	0.50	2.31	-
Nitrogen	[wt. $\%_{dry}$]	EN 15104:2011	0.11	0.21	0.40	0.90	-
Sulphur	[wt. $\%_{dry}$]	SS 187177:1991	0.06	0.02	0.60	0.42	-

Figure 8-1 shows the thermogravimetric weight loss of Lignobond particle samples at various heating rates. As in the case of biomass pyrolysis, the initial decrease in weight was due to evaporating water until 105 °C. The second weight loss was due to devolatilisation (see chapter 3.3.1). The final weights were near 40 wt. % before combustion and near 16 wt. % after combustion. The values give the fixed carbon and the ash content in percent of the weight respectively. Lignin is the component of wood with the highest decomposition temperatures and a flat devolatilisation curve (Koppejan & van Loo, 2008, p. 8), which can be seen in the results. The DTG curve serves to illustrate the weight loss over time, pointing out the peaks relative to the temperature.

Properties of the FPO are shown in Table 8-2. The values were adapted from the manufacturers website (Biomass Technology Group BV, 2018). The moisture content also suggests that water might not be necessary for a good agglomeration, as binding agents dissolve in the FPO. The carbon content is higher than LB, suggesting good reacting properties.

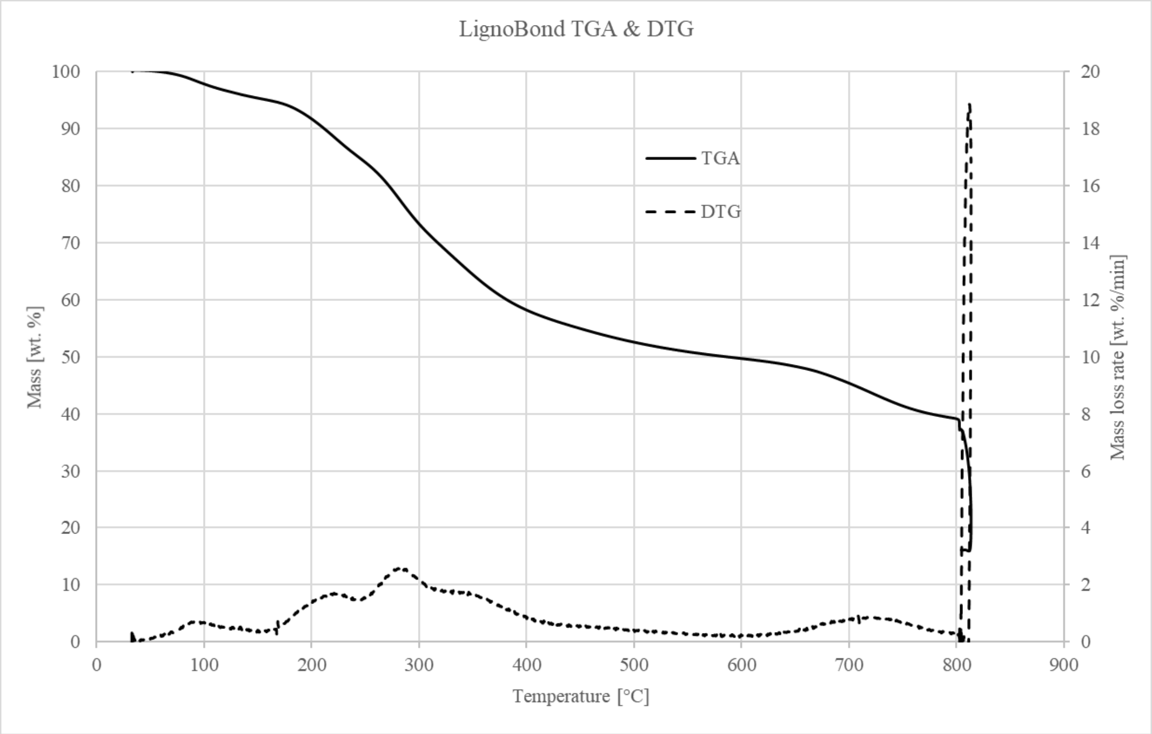


Figure 8-1: Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of pure LignoBond powder, pyrolysis at 800 °C, then combustion

TGA and DTG profiles of the pyrolysis oil are shown in Figure 8-2. From the figure, the weight loss increases rapidly between 80 – 300 °C. This is caused by volatile hydrocarbons forming during the process. 70 % of the total weight loss was in this range. During higher temperature areas, the weight loss was steadily decreasing until 800 °C were reached. This might be caused by the formation of char during this stage, since the char could not be evaporated (HU et al., 2015, p. 9).

Table 8-2: Flash pyrolysis oil properties, from (Biomass Technology Group BV, 2018)

Property	Unit	Value
Temperature level	[°C]	450 – 600
C	[wt. %]	46
H	[wt. %]	7
N	[wt. %]	< 0.01
O (balance)	[wt. %]	47
MC	[wt. %]	25
AC	[wt. %]	0.02
Solid matter	[wt. %]	0.04
Density	[kg/m³]	1,170
LHV	[MJ/kg]	16

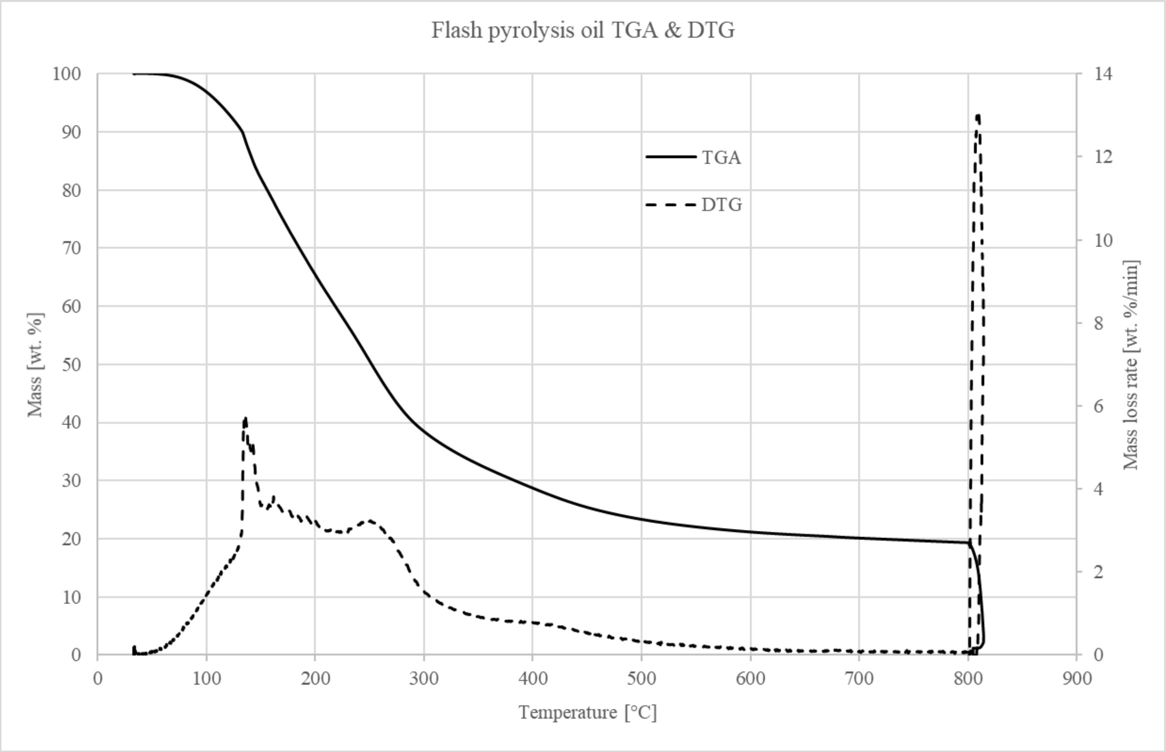


Figure 8-2: Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of pure flash pyrolysis oil (BTG), pyrolysis at 800 °C, then combustion

8.1 Results of the feedstock composition

The final water content of the compound was determined before the experiment by equation (22).

$$MC_{abs.} = \frac{0.02 \cdot Biochar + 0.25 \cdot Oil_{BTG} + 0.05 \cdot Lignin + Water}{Biochar + Oil_{BTG} + Lignin + Water} \tag{22}$$

The factors for each component were derived from the MC, which was determined from the producers' information sheet for FPO and lignin, and by TGA for Biochar. The MC of biochar is explained by moisture intake after pelletising due to storage in ambient atmosphere. This leads to the MC shown in Table 8-3.

Table 8-3: MC of all compositions before pelletising

Composition	1	2	3	4	5	6	7
MC before [wt. $\%_{wb}$]	30	30	33	33	20	15	13

The density of the pellets is determined by equation (23):

$$\rho_{Pellet} = \frac{m_{Pellet}}{\pi \cdot r_{Die}{}^{2} \cdot h_{Pellet}} \; with \; r_{Die} = \frac{0.25''}{2} = 0.3175 \, mm \tag{23}$$

The pelletising pressure covered a range from 105-520 MPa on the reading gauge. This pressure had to be transformed into the actual pressure applied on the pellet with equation (24):

$$p_{Die} = \frac{f \cdot g \cdot 10}{\pi \cdot r_{Die}{}^{2}} \cdot p_{gauge} \tag{24}$$

f	factor 0.6 to determine force (ton) applied on hydraulic cylinder, from operation manual
g	standard gravity, 9.81 $\frac{m}{s^2}$
r_{Die}	$\frac{0.25''}{2} = 0.3175 \, mm$
$p_{machine}$	pressure shown on gauge

Pressure levels of the pelletising process are shown in Table 8-4.

Table 8-4: Pressure levels shown on gauge and applied on pellet

p_{gauge}	[MPa]	0.5	0.75	1	1.25	1.5	1.75	2	2.5	2.75
p_{Die}	[MPa]	105	155	210	260	315	365	415	472	520

Water added to the pelletising compositions was mainly required to dissolve the binding agent lignin and to ensure efficient homologating of all components. The FPO was especially sticky and likely to form ball-shaped clumps of oil-biochar mix. Furthermore, the increased temperature during mixing led to evaporating water prior to pelletising and needed to be considered. Both lignin types proved to form a strong adhesive solution with heat, water, and FPO. Pressure levels below 100 MPa resulted in unreliable results. Many pellets were not stable enough to be extracted from the pellet die, as the pellets were sticking to the metal upon extraction. The exact pressure levels applied on the pellets are shown in Table 8-4. The experiments covered a range of pressures to investigate correlations between density and pressure.

8.2 Results of pelletising

A thorough table of all test samples is in Appendix 7 and Appendix 8. The observations are elaborated in the following. The measurements were taken after 30 min of resting outside of the pellet press, at laboratory conditions of 18 °C and 20-30 % humidity to ensure the same state of drying and evaporating surplus moisture.

Composition 1: The highest pellet density of 972 kg/m³ was achieved at 365 MPa, with another high point of 925 kg/m³ at 210 MPa. Pellet length and weight correlated, which was expected because of the increased pressure. Most pellets produced with less than 105 MPa fell apart or were instable. This was due to the high content of fluids of over 50 % prior to pelletising. Pressure levels over 105 MPa produced stable pellets, but small cracks and fractions were detected. The density was steadily increasing until 365 MPa. Beyond that point, the value was decreasing again, and pellets showed a spongy behaviour after extracting them from the pellet die. The best results were achieved between 210 260 MPa, where almost no cracks were detectable.

Composition 2: Like composition 1, pellets produced below 105 MPa were instable and tricky to handle without squeezing them. Cracks were detected on all pressure levels except between 260 – 315 MPa, which delivered the best results. All pellets showed spongy behaviour. The density of 909 kg/m³ peaked at 415 MPa, with a second highpoint of 879 kg/m³ at 210 MPa.

Composition 1 and 2 gave slushy results with expelling fluids. Thus, composition 5 - 7 focussed on decreasing the moisture level to gain FC and lower the MC. Before, both lignin types were added in compositions 3 and 4.

Composition 3: Like in the pre-experiments, the pellets with 5 % of LB showed excellent results regarding stability and abrasive resistance. They were stable and led to an increase of the maximum pressure to broaden the results. Density of 868 kg/m³ peaked at 472 MPa, with another highpoint of 861 kg/m³ at 260 MPa. Some pellets at various pressures showed little fractures after the resting period.

Composition 4: PellTech had a comparable binding effect. Pellets seemed to show slightly increased cracks compared to Lignobond. Both lignin types led to good results. LignoBond seemed to give slightly increased stability over PellTech. The highest density of 1,128 kg/m³ was reached at 315 MPa, followed by 1,122 kg/m³ at 210 MPa.

Composition 5: The fifth composition was still producing great amounts of excessive fluids. The pellets were like composition two, but a part water was replaced with FPO. The highest density of 1,126 kg/m³ was reached at 415 MPa, and a second peak was again found with 1,114 kg/m³ at 210 MPa. The composition led to good visual results throughout the pressure band.

Composition 6: Fluids were emerging at pressure levels above 300 MPa, which indicates that the saturation was reached. All pellets showed good qualitative results. The density peaked at 260 MPa and a value of 0,972 kg/m³.

Composition 7: The last experimental composition reached a MC, where homologating the mixture took longer than expected, as the previously applied mixing procedure did not spread the fluid over the biochar. It was assumed that the limits of the sample preparation technique were reached. The density peaked at 1,004 kg/m³ and 315 MPa.

Table 8-5: Durability test compositions 5 - 7

Composition no.	5	6	7
Abrasion of total weight [%]	9	7	broke

The first two compositions validated the previously determined approximate saturation point of oil in a coal mix. The third and fourth compositions tested both lignin types to validate the improved mechanical strength. Composition 5 - 7 served to investigate the overall minimum MC by reducing the water content further. After a drying process of 24 hrs at 105 °C, the pellets of composition 5 – 7 showed excellent stability. Results of a first durability test are shown in Table 8-5, indicating good results as well, whereas the produced number of pellets was not sufficient to fulfil the EN standard.

Overall, observations show good results for a pressure between 200 – 250 MPa. Figure 8-3 on the next page shows the measured densities of all pellet compositions and the pressure applied. It shows that even though the density of most compositions peaked at pressure levels on the die of over 300 MPa, similar densities were already achieved from 200 MPa on. The highest density was achieved with a mix of IC, low water content added and 30 wt. % FPO. The effect of high pressures is spongy behaviour of the material, as it expands after being extracted from the pellet die. Therefore, it was decided to set a resting time of thirty minutes after extraction, before measurements were taken. In the mid regions however, most pellets held their initial sizes.

The water content influenced the mixing process, pelletising and fluid excesses exiting the pelleting die. Low water contents, if not balanced out by FPO, led to problems reaching a homogenous mix. The water was measured and added by titration, giving single drops that take some effort to mix properly. Lignin required to be solved in water or FPO beforehand. Good mixing behaviour was reached at a total content of fluids at 15 wt. %. or higher. Below 10 wt. % MC, the pellets were poorly lubricated, and friction caused breaking during extraction.

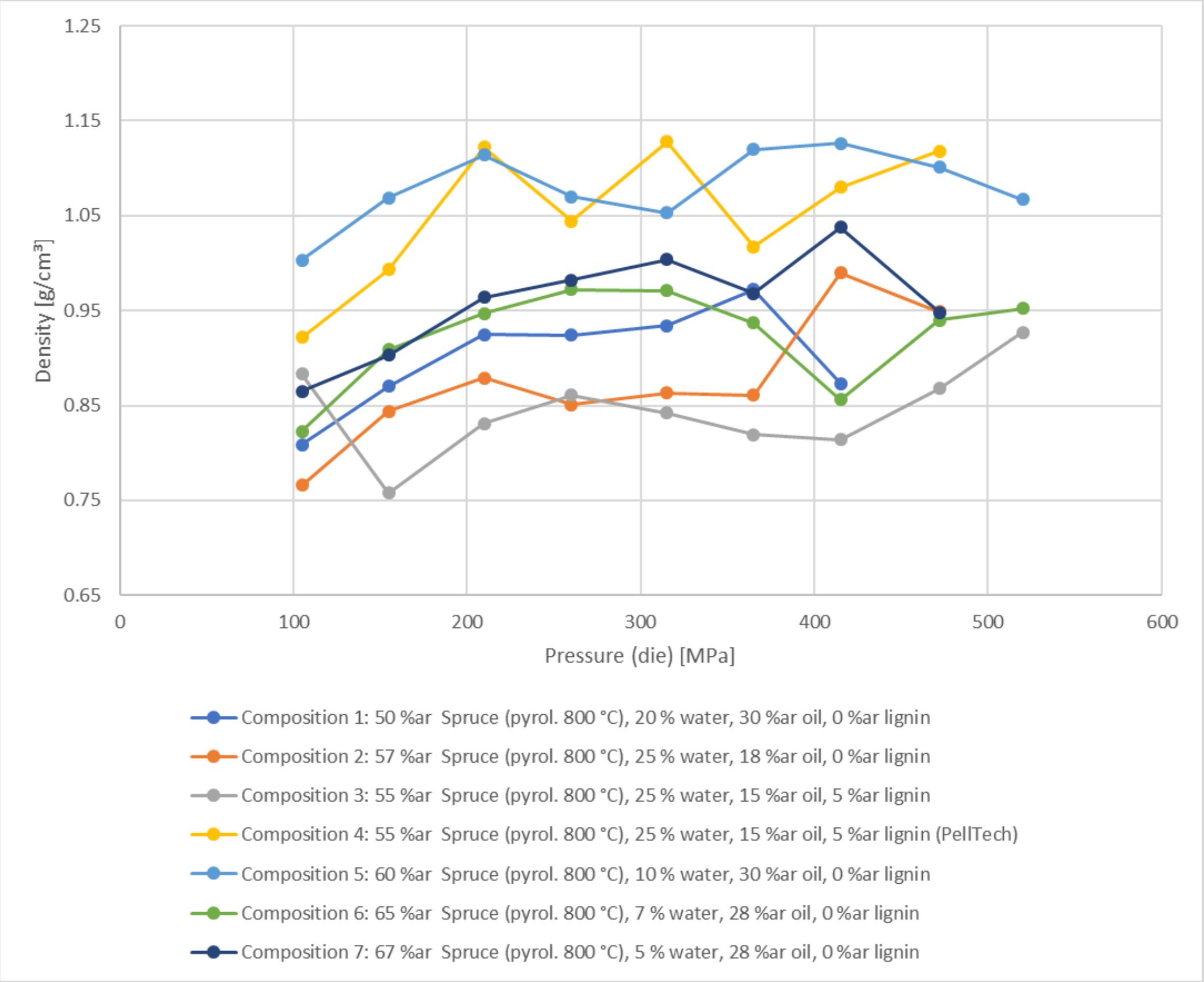


Figure 8-3: Pellet densities in (g/cm³) over pressure on the die (MPa), varying compositions

9 ECONOMIC FEASIBILITY EVALUATION

In the climate goals for 2020 by the Climate and Pollution Agency of Norway, a total of 160 potential emission reducing measures and their costs were identified. The calculated socio-economic costs per ton of CO_2 equivalents reduced range from economically profitable to very high. These measures include changing from fossil consumables and fuel to biochar and biomass. In numbers, the agency estimates a total of 4.3 million tons of CO_2 equivalents with costs up to about NOK 15 billion or 1.56 billion € (April 2018) by the year 2020. That are about 7 % of the estimated 59 million tons of emitted CO_2 in Norway in 2020 and make up to NOK 3,000 per ton CO_2 (Climate and Pollution Agency, 2010, p. 11 ff.)

To achieve these goals, the Norwegian government has elaborated examples of how the climate goals should be achieved. The country is known for being one of Europe’s pioneers in renewable energy and electromobility. As in 2016, electric vehicles made up 40 % of newly registered vehicles, and 98 % of the country’s domestic used electricity comes from hydropower (Hockenos, 2017). This leads to assume that measures are likely to be introduced for the countries second highest source of CO_2 emissions after transportation, as well (Climate and Pollution Agency, 2010, p. 12). One suggestion is implementing a general CO_2 tax to stimulate investment in climate measures and moving emission intensive industry, increasing the price for solid fuels (Climate and Pollution Agency, 2010, p. 21). The publication further determines a requirement of up to 6 TWh of timber to produce biochar for the metal industry for 2020.

For metallurgical applications, several publications have investigated the feasibility and economical effects of substituting conventional materials. Whether specific cost analyses are worthwhile is questionable, because the transport costs make a major part in overall expenses and are individual for each site. They would require an explicit analysis for each site. One of the critical issues likely to affect the use of biochar in industry is the availability of biomasses. Norgate analysed the plantation area required for biomass production versus the steel production rate by BOF (chapter 2.5.1), which makes 74 % of the worlds steel production (World Coal Association, 2018). Norgate estimates 5.2 $t_{biomass}/t_{biochar}$ for given biomass and biochar retort yields, and an overall annual steel production of 990 Mt via this route. Figure 9-1 shows the plantation area required for biochar production from timber for several yield rates. For a 47 % substitution rate by biochar and an average yield for well managed timber plantations of 15 t/ha/a, a plantation area of 50 Mha is required. It is further elaborated, that from the 3,900 Mha forest area globally about seven percent (264 Mha) are productive forest

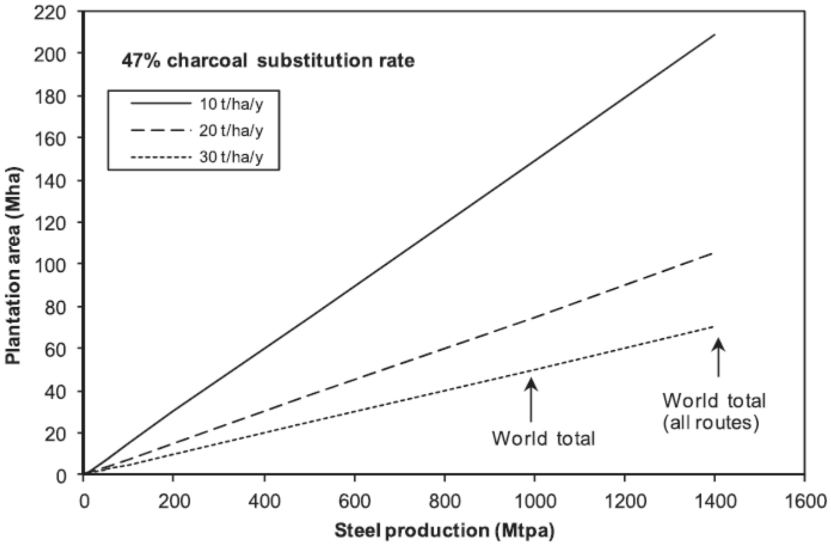


Figure 9-1: Plantation area for biochar production, 47 % substitution, different yield rates (Norgate et al., 2012)

plantations, which exceeds the requirements for biochar, despite increasing need of space for agriculture for food production (Norgate et al., 2012, p. 9). The publication further quotes a study which highlights Brazil and the Congo as possible candidates for biochar production for industrial use. This correlates with results of another study, where material costs were investigated, see Table 9-1. It shows prices for biochar compared to fossil coal in US-$ per ton. The price in Europe (Germany) is almost quadrupled, almost tripled for North-America (USA), and more than double in Brasil. It also shows, that biochar from Brazil is 25 % cheaper than from the USA and 44 % cheaper than from Germany, while both countries are considered to have a lower price level than Norway (Feliciano-Bruzual, 2014). For Norway's neighbour Finland, the price per ton for biochar is even quoted at 780 US-$/ton, which is 189 % more than from Brazil. As Germany has introduced a tax on carbon, the price for biochar could be estimated to be at least between the values for Germany and the USA, with a tendency towards Germany, as Norway is considering a carbon tax as well. This indicates, that the biochar feedstock for metal industry in Norway would probably originate from low-cost countries and be shipped in large scales. If the quality assurance would be equivalent to Norwegian standards is, to the knowledge of the author, yet to be evaluated.

Table 9-1: Costs for coal and biochar per ton (Feliciano-Bruzual, 2014)

		Brasil	Finland	USA	Germany
Coal	[USD/t]	117		124	125
Biochar	[USD/t]	270	780	360	480

Despite the CO_2 saving potential, the incorporation of biochar would have a significant impact on the final cost of metal industry depending on the application. Pelletising increases the mechanical strength, energy density, and lowers abrasion. BOF and other top-loaded smelting processes require a certain amount of mechanical stability, as well, as elaborated in chapter 3.2. Chapter 2.5.1 elaborates the varying requirements for the different systems. Blast furnaces require less physical preparation, as the reduction agent is blown in the bottom region of the kiln, thus less additional processing costs can be expected.

Table 9-2: Estimated biochar prices and taxes on coal to be competitive (blast furnace)

	Brazil	USA	Germany
USD/t	147.9	130.1	189.3

A possible cost-reducing factor is the use of waste materials as binding agents, which was a reason to choose lignin, a waste product of paper production, and pyrolysis oil. While the oil is produced by flash pyrolysis to gain high amounts of fluids, all pyrolysis processes produce a fluid phase which would be sufficient for the low amounts required. Carbonisation produces tar/oil of similar composition as FPO, which suggests recycling the oil produced during carbonization to later pelletise the biochar product (FAO, 1985).

Pre-experiments showed that < 30 wt. % of oil/water are required for good pelletising results, see chapter 6.3.2. Water proved to be a reliable binding agent and lubricant for wood pellets and will evaporate after pelletising. Experience showed, that lignin bound in water behaves like starch and water from common pelletising processes described in chapter 3.1. FPO alone and mixed with lignin led to increased clogging and sticky materials. The machinery requires to be properly cleaned after every use, meaning that commercial pelletising should be a permanent process to avoid cooling down and drying of the materials. Heating is not required, as pelletising processes usually reach temperatures of 70 – 90 °C. During the process, the oil served as improved lubricant and eased the pelletising. Drying in mass production serves as preservation and increasing the heating value, and to reduce weight and increase quality of the product (Kaltschmitt et al., 2009, p. 314). Reducing the water content of the biomass makes an expensive step during pellet production and has a great effect on the overall economic efficiency. Thus, it is a critical step for industrial applications and requires optimisation in construction and design to keep the process beneficial (Döring, 2013, p. 99).

10 DISCUSSION OF RESULTS AND RECOMMENDATIONS

As the carbonaceous component, Norway spruce was chosen, as the composition and heritage of the IC used in the pre-experiments was vague. Norway Spruce offered local character and wide availability. The analysis showed, that Norway spruce offered the highest FC and the lowest AC and VM. In addition, the literature research showed that spruce offers the highest amounts of carbon rich lignin compared to other common wood types (see Table 2-3 and Table 2-4 in chapter 2.5). Further investigations of the feedstock were not necessary, as the practical experience shows, that for industrial applications the detailed quality of the feedstock is less important than the heritage, hence the material price (Norgate et al., 2012).

Biochar and wood profited from pelletising with binding agents. The addition of moisturising binders decreased the energy requirement for pelletising the feedstock significantly. For both pellet presses, lubrication eases the pelletising just as the extraction process as well.

The FPO showed excellent behaviour during pelletising. It offered a higher viscosity compared to the tar pitch used in another study about coke breeze pellets (Benk & Coban, 2011). It inspired to use pyrolysis oil as a binding agent, and the fact that oil or tar is a side product within the production line of biochar underlined the feasibility for commercial use. The higher viscosity of FPO allowed to use little amounts of water to achieve the required MC to homologate, pelletise, and extract the pellets. The pellet die was lubricated better than with water only. The process caused it automatically during pelletising, which led to a difference in energy required to handle the process. On the other hand, drying FPO caused the pelletising unit to clog, and required thorough cleaning with acetone.

Lignin showed good results as well. It was previously used by Stevens for wood pellets, by Hu et al. for biochar pellets, and confirmed these results. The high ash content of 16 wt. % measured during TGA analysis highlights the importance of a low content of lignin to stay within the requirements for reduction agents (see Table 2-10). The results confirmed the study of Hu et al., that low contents can improve the characteristics of biochar pellets already (Hu et al., 2015, p. 8).

Starch was discontinued after the pre-experiments, as it showed similar, but inferior effects compared to lignin. Hu et al. states that starch pellets show low mechanical strength and volume density, indicating that starch was not suitable as binding agent for biochar pellets. The pre-experiments showed mostly similar results after drying. It is assumed, that starch is more suitable for a woody feedstock.

Water was required for pelletising the dry binding agents as well as the raw feedstock. The literature review already showed, that starch as well as lignin solve in water. With the use of FPO, the amounts of pure water were limited. Too much MC led to a loss of stability after drying for pellets produced without bridge-building binding agents lignin and FPO. This was another advantage of said binders.

The overall MC delivered mostly by water and FPO was required for efficient agglomeration and homologation. This finding was not found in the literature review but is seen as an essential result of the laboratory-scale experiments. For industrial applications, larger amounts of materials can be used, and the even spread of all materials is easier to achieve. The experimental work used a heated magnetic stirrer to simulate large scale conditions. The pellet extraction required skilled handling to avoid breaking the pellets, as they were sticking to the pelletising die. Pellets further required a resting phase, which requires further investigation, about how they change, e.g. their moisture content and if the difference can be reduced.

Increasing the pressure showed the interesting effect of a spongy behaviour, especially for pellets with a high MC. The best results were made at pressures of 200 – 260 MPa, which is higher than in relevant publications. The density peaked at higher pressure levels, but the second peak in said pressure area posed as a good compromise of effort and result. Hu et al. names 125 MPa for densifying biochar with different binders. The experiments showed stable results for that pressure level, even though they were at the lower end of the results. The overall result for densities was higher than the requirements for wood pellets at 600 kg/m³ (ENplus, 2015). Several compositions did not reach the values of relevant publications. Hu et al. lists volume densities between 1130 kg/m³ and 1150 kg/m³for biochar pellets with lignin, which was only achieved by pellets with FPO.

The mechanical strength of the lignin pellets was mainly related to bonding and mixing in the biochar. Hydrogen bonds, Van-der-Waals forces and mechanical interlock are combined to form strong agglomeration. The soft lignin particles function as a bridge between the harder biochar particles, forming bridges in between (Hu et al., 2015). An improvement for this thesis would have been a standardised durability test. The system at hand was designed for a minimum amount of 500 g of pellets, which was impossible to produce with either of the single unit pellet presses. The results regarding strength are of limited significance, as no exact values could be measured.

Regarding the economical aspect, the evaluation showed that the political direction towards renewable energy and emission-reducing measures goes ahead of technological advantages of biomass. The emission saving potential for the metal industry is one of the largest in the study Climate Cure 2020. A CO_2 tax would increase the importance of biochar for the metal industry significantly. The results posted in the previous chapter indicate, that biochar is a feasible initiative to reduce CO_2 emissions in blast furnaces. For other applications, the required mechanical strength and durability require more research, before a definite statement can be made. Lignin solved in water and pelletised with biochar showed similar characteristics as with starch for wood pellets. It was assumed, that the process is like commercial wood pelletising. Only pelletising with FPO would require thorough research towards the mechanical feasibility.

This thesis served to initially screen, which binding agents would work with biochar for use in metallurgical industry. The pelletising showed good results for the experimental use of binding agents to increase certain characteristics and laid the groundwork for additional research projects. The investigative binding agents produced good results, but some drawbacks are still to overcome and several questions are yet to be answered. The results give a good direction, how biochar could be treated to achieve the required quality standards. For future research, it is planned to investigate further, how the binding agents behave in a detailed study. Afterwards, the pellets behaviour during pyrolytic processes with different variables will be investigated to be able to tell, how the different metallurgical processes will influence the pellet quality. A proper durability test method will be established to validate results regarding the mechanical strength. Further, the use of hardeners such as calcium hydroxide is planned. The pellet press is capable of pelletising at temperatures up to 1,000 °C, which will enable the research team to simulate pelletising under more intense conditions, as well.

11 SUMMARY

For metallurgic smelting processes, a reducing agent with a high carbon content and other process-specific characteristics is necessary. With growing concerns over global warming, the substitution of carbon dioxide (CO_2)-heavy fossil coal or coke gains importance. Biochar from biomass is a possible alternative, as the CO_2 emitted during combustion is compensated for by photosynthesis of the growing biomass. This thesis served to initially screen, if pelletising with varying binding agents could achieve equivalent characteristics for the biochar compared to a fossil feedstock.

Reviewing relevant literature showed, that fossil coal is one of the main pollutants in Norway, as the countries electrical power is almost entirely based on CO_2-neutral hydropower. Reducing emissions from industrial applications is a major goal of the countries climate goals until 2020 (Climate and Pollution Agency, 2010). Analyses of a biochar feedstock showed similar values for fixed carbon and volatile matter compared to characteristics of fossil coal and coke. Carbon is the main reducing component required for metal production. Main drawbacks of biochar are the lower energy density and low mechanical strength. To achieve sufficient properties, the use of binding agents was elaborated from relevant publications. Literature review pointed out several interesting materials like water, starch, lignin and Oil/tar pitch might lead to good results.

A pre-experiment served to investigate the behaviour of a feedstock of wood meal and biochar when pelletised with different compositions of binders. Water, starch, lignin powder, and oil from a flash-pyrolysis process were selected for the experiment. The pellets were produced with a simple pellet press produced for a bomb-calorimeter to simplify the process. From observations during the experiment, wood was ruled out as a possible feedstock due to insufficient behaviour at higher temperatures. Even though a pyrolytic process lowered the content of volatiles and increased the fixed carbon, the pellets were too instable and mechanically weak. Starch showed best results when pelletised with wood but failed to properly bind hydrophobic biochar. However, the biochar-pellets showed good results. When mixed with starch dissolved in water, biochar achieved improved stability and abrasion, but the mix of binders was not able to reach the same binding effects as with the hydrophobic wood. The most promising materials, lignin and pyrolysis oil, showed both good results. They were achieved by composing biochar with pyrolysis oil and with lignin dissolved in either pyrolysis oil or water. Best properties were found to require an overall moisture content of all ingredients of 25 – 30 wt. %. This enabled the liquid to lubricate the system, homogenise the mixture prior to pelletising and extract the pellet from the die with ease.

A main experiment was conducted according to the previously made observations. Pyrolysed Norway spruce served as a feedstock, as analyses showed excellent properties compared to other resources and fossil coal/coke. As binding agents served water, lignin powder and pyrolysis oil. The main experiment was conducted with a laboratory grade single unit hot pellet press, improving the pelletising process and giving scientifically relevant results. The pelletising resulted in varying results, depending on the composition and applied pressure. The pellets showed similar results compared to other publications. Lignin and pyrolysis oil confirmed the observations of the previous experiment. In addition, water and pyrolysis oil showed excellent lubricating characteristics. Problems were discovered with the sticky characteristics of lignin dissolved in water or pyrolysis oil, and when the compositions were pelletised at low pressures. The machinery clogged regularly and required proper cleaning with acetone. Further investigation of how to optimise the mixture is required.

Evaluating the economic feasibility showed, that biochar has costs several times higher compared to fossil coal. The exact value depends mainly on country of origin and transport costs. The binding agents lignin and pyrolysis oil were waste or side products from other processes to increase feasibility. Only biochar from Brazil is currently economically relevant. But results of investigative research showed, that by implementing a CO_2-tax, and under consideration of the growing concerns over global warming, biochar could become an economic-feasible substitution to fossil coal. Results of the experiments showed that pelletised biochar can be a possible substitution for fossil coal and coke for the smelting processes as reducing agent. The thesis narrowed down possibilities to pelletise biochar with binding agents and laid the groundwork for additional research projects.

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13 LISTS

15.1 List of figures

15.2 List of tables

15.3 List of abbreviations

13.2 List of figures

13.4 List of tables

13.6 List of abbreviations

AC	Ash content
Al	Aluminium
amb	ambivalent
ar	as received
C	Carbon
CEN	European Committee for Standardisation
Cl	Chlorine
cm	Centimetre
CO	Carbon monoxide
CO_2	Carbon dioxide
db	dry basis
DTG	Derivative thermo-gravimetric
EN	European Norm
EU	European Union
FC	Fixed carbon
Fe	Iron
Fe_2O_3	Iron (III) oxide
GCV	Gross calorific value
GHG	Greenhouse gas
ΔH_f^0	Standard enthalpy of formation
$\Delta H_{r,comb.}^0$	Heat of combustion
H	Hydrogen
HHV	Higher heating value
H_2O	Water
HTA	Hydrothermal activation
HTC	Hydrothermal carbonisation
HTG	Hydrothermal gasification
HTL	Hydrothermal liquefaction
IC	Industrial grade biochar
IGCC	Integrated gasification combined cycle
ISO	International Organisation for Standardisation
J	Joule
K	Potassium
kg	Kilogramm
LB	LignoBond lignin
LCA	Life cycle analysis
LHV	Lower heating value
MC	Moisture content
Me	Alkaline earth metal
Mg	Magnesium
MJ	Megajoule
m	metre

mm	Millimetre
Mn	Manganese
MnO	Manganese oxide
N	Nitrogen
Na	Sodium
Nm	Newton metre
NCV	Net calorific value
O	Oxygen
PT	PellTech lignin
PC	Pulverised coal
RES	Renewable energy source
S	Sulphur
Si	Silicon
SiC	Silicon carbide
SiO	Silicon oxide
t	metric tons
TGA	Thermogravimetric analysis
VM	Volatile matter
VTC	Vapothermal carbonisation
wb	wet basis
wt. %	Weight in percent

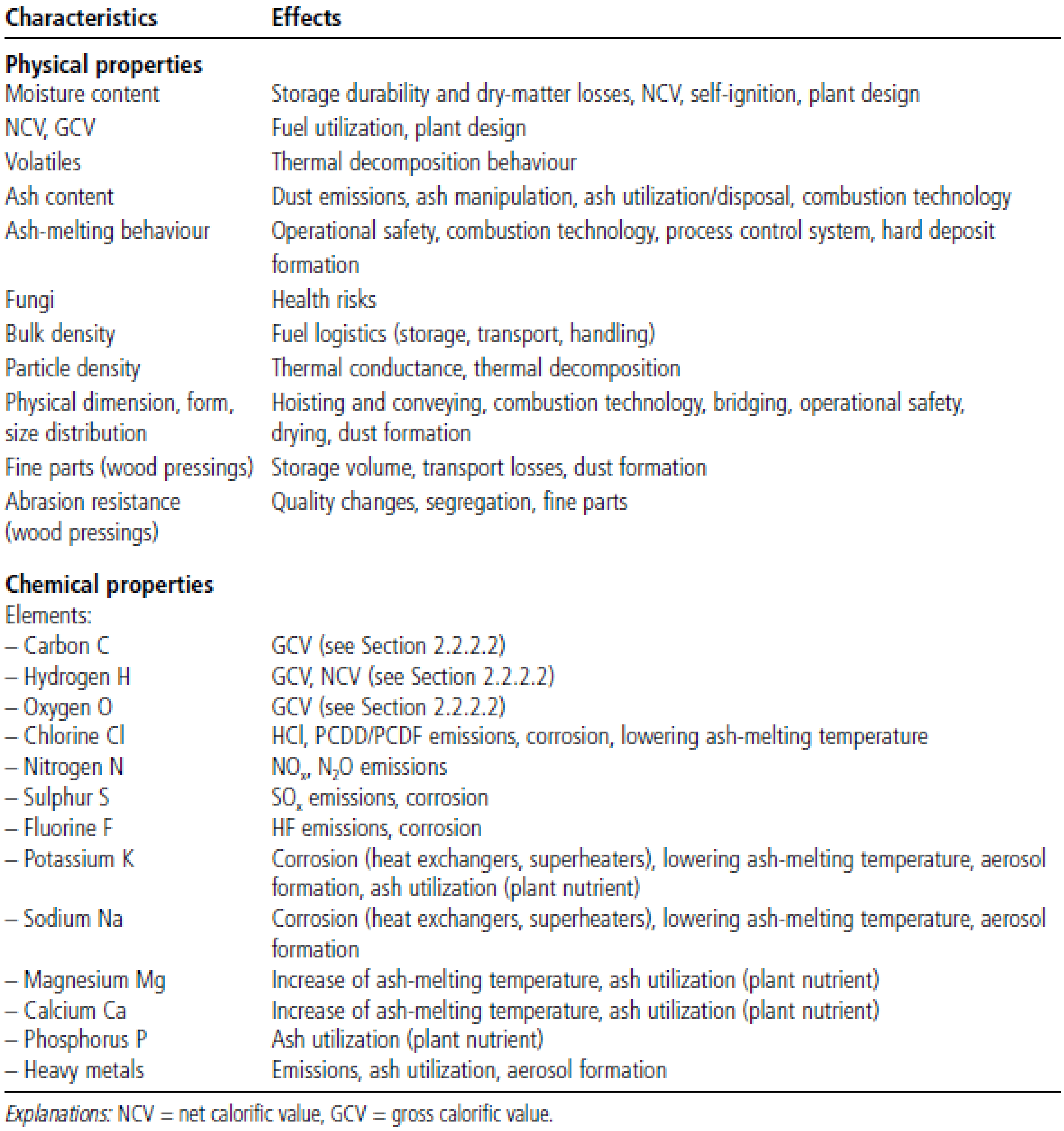
APPENDIX

List of appendixes

Appendix 1: Classification of woody biomasses (CEN, 2010)

1.1 Forest, plantation and other virgin wood	1.1.1 Whole trees without roots	1.1.1.1 Broadleaf 1.1.1.2 Coniferous 1.1.1.3 Short rotation coppice 1.1.1.4 Bushes 1.1.1.5 Blends and mixtures
	1.1.2 Whole trees with roots	1.1.2.1 Broadleaf 1.1.2.2 Coniferous 1.1.2.3Short rotation coppice 1.1.2.4 Bushes 1.1.2.5 Blends and mixtures
	1.1.3 Stem wood	1.1.3.1 Broadleaf 1.1.3.2 Coniferous 1.1.3.3 Blends and mixtures
	1.1.3 Logging residues	1.1.4.1 Fresh/Green, broadleaf (including leaves) 1.1.4.2 Fresh/Green, coniferous (including needles) 1.1.4.3 Stored, broadleaf 1.1.4.4 Stored, coniferous 1.1.4.5 Blends and mixtures
	1.1.5 Stumps/Roots	1.1.5.1 Broadleaf 1.1.5.2 Coniferous 1.1.5.3 Short rotation coppice 1.1.5.4 Bushes 1.1.5.5 Blends and mixtures
	1.1.6 Bark (from forestry operations)	
	1.1.7 Segregated wood from gardens, parks, roadside maintenance, vineyards and fruit orchards	
	1.1.8 Blends and mixtures	
1.2 By-products and residues from wood processing industry	1.2.1 Chemically untreated wood residues	1.2.1.1 Without bark, broadleaf 1.2.1.2 Without bark, coniferous 1.2.1.3 With bark, broadleaf 1.2.1.4 With bark, coniferous 1.2.1.5 Bark (from industry operation)[a]
	1.2.2 Chemically treated wood residues, fibres and wood constituents	1.2.2.1 Without bark 1.2.2.2 With bark 1.2.2.3 Bark (from industry operation)[a] 1.2.2.4 Fibres and wood constituents
	1.2.3 Blends and mixtures	
1.3 Used wood	1.3.1 Chemically untreated wood	1.3.1.1 Without bark 1.3.1.2 With bark 1.3.1.3 Bark[a]
	1.3.2 Chemically treated wood	1.3.2.1 Without bark 1.3.2.2 With bark 1.3.2.3 Bark[a]
	1.3.3 Blends and mixtures	
1.4 Blends and mixtures		
[a] Cord is included in bark		

Appendix 2: Characteristics of solid biomass fuels and effects (Koppejan & van Loo, 2008)



Characteristics	**Effects**
Physical properties	
Moisture content	Storage durability and dry-matter losses, NCV, self-ignition, plant design
NCV, GCV	Fuel utilization, plant design
Volatiles	Thermal decomposition behaviour
Ash content	Dust emissions, ash manipulation, ash utilization/disposal, combustion technology
Ash-melting behaviour	Operational safety, combustion technology, process control system, hard deposit formation
Fungi	Health risks
Bulk density	Fuel logistics (storage, transport, handling)
Particle density	Thermal conductance, thermal decomposition
Physical dimension, form, size distribution	Hoisting and conveying, combustion technology, bridging, operational safety, drying, dust formation
Fine parts (wood pressings)	Storage volume, transport losses, dust formation
Abrasion resistance (wood pressings)	Quality changes, segregation, fine parts
Chemical properties	
Elements:	
– Carbon C	GCV (see Section 2.2.2.2)
– Hydrogen H	GCV, NCV (see Section 2.2.2.2)
– Oxygen O	GCV (see Section 2.2.2.2)
– Chlorine Cl	HCl, PCDD/PCDF emissions, corrosion, lowering ash-melting temperature
– Nitrogen N	NO_x, N_2O emissions
– Sulphur S	SO_x emissions, corrosion
– Fluorine F	HF emissions, corrosion
– Potassium K	Corrosion (heat exchangers, superheaters), lowering ash-melting temperature, aerosol formation, ash utilization (plant nutrient)
– Sodium Na	Corrosion (heat exchangers, superheaters), lowering ash-melting temperature, aerosol formation
– Magnesium Mg	Increase of ash-melting temperature, ash utilization (plant nutrient)
– Calcium Ca	Increase of ash-melting temperature, ash utilization (plant nutrient)
– Phosphorus P	Ash utilization (plant nutrient)
– Heavy metals	Emissions, ash utilization, aerosol formation

Explanations: NCV = net calorific value, GCV = gross calorific value.

Appendix 3: Results pelletised biochar with varying particle size, no binders

Size	Length	Diameter
< 125 mm		
0.125 mm < size < 0.250 mm		
0.250 mm < size < 0.5 mm		
0.5 mm < size < 1 mm		
Mixed (< 2 mm)		

Appendix 4: Biochar pellets with different amounts of water in % of total weight as binding agent

Water added	Length	Diameter
30%		
50%		
70%		
90%		

Appendix 5: Results and conditions in % of total weight of the pelletising pre-experiments

- Wood meal
- 20 % MC
- 5 % starch

- Industrial biochar
- 10/20/30 % starch

- Industrial biochar
- 20 % starch
- 500/800 °C pyrolysis for seven minutes

- Industrial biochar
- 40 % FPO
- Dried/500/800 °C pyrolysis
- Durability tested

- Industrial biochar
- 40 % FPO
- 900 °C pyrolysis/with starch
- Durability tested

- 60/70 % industrial biochar
- 20 % lignin (LignoBond) and 20 % water for pellet 1
- 30 % lignin (LignoBond) plus 30 % water added to total mix

Appendix 6: Results and conditions in % of total weight of the pelletising pre-experiments, part 2

- 10/15 % lignin (LignoBond)
- 20 % flash pyrolysis oil (BTG)
- 70/50 % industrial biochar
- Second pellet with 15 % water

- 5 % lignin (LignoBond)
- 30 % flash pyrolysis oil (BTG)
- Second pellet after durability test

Appendix 7: Measured results of the main pelletising run, averages out of three, compositions 1-4

$P_{machine}$	[MPa]	0.5	0.75	1	1.25	1.5	1.75	2	2.5	2.75
P_{die}	[MPa]	105	155	210	260	315	365	415	472	520
Composition 1:	50 wt. $\%_{ar}$	Spruce (pyrol. 800 °C)								
	20 wt. %	Water								
	30 wt. $\%_{ar}$	Flash pyrolysis oil								
	0 wt. $\%_{ar}$	Lignin								
Weight	[g]	0.1999	0.2342	0.2079	0.2065	0.1598	0.1725	0.1437	-	-
Length	[cm]	0.78	0.85	0.71	0.706	0.54	0.56	0.52	.	.
Density	[g/cm^3]	0.809	0.87	0.925	0.924	0.934	0.972	0.873	-	-
Composition 2:	57 wt. $\%_{ar}$	Spruce (pyrol. 800 °C)								
	25 wt. %	Water								
	18 wt. $\%_{ar}$	Flash pyrolysis oil								
	0 wt. $\%_{ar}$	Lignin								
Weight	[g]	0.1867	0.1550	0.1642	0.1429	0.1776	0.1227	0.0864	0.3097	-
Length	[cm]	0.77	0.58	0.59	0.53	0.65	0.45	0.30	0.103	-
Density	[g/cm^3]	0.766	0.844	0.879	0.851	0.863	0.861	0.99	0.949	-
Composition 3:	55 wt. $\%_{ar}$	Spruce (pyrol. 800 °C)								
	25 wt. %	Water								
	15 wt. $\%_{ar}$	Flash pyrolysis oil								
	5 wt. $\%_{ar}$	Lignin (LignoBond)								
Weight	[g]	0.1594	0.1728	0.1579	0.1364	0.2480	0.1064	0.1649	0.2050	0.0998
Length	[cm]	0.57	0.72	0.60	0.50	0.93	0.41	0.64	0.746	0.34
Density	[g/cm^3]	0.883	0.758	0.831	0.861	0.842	0.819	0.814	0.868	0.927
Composition 4:	55 wt. $\%_{ar}$	Spruce (pyrol. 800 °C)								
	25 wt. %	Water								
	15 wt. $\%_{ar}$	Flash pyrolysis oil								
	5 wt. $\%_{ar}$	Lignin (PellTech)								
Weight	[g]	0.0532	0.0584	0.0643	0.0569	0.0678	0.0602	0.0592	0.0666	-
Length	[cm]	0.1823	0.1857	0.1810	0.1721	0.1898	0.1870	0.1731	0.1881	-
Density	[g/cm^3]	0.922	0.993	1.122	1.044	1.128	1.017	1.080	1.118	-

Appendix 8: Measured results of the main pelletising run with averages out of three, compositions 5 - 7

$P_{machine}$	[MPa]	0.5	0.75	1	1.25	1.5	1.75	2	2.5	2.75
P_{die}	[MPa]	105	155	210	260	315	365	415	472	520
Composition 5:	60 wt. $\%_{ar}$	Spruce (pyrol. 800 °C)								
	10 wt. %	Water								
	30 wt. $\%_{ar}$	Flash pyrolysis oil								
	0 wt. $\%_{ar}$	Lignin								
Weight	[g]	0.1908	0.1956	0.1840	0.1902	0.1871	0.1716	0.2140	0.1499	0.1830
Length	[cm]	0.61	0.59	0.53	0.57	0.57	0.49	0.60	0.43	0.53
Density	[g/cm³]	1.003	1.069	1.114	1.070	1.053	1.12	1.126	1.101	1.067
Composition 6:	65 wt. $\%_{ar}$	Spruce (pyrol. 800 °C)								
	7 wt. %	Water								
	28 wt. $\%_{ar}$	Flash pyrolysis oil								
	0 wt. $\%_{ar}$	Lignin								
Weight	[g]	0.1486	0.1699	0.1710	0.1586	0.1722	0.1885	0.1605	0.1563	0.1537
Length	[cm]	0.57	0.59	0.57	0.515	0.56	0.635	0.53	0.525	0.51
Density	[g/cm³]	0.823	0.909	0.947	0.972	0.971	0.937	0.856	0.940	0.952
Composition 7:	67 wt. $\%_{ar}$	Spruce (pyrol. 800 °C)								
	5 wt. %	Water								
	28 wt. $\%_{ar}$	Flash pyrolysis oil								
	0 wt. $\%_{ar}$	Lignin								
Weight	[g]	0.1973	0.1687	0.1862	0.1524	0.1653	0.1456	0.1791	0.2087	-
Length	[cm]	0.72	0.59	0.61	0.49	0.52	0.475	0.545	0.695	-
Density	[g/cm³]	0.865	0.903	0.964	0.982	1.004	0.968	0.1038	0.948	-