Utilisation Possibilities of Biochar Produced by Pyrolysis

Mirva Viitasaari

BACHELOR’S THESIS
May 2021

Bioproduct and Process Engineering

ABSTRACT

Tampereen ammattikorkeakoulu
Tampere University of Applied Sciences
Bioproduct and Process Engineering

VIITASAARI, MIRVA:
Utilisation Possibilities of Biochar Produced by Pyrolysis

Bachelor's thesis 51 pages
May 2021

In the past decades there have been many efforts to reduce the burden humans have caused to the environment. One of these efforts is the utilisation of biomass as both energy and raw material, which offers a more sustainable option to meet the increased demand. This conversion of biomass can be achieved by pyrolysis which produces bio-oil, syngas, and biochar. Because of the unique properties and environmental benefits of biomass derived biochar, its utilisation possibilities seem to be very abundant.

The purpose of this thesis was to collect information on biochar characteristics and evaluate the chosen utilisation possibilities and their potential scalability. The theoretical section explores the pyrolysis process, biochar characteristics, the effect of pyrolysis, feedstock and upgrading methods to biochar properties. Also, evaluations of biochar use in blast furnace injection in metallurgy and as a catalyst in the concept of biomass refinery are conducted.

The key results indicate that the main parameters affecting biochar properties are pyrolysis temperature and feedstock. Generally important properties of biochar are mineral and ash content, porosity, pH, and density. The findings indicate that biochar can be a realistic commercial substitute for pulverized coal in blast furnace injection. Biochar can meet the quality requirement and was found to be comparable to pulverized coal. It offers a possibility to decrease emissions as a substitute of fossil coal and increase productivity in iron and steel industry. Biochar as a catalyst in thermochemical conversion of biomass offers a low-cost, more effective, and economic option for common catalysts used.

There are markets for biochar in worldwide and they are expected to grow. In Finland, markets also have a great potential, but large-scale production of biochar is missing. Thus, further studies are required to design an active and selective biochar catalyst. Moreover, the challenge of how to maintain certain biochar properties in a large-scale production needs to be met.

Key words: biochar, biochar utilisation, pyrolysis, biochar catalyst, blast furnace

CONTENTS

ABBREVIATIONS AND TERMS

BC	Biochar
BF	Blast furnace
BFB	Bubbling fluidized bed
CFB	Circulating fluidized bed
CCA	Carbon composite agglomerate
CEC	Cation exchange capacity
EC	Electrical conductivity
Ex-situ	Away from its original location, e.g. “off-site”
Half-life	The time required for a quantity to reduce to half of its initial value
Heating rate	The rate at which temperature is raised, expressed in temperature per time
Heating value	The amount of heat released during combustion of a specified amount of it
HHV	Higher heating value
Higher heating value	The upper limit of the available thermal energy produced by a complete combustion of fuel
In-situ	In the natural or original place, e.g. “on site”
PAH	Polycyclic aromatic hydrocarbon
PC	Pulverized coal
Residence time	Duration of persistence of a mass or a substance in a medium or a place
VM	Volatile matter

INTRODUCTION

Constantly increasing demand of energy and raw materials together with various environmental issues pushes us towards more sustainable living. Substitutes for fossil resources are constantly being developed and biomass fulfils a lot of requirements related to sustainability and economic. Pyrolysis is a straightforward process for converting biomass into useful products such as bio-oil, synthesis gas, and biochar.

Biochar unique properties allow its wide range of utilisation possibilities now and in the future. Biochar properties, process conditions, and their tailor ability provide new possibilities, and understanding of these relations is necessary for its exploit. It has huge environmentally healing potential as a reducer of CO_2 emissions in the industry or as a carbon sequester e.g. in soils or materials.

Aim of the thesis is understanding of biochar characteristics and quality requirements related to different end-use applications. Purpose is to evaluate utilisation possibilities and their potential now and in the future. Focus is on the quality requirements of biochar, how it can be affected and how it affects to the utilisation possibilities. All possible end-uses cannot be considered and evaluated due to limited scope. Biochar quality requirements in metallurgy and as a catalyst in the thermochemical process are chosen for further investigation.

Term biochar in this thesis refers to a solid product of biomass pyrolysis with no limitations regarding its end-use purposes. Terminology related to this matter includes multiple options such as biochar, biocoal, activated carbon, charcoal, and biocarbon. These terms often are classified by the pyrolysis feedstock or the end-use application. As an example, biochar may refer to solid char used for soil amendment or biocoal to coal-like substance that is used as a fuel.

1 PYROLYSIS

Pyrolysis process is thermochemical decomposition of biomass into different products. It occurs either in the total absence of oxygen or with a bounded supply of oxygen that will not permit gasification. In the process biomass is rapidly heated to around 300–650 °C. Typically, primary focus of pyrolysis is the production of liquids for chemical or fuel production, but products also include gases and char. (Basu 2018, 155)

Major thermochemical conversion processes are combustion, gasification, pyrolysis, and torrefaction. Combustion includes high-temperature (700–1400 °C) exothermic oxidation in the presence of oxygen to hot flue gas. Unlike combustion, gasification involves different chemical reactions in limited supply of oxygen at high temperature (500–1300 °C) producing product gases with heating values. Torrefaction includes slow heating of biomass to 200–300 °C without or a bit contact with oxygen. (Basu 2018, 10–12)

1.1 Process

Pyrolysis is a process for biomass rapid heating without air or oxygen at a specific temperature. In pyrolysis process biomass large and complex hydrocarbon molecules start to break down into small and simple molecules of gas, liquid, and char. Nature of its products is dependent on different factors such as pyrolysis heating rate and temperature. (Basu 2018, 155, 157)

Figure 1. presents pyrolysis process of a fluidized bed pyrolysis process. Biomass is fed to the chamber that contains high temperature solids (fluidized bed), which then heats the biomass to the peak temperature. Pyrolysis temperature is the temperature in which the biomass decomposition starts. Vapors that are released from biomass will leave the pyrolysis chamber. Char that is produced will stay partially in the chamber and partially in the vapor that is released. Gas is separated from the char and cooled down. Solid char can be collected for commercial purposes or burned for heat in a separate chamber. Gas separated

is divided into condensable and noncondensable gas. After char separation condensable gas condenses as biooil or pyrolysis oil. Noncondensable gases will leave the pyrolysis chamber as product gas. Gas leaving is free from oxygen meaning that part of it can be recycled into pyrolysis chamber as a fluidizing medium or as a heat carrier. This description of pyrolysis with bubbling fluidized bed (BFB) is only one variation of the process. (Basu 2018, 158–160)

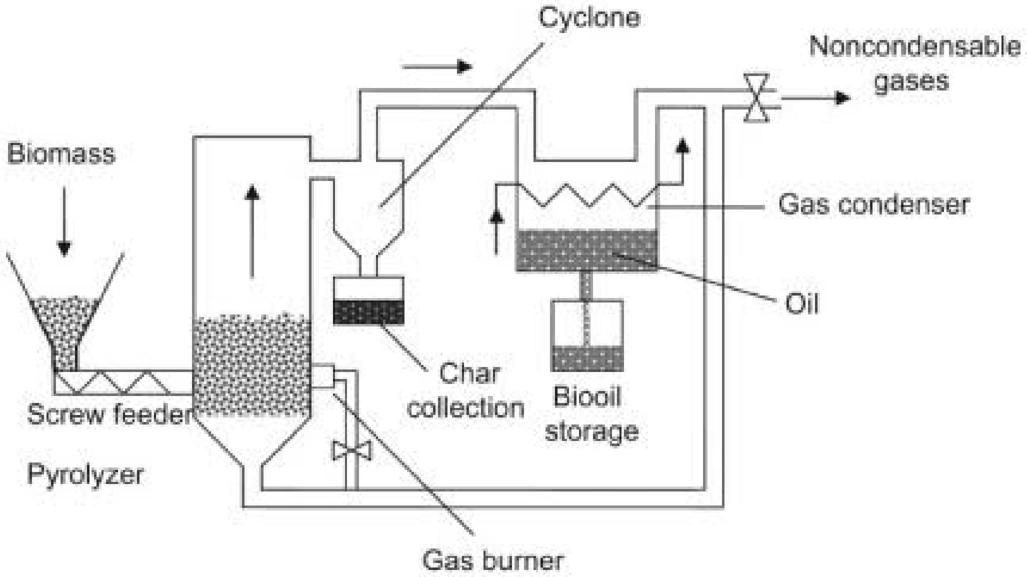


FIGURE 1. Simplified production process of pyrolysis plant with BFB (Basu 2018, 160)

Figure 2 shows simplified process steps in circulating fluidized bed (CFB) pyrolyzer. Principle is like BFB other than the bed is enlarged, and solids will repeatedly recycle around a separate loop. Loop seal and cyclone form the external loop. Gas velocity is higher in CFB than BFB. Advantage in CFB is the fact that the char entrained from the pyrolyzer is effortlessly separated and often it can be for example burnt for heat in an external chamber. Fluidized beds in figures 1 and 2 are used for fast pyrolysis. (Basu 2018, 180)

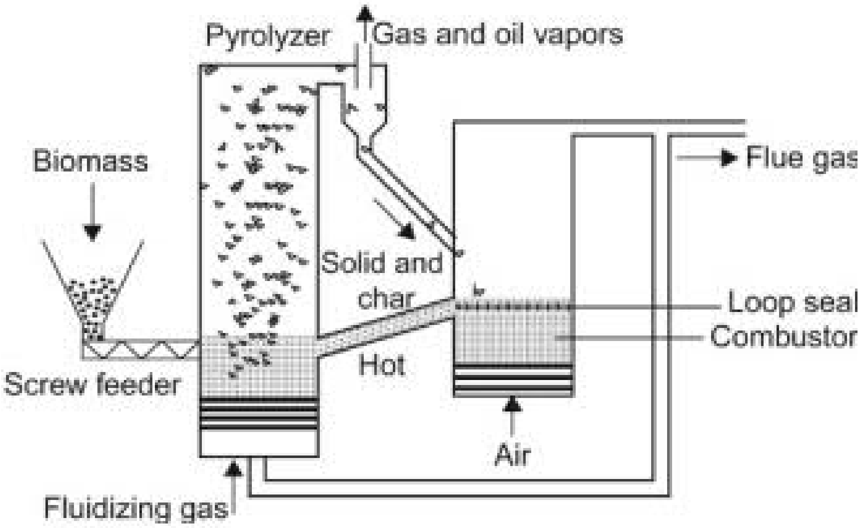


FIGURE 2. Pyrolysis process in CFB (Basu 2018, 177)

Pyrolysis process can be categorized as fast or slow based on the heating rate and residence time. Heating rate is the rate at which temperature is raised and it is usually expressed in °C/s or °C/h. The residence time in fast pyrolysis of vapor is just seconds when in slow pyrolysis it can be from minutes to hours. In fast pyrolysis biomass heats so swiftly that it will reach the pyrolysis (peak) temperature before it starts to decompose. Heating rate varies from 10–200 °C/s up to 1 000–10 000 °C/s, but the pyrolysis (peak) temperature should be under 650 °C if interest is biooil production. Residence time is the duration of biomass in the pyrolyzer. Typical pyrolysis residence times are visible in the table 1. The aim of fast pyrolysis is the maximized bio-oil production. (Basu 2018, 162–163; Kan et al. 2015, 1126)

Slow pyrolysis is traditionally applied to produce char. Typical for slow pyrolysis is long residence time from hours to days, temperature range 300–700 °C, and broad range of particle size (5–50 mm). Biomass thermal decomposition occurs under very low heating rate with enough time for repolymerisation reactions that maximises the solid yields. (Kan et al. 2015, 1127)

Three main pyrolyzer types used for slow pyrolysis are fixed-bed, screw reactor and rotary kiln. A cylinder body and two convex heads form a fixed bed reactor. Usually they are placed vertically so reactants/biomass passes through the reactor using gravitational force. Carrier gas will carry out the products. In fixed bed reactors heating rate is low and heat transfer is often not distributed uniformly. Fixed bed pyrolyzer operates in batch mode. For previous reasons reactors are often used only on a lab scale. Rotary kilns process is simple to operate and can be used on an industrial scale. Reactor consists of cylinder vessel, which is usually inclined horizontally. Biomass will be fed from the top and the rotation of the reactor together with hot gas moves it downwards while biomass is being pyrolyzed. (Gholizadeh et al. 2020, 5888, 5891) Screw drum reactor consists of feeding system and a screw, which slowly moves the biomass in the pyrolyzer converting it to biochar and vapours (figure 3). Feeding system makes it a continuous process. Industrial-scale installation of screw drum reactors are available and in operation e.g. Pyreg (Germany) and Biogreen (France). (Jeguirim & Limousy 2019, 55)

Mašek et al. (2018, 1) found that slow pyrolysis units (fixed bed, screw reactor and rotary kiln) for the use of biochar production are possible to scale up from grams to hundreds of kilograms without impairing biochar quality parameters. Residence times of the slow pyrolysis units were under 30 minutes. Problematic in production capacity increase is that even heat transfer to feedstock may be insufficient and cause uneven biochar at a large scale. (Mašek et al. 2018, 1)

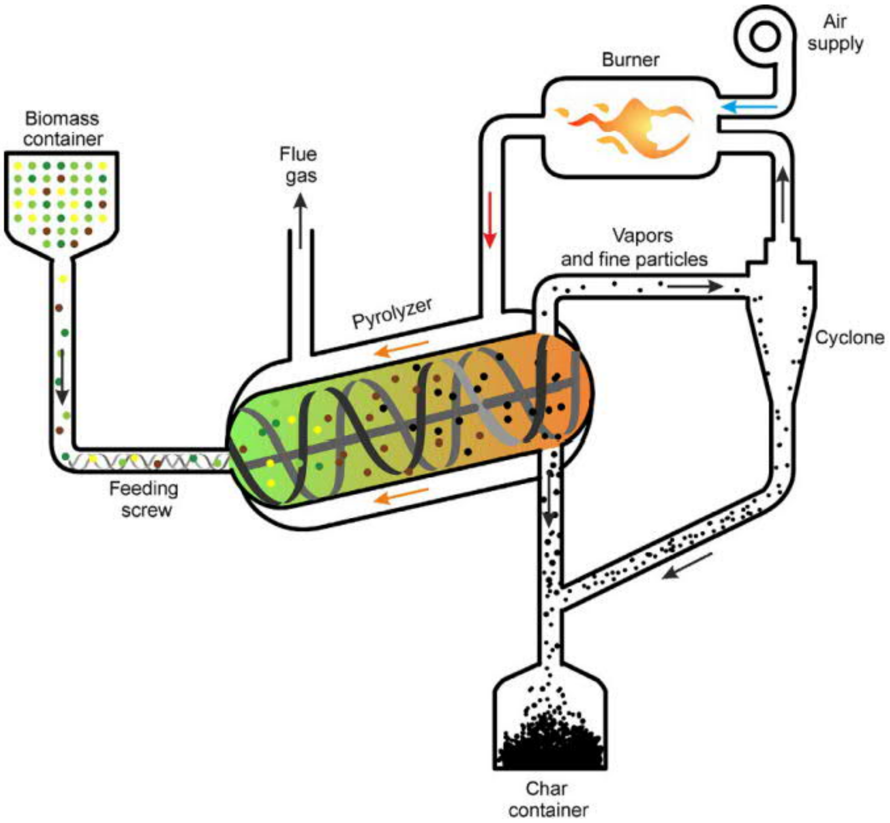


FIGURE 3. Continuous screw reactor used in slow pyrolysis (Jeguirim & Limousy 2019, 55)

Main operating parameters affecting the pyrolysis product yield are heating rate, final pyrolysis temperature and residence time (table 1). Alternative causes for example pressure, pyrolysis medium and catalysts will make a difference on the product yield. Besides, previously mentioned factors also pyrolyzer design and the physical and chemical properties of biomass are crucial factors. (Basu 2018, 165)

TABLE 1. Typical product yield and parameters of different pyrolysis type (Ahmad et al. 2014, 21; Bolan et al. 2013, 585, modified)

Process	Temperature (°C)	Residence time	Products		
			Liquid (%)	Solid (%)	Gas (%)
Fast pyrolysis	300–1000, typically ~ 500	Short (<2 s)	75	12	13
Intermediate pyrolysis	~ 500	Moderate (10–20 s)	50	25	25
Slow pyrolysis	100–1000 typically ~ 400	Long (5–30 min to hours)	30	35	35

1.2 Feedstock and products

Solid fuels as feedstock can be divided roughly into to non-renewable and renewable. Feedstock reviewed on this thesis is biomass, which is renewable feedstock. Biomass is plant or animal derived organic material. Biomass forms by the synergy of carbon dioxide (CO_2), water, air, soil and sunlight with plants and animals. Common sources are related to agricultural, forest, municipal (e.g. sewage sludge, food waste and wastepaper), energy crops (e.g. poplars, willow, and corn) and biological (e.g. animal waste, aquatic species, and biological waste). Biomass comes from variety of sources and it can also be classified to virgin biomass and waste biomass. (Basu 2018, 49–50, 54)

Considerable part of biomass used is lignocellulose and classification of lignocellulosic biomass is visible in the table 2. Lignocellulosic material refers to part of the plant that is nonstarch and fibrous. Lignocellulosic biomass dominant components are cellulose (40–50 %), hemicellulose (20–40 %) and lignin (10–40 %) (Chemerys & Baltrėnaitė 2018, 22). Cellulose is the primary component of biomass cell walls. It is main component for example in wood, cotton, and many other plants. Structure of cellulose is strong, crystalline, and hydrolysis resistant. Hemicellulose contains variations in the composition among different biomass. Structure is described as random and amorphous without strength properties. Hemicellulose has the tendency to produce less tar and more gases than cellulose. Lignin is very insoluble even in sulphuric acid and it is the strengthening agent for holding cellulose fiber cells together. (Basu 2018, 55, 61–63)

TABLE 2. Categorization of lignocellulosic biomass (Yaashikaa et al. 2019, 3)

Lignocellulosic biomass	Examples
Agricultural residues	straw, sugarcane, bagasse, and husk
Forest residues	roots, bark, wood chips, and sawdust
Herbaceous biomass	switchgrass, and elephant grass

Pyrolysis products are categorized into liquid (water, tars, and heavier hydrocarbons), solid (mainly biochar) and gas (e.g. CO_2, H_2O, CO, C_2H_2, C_2H_4, ethylene, ethane, propylene, propane, and butane). Pyrolysis liquid product is better known as biooil, tar or biocrude. Biooil is tarry black fluid that contains mainly of homologous phenolic compound and up to 20 % water. Biooil is produced by simultaneous and fast fragmentation and depolymerization of cellulose, hemicellulose, and lignin. Solid yield of pyrolysis is biochar, which is introduced in detail in the chapter 2. Primary decomposition of biomass produces gases that are condensable gases (vapor) and noncondensable gases (primary gas). Vapors will condense on cooling part and will add the yield of liquid. Figure 4 shows biomass particle in pyrolysis process and its products after pyrolysis. (Basu 2018, 160–162; Abou Rjeily et al. 2021, 3)

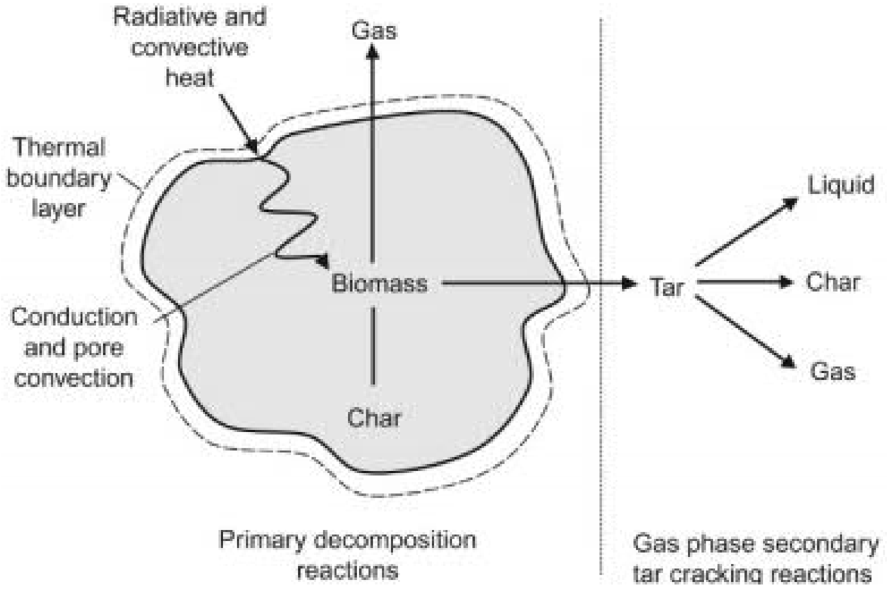
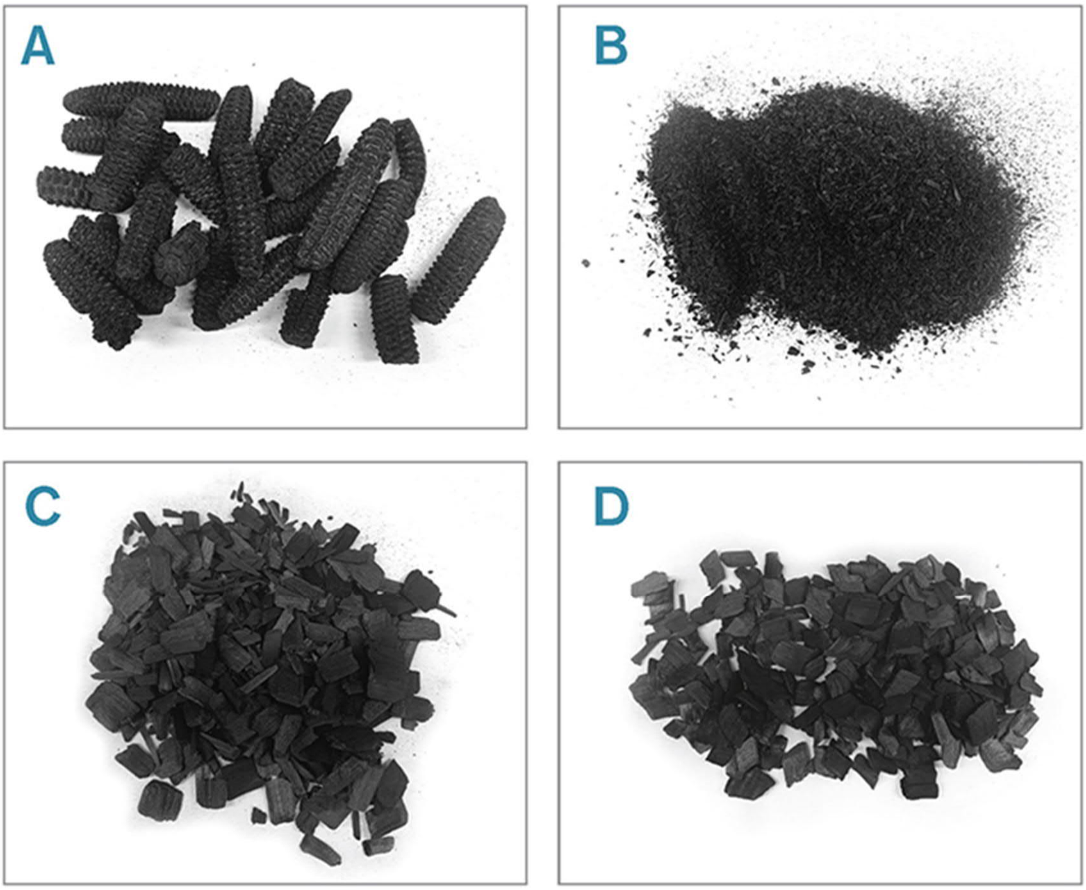


FIGURE 4. Biomass particle in pyrolysis process (Basu 2018, 159)

2 BIOCHAR

Biochar is a solid product of thermal decomposition of biomass and a product in the biorefinery concept. Picture 1 shows biochar appearance from different feedstocks. Biochar is mostly known as a great soil amendment or fuel. Rather than burning entirely forest residues or agricultural products that releases the entire carbon to the atmosphere, production of biochar retains that carbon partially in a solid form. Pyrolysis provides efficient biochar production as the harmful volatiles are not released straight to the atmosphere while producing chemicals and energy feedstock. Biochar also, has a growing importance in carbon sequestration. (Basu 2018, 184; Jeguirim & Limousy 2019, 63)



PICTURE 1. Biochar from different feedstocks: A. corncob, B. manure, C. poplar wood and D. birch wood (Larson & Sandford 2020)

Biochar can be produced either in large scale industrial facilities or individual small scale farms. History shows that biochar has been used in many different pre-industrial cultures for example added to the soil or for filtration. Biochar utilisation possibilities have multiplied through developed technology (figure 5). It is essential to understand the structure, texture, and chemical composition of biochar to be able to exploit it. (Schmidt & Wilson 2014) Figure 5 shows also primary and secondary properties of biochar. Primary properties are influenced direct by process conditions and feedstock and secondary properties are factors of primary properties.

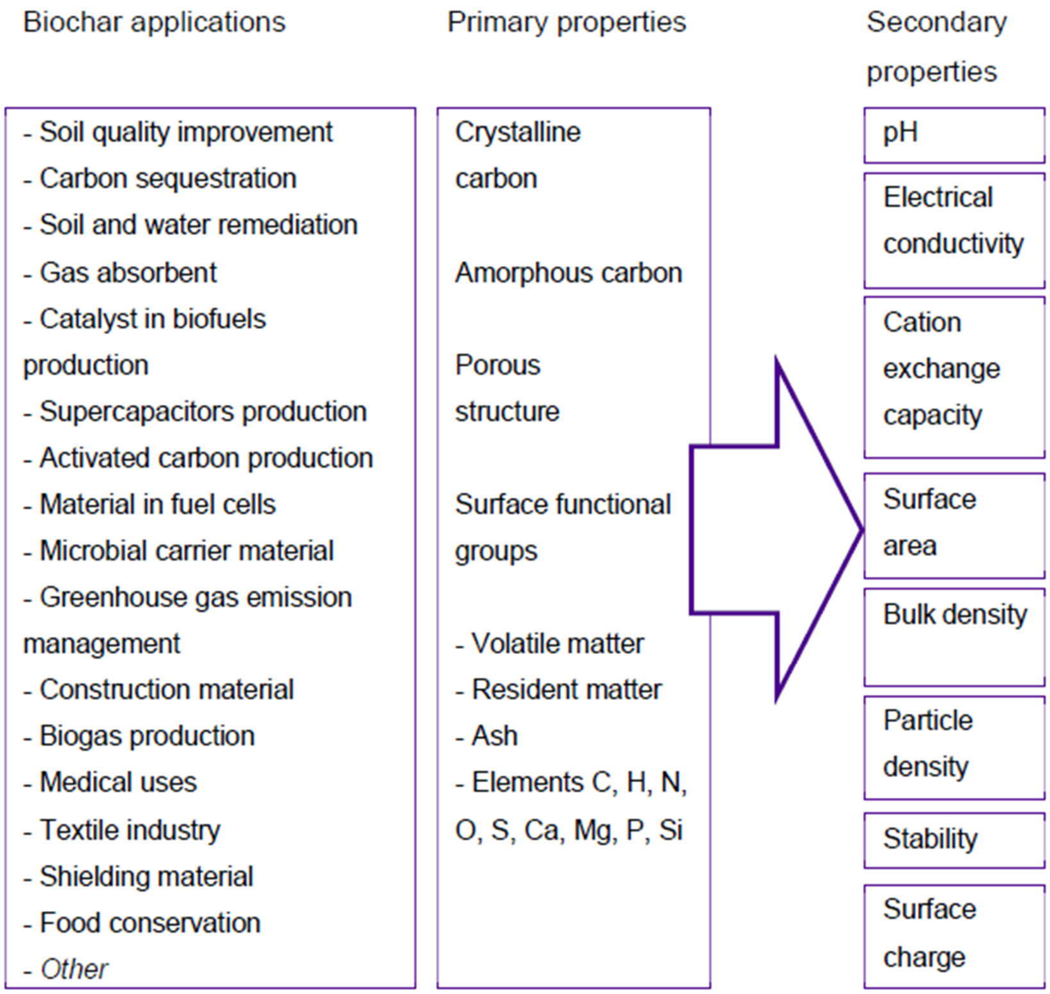


FIGURE 5. Biochar applications and properties in general (Igalavithana et al. 2017, 2276, modified)

2.1 Utilisation

Part of biochar attractiveness is that it is low-cost and sustainable material choice for replacing other materials from petrochemical or other chemical processes. Application possibilities are all the time further developed, but already it can be used in many different applications. (Qian et al. 2015, 1057) Different utilisation possibilities and their focal points in biochar properties are presented in the table 3.

Traditional application of biochar is for soil improvements, carbon sequestration in water/soil and soil remediation. Large portion of biochar is used for the cascaded use of biochar in animal farming. These uses are for example, silage agent, feed and litter additive, slurry, manure, and water treatment. Other traditional application is as a soil conditioner. These uses are for example, carbon fertilizer, additive, substitute for peat, plant protection and fertilizer for trace elements. (Schmidt & Wilson 2014; Igalavithana et al. 2017, 2277) Requirements for soil improvement from biochar are high pH, high C content, available N and P content, high surface area and porosity. Important properties for biochar applications in soils are also, electrical conductivity (EC) and cation exchange capacity (CEC), which affects plant growth and soil microbial communities. Increase in CEC in soil improves its fertility by reducing leaching of nutrients. (Jeguirim & Limousy 2019, 74–75, 130; Igalavithana et al. 2017, 2292)

Next generation applications for example catalyst, supercapacitors, gas absorbent, fuel cell systems, medicinal uses and energy/gas storage are still in development (Igalavithana et al. 2017, 2277). Biochar use as energy storage or in supercapacitors requires high porosity and surface area, EC and CEC and surface chemistry properties (Jeguirim & Limousy 2019, 389). Biochar with high EC, porosity, and stability at low temperatures is good as electrodes material in microbial fuel cells. (Qian et al. 2015)

Applications in the building sector are uses as insulation, air or earth foundation decontamination, humidity regulation or protection against electromagnetic radiation. Decontamination uses for biochar are as soil additive for soil remediation and soil substrate. Also, it is considered in biogas production as a additive or in slurry treatment. Water treatment includes biochar use as an active carbon filter, pre-rinsing additive, micro-filters, or macro-filters in developing countries. Other industrial uses include biochar use in exhaust filters, materials for example carbon filters or plastics, electronics, metallurgy, cosmetics paints and colouring and energy production for example pellets or substitute for lignite. (Schmidt & Wilson 2014) In combustion important biochar properties are volatile matter (VM), fixed carbon, and ashes. If biochar has low content in volatiles, it will not ignite. If biochar has high volatile percentage combustion will start to release smoke and bad odours. (Jeguirim & Limousy 2019, 78) In chapter 3 biochar utilisation in metallurgy and as a catalyst are discussed in detail.

TABLE 3. Important focal points of biochar characterization in different applications (Igalavithana et al. 2017, 2213, modified)

	Biochar properties											
	Proximate analysis			Elemental analysis								
	Moisture	VM	Ash	C,H,O, N,S	In ash	pH	EC	CEC	Surface area	Bulk density	Porosity	Surface functional groups
Soil quality improvement	+	+++	+++	+++	+++	+++	+++	++	+	(+)	(+)	+
Soil carbon sequestration	+++	+++	+++	+++	++	+++	+++	+	+++	(+)	(+)	+++
Soil and water remediation	+++	+++	+++	+++	++	+++	++	+++	+++	(+)	(+)	+++
Catalyst in biorefinery	++	+++	+++	+++	+++	+	(+)	(+)	+++	+	+++	+++
Super capasitor production	nk	+++	+++	+++	nk	(+)	(+)	nk	+++	(+)	+	+++
Acticated carbon production	+++	+++	+++	+++	++	(+)	(+)	(+)	+++	(+)	(+)	+++
Material in fuel cells	++	+++	+++	+++	(+)	(+)	(+)	(+)	+++	(+)	+	+++
Green house gas management	+	+++	+	+++	+	+++	nk	+	+++	+	(+)	+++
Construction material	++	+++	+++	+++	nk	nk	nk	nk	+++	+++	+++	nk
Analysis requirements: + = low, ++ = medium, +++ = high, (+) = not essential, nk = not known												

2.2 Characteristics of biochar

Biochar characterization is always dependent on the used feedstock and production methods, conditions, and different properties of the end-product. Biochar characterization can be divided in several different ways. In this thesis characteristics are divided into proximate and elemental analyses and to physicochemical properties (figure 6). (Igalavithana et al. 2017, 2277

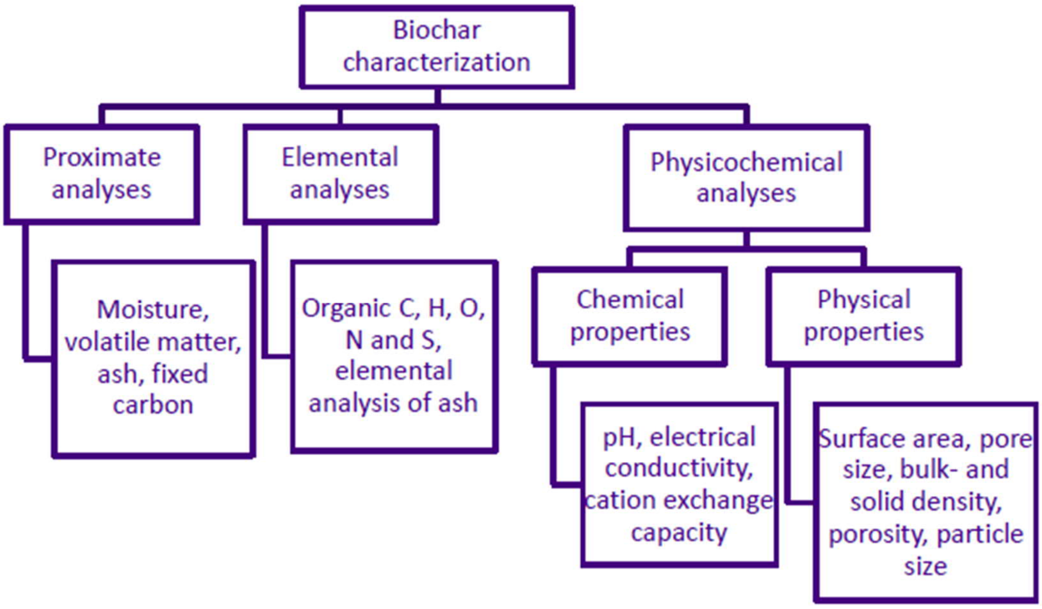


FIGURE 6. Graphical overview of biochar characterization (Igalavithana et al. 2017, 2281, modified)

2.2.1 Proximate and elemental analyses

Proximate analysis includes mass percentages of volatile matter (VM), fixed carbon/resident matter, moisture, and ash content in biochar. Elemental analysis of biochar primary focuses on element and chemical compounds. Main concerns are amounts of carbon C, hydrogen H and oxygen O and minimal amount of nitrogen N and sulfur S. Mostly the amount of S is negligible and N content of biochar is often very low (higher in high N content feedstock). (Igalavithana et al. 2017, 2286)

O/C and H/C ratios give information of biochar structure and low ratios indicate good stability of biochar. Spokas (2010, 296) claims that biochar with less than 0.2 O/C ratio are most stable and have a half-life of 1000 years and O/C ratio greater than 0.6 obtains a half-life of <100 years. Low H/C ratio means high stability and fused aromatic ring structures in biochar. Oxygen content indicates biochar surface chemistry behavior, which is in close relationship with functional groups, which are important driver for degradation potential. (Leng & Huang 2018, 628–629)

Biochar ash composes of minerals and therefore it is included also in the elemental analysis. Biochar ash is divided into acid-soluble and acid-non-soluble ash. Dimension of these fractions is dependent on the feedstock for example, lignocellulosic derived biochar has high percentage of acid-soluble ash (0.5–25 %) rather than acid-non-soluble (0–8 % of biochar composition). (Igalavithana et al. 2017, 2287) Biochar contains different mineral impurities e.g. Ca, K, P, Si, Mg, Na, Fe and Zn. Biochar ash is reported as these minerals and they can be beneficial, for example in catalytic applications, but also limit applications possibilities as minerals can block the biochar pore structure (Ohra-aho et al. 2020, 2). Minerals influence the C content and distribution in the surface and bulk of biochar. Biochar ash content is correlated positively to alkalinity but faintly to pH. (Jeguirim & Limousy 2019, 71, 75) In the table 4 are mineral contents of pine, birch and willow biochar. Willow biochar contains more K, Ca and P than pine and birch due to willow being unbarked that was used as a feedstock. For the same biochar elemental analysis results are visible in the chapter 4.2.

TABLE 4. Minerals content of wood derived biochar from fast pyrolysis in BFB pyrolyzer at 480°C with residence time of 0.8 s (Ohra-aho et al. 2020, 5)

	Ca	Mg	Na	K	P	S	Fe	Si
Pine mg/kg	3800	970	150	3500	530	130	460	280
Birch mg/kg	5900	1700	97	5100	640	110	160	100
Willow mg/kg	10,300	2100	530	17,400	4900	500	240	360

2.2.2 Physicochemical properties

The pH of biochar is essential property. Commonly it is reported to be alkaline (pH>7), but range can vary from acidic to alkaline (pH ~ 4–12). Biochar can be a buffer toward pH changes and after addition to the pH it rebounds to the original level and after that (2 h) stabilize to the new value. Electric conductivity (EC) in biochar is due to its water-soluble ions. It is a measurement of biochar salinity. EC is dependent on biochar porous structure, surface area and crystalline C structure. CEC measures negative charge of biochar that exchangeable cations can neutralize. (Jiang et al. 2013, 482; Igalavithana et al. 2017, 2290–2292; Jeguirim & Limousy 2019, 74)

Surface properties include surface area, charge density, pore structure and distribution. Porosity together with pore volume and distribution is important because it influences directly to so many other properties such as density, mechanical stability, CEC, and water uptake of biochar. Development of micropores (<2 nm) makes the greatest contribution to total surface area (Ok 2019, 22). Surface area is often measured by Brunauer–Emmett–Teller (BET) surface area method. Functional group chemistry causes the surface properties of biochar. Functional groups include for example, phenolic, carboxylic, aliphatic, amine and aromatic functional groups. These functional groups and their direct interaction with other chemical and surfaces create surface properties. (Li et al. 2013, 1; Igalavithana et al. 2017, 2296)

Biochar density is essential physical property that can be categorized into solid density and bulk density. Ratio between solid volume to weight is called solid density and it is associated with biochar C structure and its level of packing. The ratio of total volume to weight is bulk density. It is related to porosity and particle size and weight. Particle size distribution affects greatly to physicochemical properties of biochar. For example, volatile matter, ash content, pH, and water holding capacity of biochar are influenced by its particle size distribution. (Igalavithana et al. 2017, 2295–2296; Liao & Thomas 2019, 2)

2.3 Factors affecting properties

During pyrolysis process the reaction conditions are in key role for production of biochar. Previous characteristics are influenced mostly by temperature, type of biomass, and reaction time. Process parameters like particle size, processing time, heating rate, and temperature does not affect only on the biochar properties but also control the yield. Yield of biochar in pyrolysis process is highly dependent on feedstock, pyrolysis type and processing temperature. (Amin et al. 2016, 1460; Basu 2018, 185)

2.3.1 Pyrolysis type

Main parameter impacting the properties of biochar is pyrolysis temperature. Pyrolysis temperature contributes to properties like surface area, surface charge pH, carbon content, stability, and volatile fraction. Increase in pyrolysis temperature will decrease the biochar content of hemicellulose, cellulose, lignin, and others such as protein, polysaccharide, and other macromolecules, which will create changes in biochar. (Ahmad et al. 2014, 25; Li et al. 2020, 4)

Biochar produced by slow pyrolysis has higher C content, lower ash content, lower surface area and larger particle size than fast pyrolysis biochar (Chang et al. 2019, 589). Long residence time is optimal for great biochar yield due to longer residence time of volatiles. Hodgson et al. (2016) noticed that increase in residence time (120–360 min) decreases total carbon production but increase the fixed carbon content. Residence time affects surface area and porosity of biochar, trend is that at first it increases and after hours it can start to decrease. (Jeguirim & Limousy 2019, 45) Fast pyrolysis biochar have finer structure than slow pyrolysis biochar due to rapid change in the reactor. Biochar produced by fast pyrolysis hold higher grade of thermal modification which its low C and H ratio is an indication of. (Amin et al. 2016, 1461)

Low pyrolysis temperature results in greater amount of solid char. Yield decreases are seen in the tables 4 and 5 in which drastic decreases are seen in lower temperatures and more modest decreases between higher temperatures.

Finding is due to a fact that devolatilization and decomposition of biomass takes place around at 250–400°C. (Wang et al. 2017, 492) Biochar produced in low temperatures has high acidity, high polarity, low aromatic content, and hydrophobicity (Li et al. 2020, 4).

Biochar pH increases as the pyrolysis temperature increase due to removal of acid functional groups (–COOH, –OH) and mineral separation from the biochar. Electric conductivity also increases as pyrolysis temperature increases, but mainly EC of biochar is affected by the choice of feedstock. Loss of acidic surface functional groups will also decrease volatile matter and cation exchange capacity. (Jeguirim & Limousy 2019, 71–72)

High temperatures yield less biochar than low temperatures (figure 7). As pyrolysis temperature increases biochar heating value increases. Heating value tells how much heat will release during combustion. Fixed carbon content, which has high heating value will increase as temperature increases, while at the same time volatile content of biochar decreases. High temperatures decrease H and O content of biochar, which results in low H/C and O/C ratio. High temperature biochar can contain higher concentrations of condensed aromatic carbon when low temperature produced biochar may contain remnants of biopolymers (Chu et al. 2018, 3). High pyrolysis temperatures typically produce biochar that are good in the sorption of organic materials as it increases surface area, micro-porosity and hydrophobicity (Ahmad et al. 2014, 27; Basu 2018, 166, 184). Toloue Farrokh et al. 2020 found that until to 500 °C pyrolysis temperature moisture absorption capacity of biochar decreased compared to raw material but after that it started to increase again.

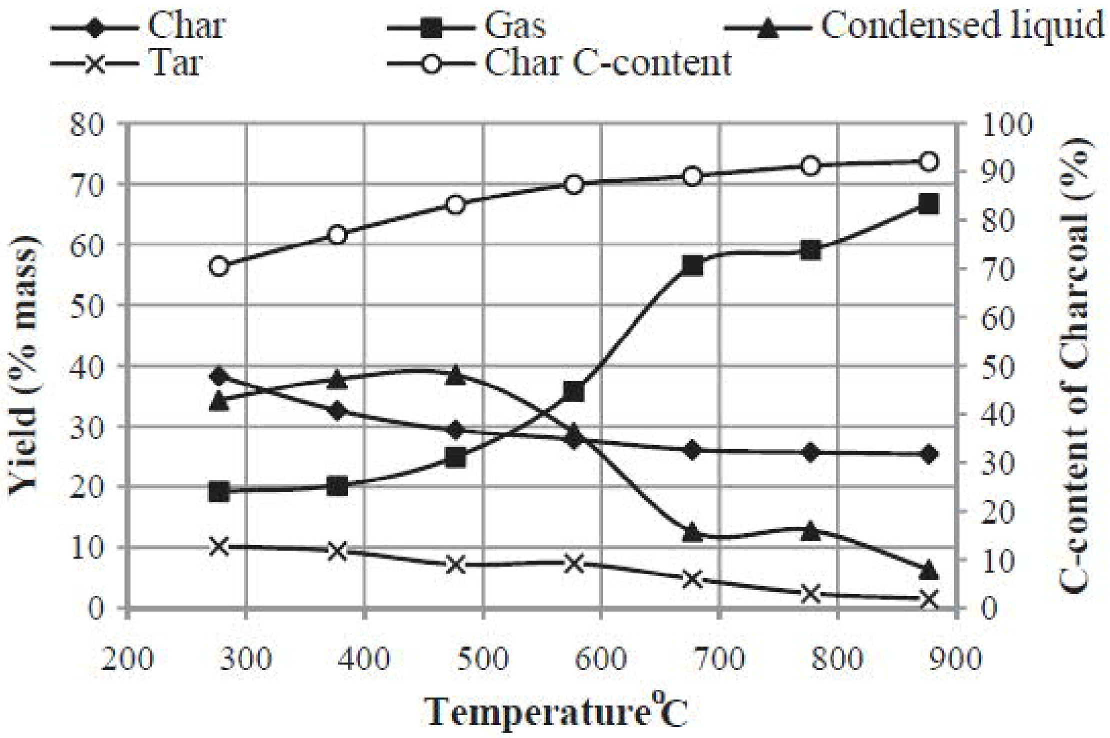
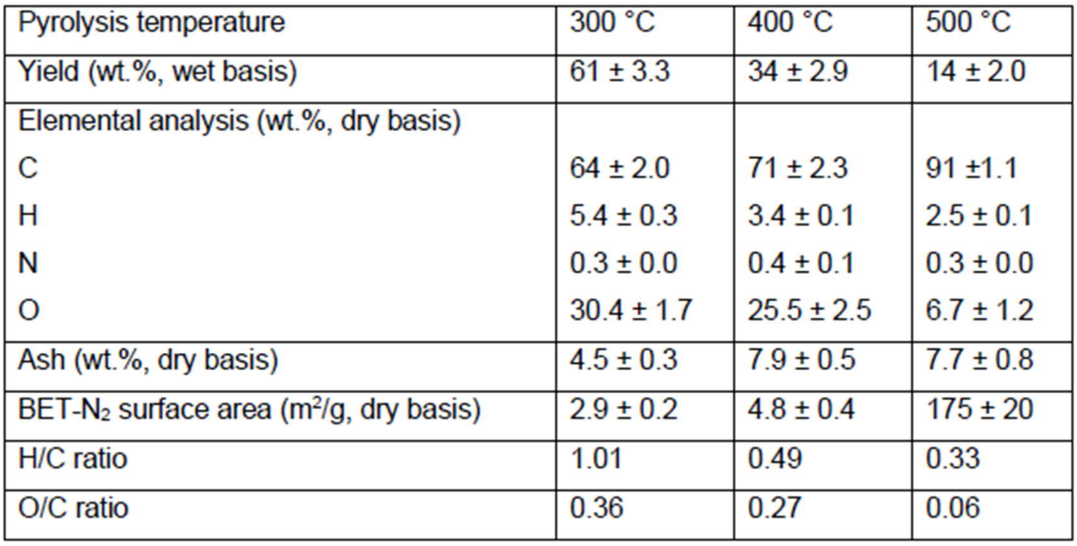


FIGURE 7. Yield % (dry basis) of product from slow pyrolysis and C content of biochar. C-content it the total carbon content of the char (Suopajärvi et al. 2013, 516; data from Demirbas, 2001)

Surface area is found to increase in higher temperatures with the release of volatiles from biomass, but with continuous increase of temperature bulk density will start to decrease. Bulk density increase occurs because structure experiences densification and shrinkage. Low bulk density is result of asymmetrical and shape of the biochar particles. Microporosity develops with high temperatures and long residence time (Ok 2019, 25). Biochar produced at 700 °C or higher temperatures may possess a lower surface area. It has been reported that at extremely high temperatures (>900 °C) microporous structure changes will lead to a reduction of surface area. (Li et al. 2020, 4; Toloue Farrokh et al. 2020, 4)

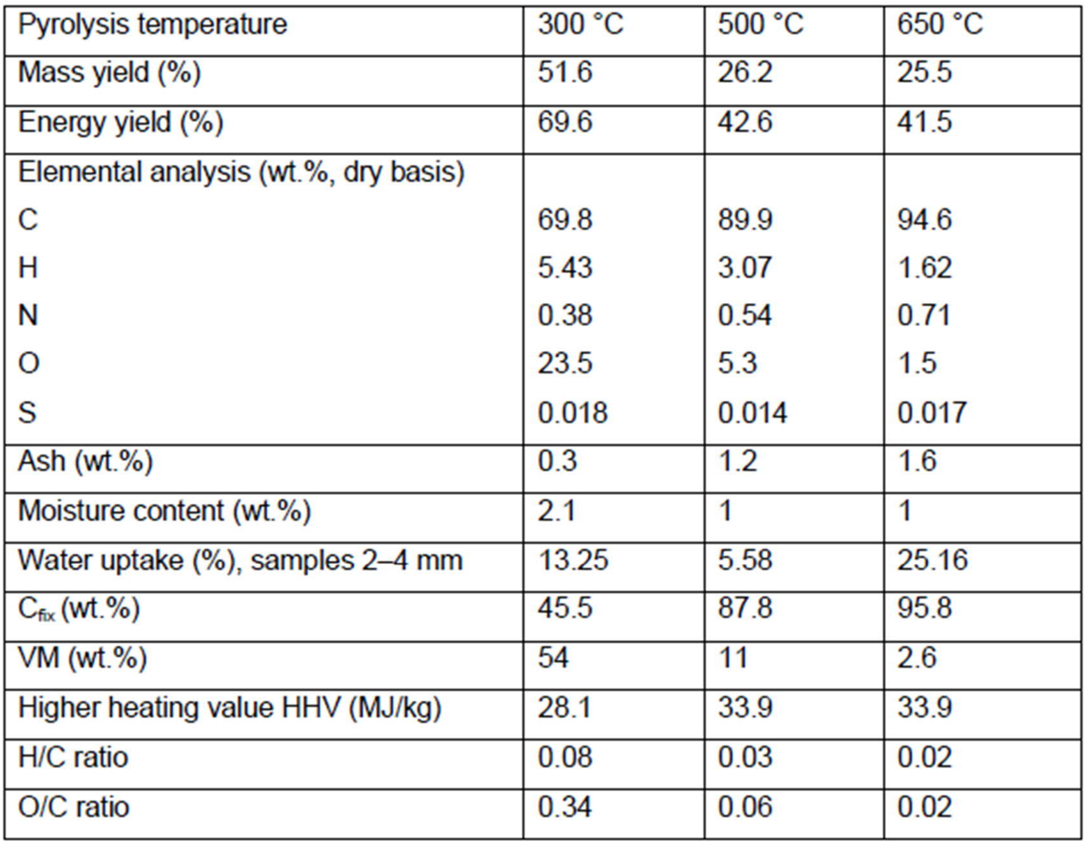
Table 5 and 6 can be used to compare possible differences in pyrolysis temperature, slow/fast pyrolysis, or woody feedstock (hardwood/softwood). In the table results pyrolysis occurs at the same heating rate of 5 °C min^{-1} under N_2 (200 mL min^{-1}). Residence time in slow pyrolysis is 8 h and in the fast pyrolysis it is 2 s. These lab-scale studies support the theory presented in this chapter. Gathered results on pyrolysis temperature effects on characteristics are on the table 7.

TABLE 5. Biochar collected from fast pyrolysis of pitch pine wood chips in different temperatures (Kim et al. 2012, 160)



Pyrolysis temperature	300 °C	400 °C	500 °C
Yield (wt.%, wet basis)	61 ± 3.3	34 ± 2.9	14 ± 2.0
Elemental analysis (wt.%, dry basis)			
C	64 ± 2.0	71 ± 2.3	91 ±1.1
H	5.4 ± 0.3	3.4 ± 0.1	2.5 ± 0.1
N	0.3 ± 0.0	0.4 ± 0.1	0.3 ± 0.0
O	30.4 ± 1.7	25.5 ± 2.5	6.7 ± 1.2
Ash (wt.%, dry basis)	4.5 ± 0.3	7.9 ± 0.5	7.7 ± 0.8
BET-N_2 surface area (m^2/g, dry basis)	2.9 ± 0.2	4.8 ± 0.4	175 ± 20
H/C ratio	1.01	0.49	0.33
O/C ratio	0.36	0.27	0.06

TABLE 6. Effect of slow pyrolysis temperature on biochar properties from birch wood chips (Toloue Farrokh et al. 2020, 4)



Pyrolysis temperature	300 °C	500 °C	650 °C
Mass yield (%)	51.6	26.2	25.5
Energy yield (%)	69.6	42.6	41.5
Elemental analysis (wt.%, dry basis)			
C	69.8	89.9	94.6
H	5.43	3.07	1.62
N	0.38	0.54	0.71
O	23.5	5.3	1.5
S	0.018	0.014	0.017
Ash (wt.%)	0.3	1.2	1.6
Moisture content (wt.%)	2.1	1	1
Water uptake (%), samples 2–4 mm	13.25	5.58	25.16
C_{fix} (wt.%)	45.5	87.8	95.8
VM (wt.%)	54	11	2.6
Higher heating value HHV (MJ/kg)	28.1	33.9	33.9
H/C ratio	0.08	0.03	0.02
O/C ratio	0.34	0.06	0.02

TABLE 7. Characteristics of biochar depending on the pyrolysis temperature (Li et al. 2016, 3272; Ahmad et al. 2014, 25) Arrow indicates if characteristics is at a lower or higher level in two different temperatures.

Pyrolysis temperature	Low (~300 °C)	High (~500 °C)
Yield	↑	↓
C	↓	↑
H	↑	↓
O	↑	↓
Ash content	↓	↑
Surface area	↓	↑
pH	↓	↑
C_{fix}	↓	↑
VM	↑	↓
Heating value	↓	↑
Porosity	↓	↑
Moisture absorption	↓	↑
Polymerization degree	↓	↑
Graphite degree	↓	↑

Heating rate adjusts biochar porosity and surface area. It is important in controlling the yields of pyrolysis products. Relatively low heating rate minimised decomposition process, which is the reason for higher biochar yield. Favourable for construction of aromatic structures in biochar is low heating rate. (Leng & Huang 2018, 638; Li et al. 2020, 5) Biochar collected at high heating rates have high O content and low caloric value (Chu et al. 2018, 3).

Decomposition rate increases as pyrolysis pressure expanses the retention time of pyrolysis steam. Development in the pyrolysis pressure (5, 10 and 20 bar under normal pressure) will raise the biochar particle size and decrease biochar activity. Increase in pressure will decrease surface area due to clogging of pores with trapped tar. Pressurized pyrolysis will most likely stabilize the production and increase the yield of biochar. (Li et al 2020, 5; Jeguirim & Limousy 2019, 45)

If target is only to maximize high char yields following biochar conditions are preferred; high lignin content and N content in biomass, low moisture content, pyrolysis temperature below 400 °C (note lower fixed C content), elevated process pressure (1 MPa), long vapor residence time, low heating rate, large biomass particle size and efficient heat transfer to feedstock. (Jeguirim & Limousy 2019, 44)

2.3.2 Feedstock

Type of biomass feedstock affects properties, for example porosity, surface area and surface function. Lignocellulosic biomass composes primarily from cellulose, hemicellulose, and lignin, which are in contact during pyrolysis. Decomposition of components occurs in different temperatures, which affects biochar properties greatly. Moisture content of biomass affects biochar due to high energy and temperature requirements for decomposition and increases the energy demand of the process (Yaashikaa et al. 2019, 4). Hemicellulose degrades easily at pyrolysis temperature 220–315 °C and cellulose at 315–400 °C. Lignin is more challenging to decompose and the temperature range is from 160–900 °C (typical ~500 °C). (Li et al. 2020, 2; Yang et al. 2007, 1787)

Porous structure of biochar is improved by high loss rate of cellulose. Raw material with high lignin content is e.g. woody biomass from softwood (pine and spruce), biomass from agricultural (e.g. corn stover, sugarcane bagasse) or forest residues (e.g. branches, leaves) are cellulose rich and rich in lipid (>10 %) are especially aquatic biomasses e.g. microalgae (figure 8). Woody biomass and biochar derived from that are rich in lignin and resemble the structure of raw wood with upright micro-channels and fibrous crinkled surfaces. According to Da et al. (2017) cellulose-rich biomass favours graphitic structure biochar. In slow pyrolysis softwood yielded ~5 % more char than hardwood due to higher lignin content. (Jeguirim & Limousy 2019, 15; Suopajärvi et al. 2018, 389)

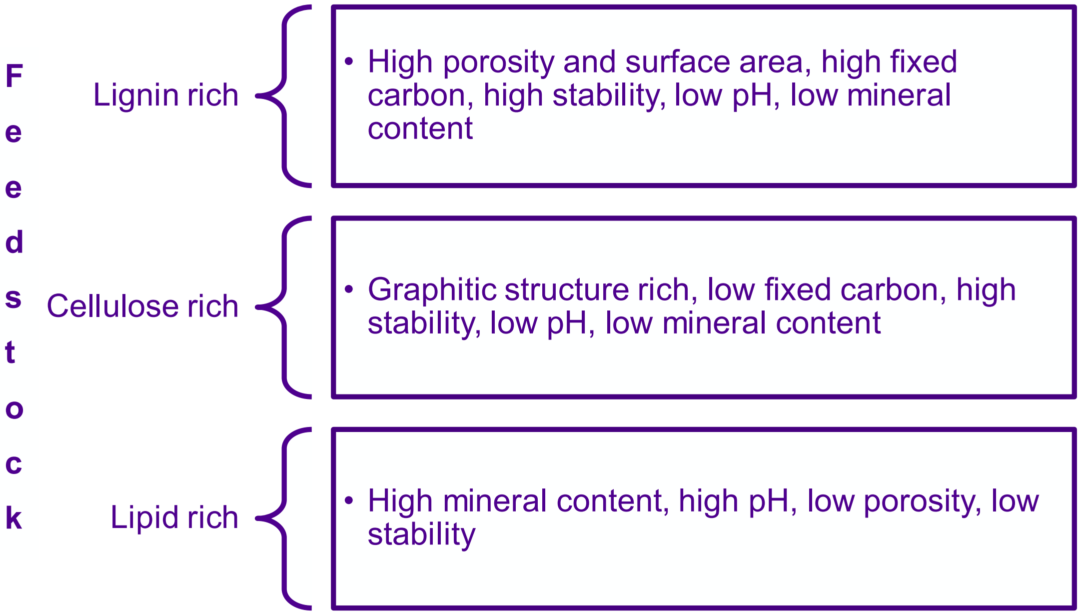


FIGURE 8. Biochar properties by the influence of feedstock (Kumar et al. 2020, 5, modified)

Lignocellulosic biomass has typically higher O, C, and H content but lower N content compared to marine algae. Algae and crop residue derived biochar has poor stability, high pH and ash content compared to wood-based biochar. N-content in biochar is highly dependent on the feedstock and cannot be affected greatly by the pyrolysis process conditions (Ahmad et al. 2014, 25). High mineral content of feedstock results in high pH, and low porosity of biochar. High ash content is problematic as a property of biochar for example, it can block the biochar micropores. (Kumar et al. 2020, 4–5)

Biochar ash content is exceptionally dependent on feedstock. Usually softwood biochar has low ash content, hardwood biochar has intermediate ash content and corn and wheat stover biochar has rather high ash content. (Li et al. 2020, 2–4) Xu et al. (2017) indicates that ash content is 3–4 higher for grass chars than woody chars due to higher content of K, Ca, and Mg in grass biomass. High ash content in raw material biomass prevents the formation of polycyclic aromatic carbon (PAH), which will result in unstable biochar. Li et al. (2017) conducted a study of fast pyrolysis and the feedstock sensitivity of biochar. They summarized that as ash content of biomass increases it will add to biochar yield. (Li et al. 2017, 961; Li et al. 2020, 2–4)

2.3.3 Upgrading methods

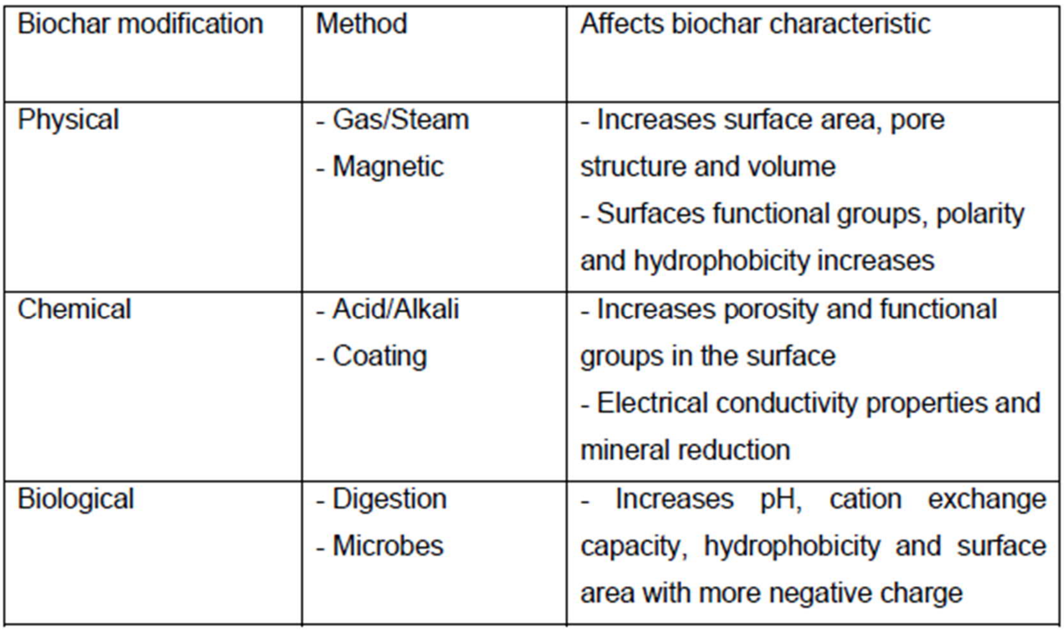
Several modification methods have been developed to broaden biochar utilization possibilities. Pre- and post-treatments of biochar are done to enhance or minimize certain properties that are wanted in an application. Material can be modified in a biological, chemical or physical way (table 8). (Wang et al. 2017, 2160)

Properties like surface area, pore structure and volume can be improved through physical modification. Chemical properties (e.g. functional groups, polarity, hydrophobicity) especially at biochar surface can be enhanced by physical activation. Methods will not need expensive chemicals and the process is simple. Surface area and pore volume is build up by modifying with gas such as oxygen, carbon dioxide, or nitrogen. Also, carbon content was increases when using oxygen gas instead of nitrogen. Steam applied to carbon surface will produce carbon dioxide and hydrogen and the released gas assists the biochar upgrading. When volatile compounds are removed the pores will increase. Essential parts in steam modification are steam, temperature and time. (Yaashikaa et al. 2019, 4–5)

Biochar chemical activation is either done chemically to biomass before pyrolysis or after pyrolysis to biochar. Chemically activated biochar has better porosity, more surface functional groups, anion/cation exchange properties and mineral reduction. Acid treatments include adding acids like sulfuric or phosphoric acid, or inorganic salts and hydroxides. Chemical modification does not require that much time but are more expensive than physical modification. (Yaashikaa et al. 2019, 5)

Biological modification means that the feedstock used is biologically pretreated biomass. Feedstock can be modified through bacterial conversion or through anaerobic digestion. After anaerobic digestion of biomass and pyrolysis of it will result in an increase of pH, CEC, hydrophobicity and surface area. (Wang et al. 2017, 2160; Yaashikaa et al. 2019, 6)

TABLE 8. Typical biochar upgrading methods (Yaashikaa et al. 2019, 4)



Biochar modification	Method	Affects biochar characteristic
Physical	- Gas/Steam - Magnetic	- Increases surface area, pore structure and volume - Surfaces functional groups, polarity and hydrophobicity increases
Chemical	- Acid/Alkali - Coating	- Increases porosity and functional groups in the surface - Electrical conductivity properties and mineral reduction
Biological	- Digestion - Microbes	- Increases pH, cation exchange capacity, hydrophobicity and surface area with more negative charge

3 QUALITY REQUIREMENTS FOR DIFFERENT PURPOSES

3.1 Steel and iron production

Steel production can be considered as a carbon and energy intensive industry with total of 5–7 % of the universal CO_2 emissions. Decarbonization of the steel and iron industry is under development. Biomass and biochar have been detected as a possible raw material for replacement of different fossil-based reducing agents in the steel and iron industry (Babich & Senk 2013, 57). Currently coal and coke are the most popular reducing agents used in metallurgy. (Suopajärvi et al. 2017, 710)

3.1.1 Blast furnace injection

Technologies to produce iron and steel are divided into four categories: blast furnace/basic oxygen furnace (BF-BOF route, figure 9), melting of recycled scrap in an electric arc furnace (mini mill route), direct reduction iron/electric arc furnace and smelting reduction/basic oxygen furnace. The most used method for steel production (70 % worldwide) is BF-BOF route, which is also called integrated steel production. Mini mill route accounts of 25 % of global steel production and other two method are not commonly used. (Suopajärvi et al. 2018, 385)

Parts of an integrated steel plant are cokemaking, sintering, BF, BOF, continuous casting, hot and cold rolling. Main process part of integrated steel production is the BF. It produces hot metal by reducing and melting iron oxides with reducing agents. Inputs at the top of the BF are iron-bearing burden, coke and flux while at the lower part injected through tuyeres are reducing agents and hot blast. Outputs of BF are liquid metal and slag and off-gases. The most used reducing agents in the process are metallurgical coke and pulverized coal (PC), but also natural gas or oil can be used. As an iron source in the process are pellets and sinter. These ironmaking processes (sintering, cokemaking and BF) produce 90 % of the CO_2 emissions of the end-product (hot rolled coil). (Suopajärvi et al. 2017, 711; Suopajärvi et al. 2018, 386)

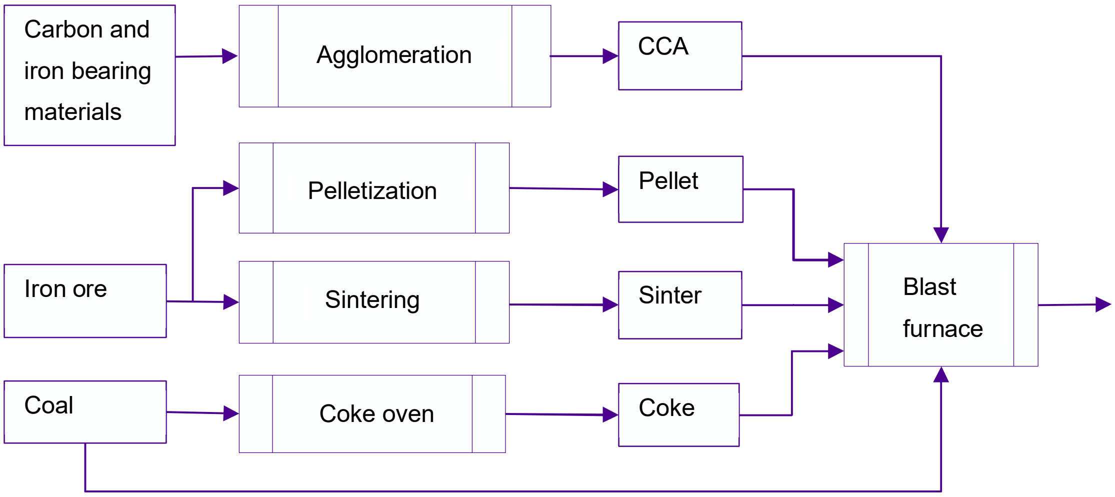


FIGURE 9. BF-BOF route production processes before BF (Hasanbeigi et al. 2014, 647, modified)

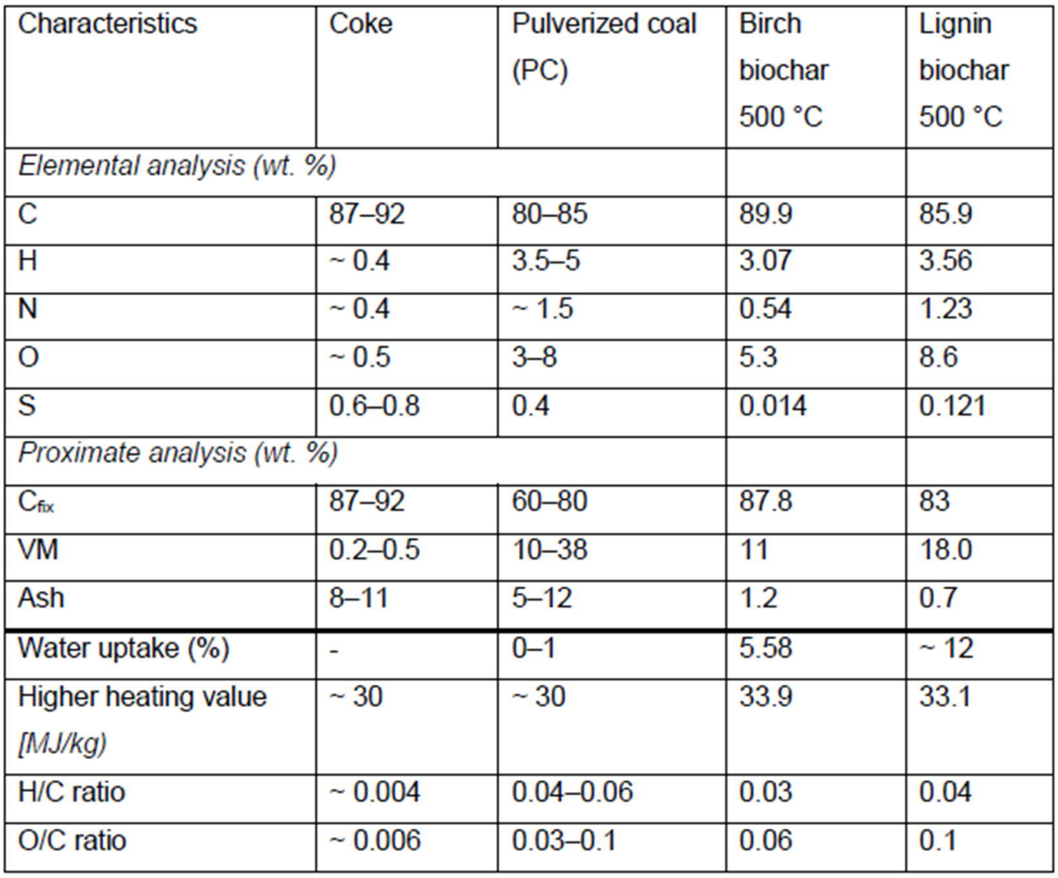
Biochar injection to the blast furnace (BF) has the largest potential in reducing the use of fossil-based reducing agents. Currently pulverized coal (PC) is used to partially replace expensive metallurgical coke injection to BF, but biochar has been found suitable for even 100 % replacement of injected PC and with a higher coke replacement ratio than PC. (Suopajärvi et al. 2018, 394; Suopajärvi et al. 2017; 729)

3.1.2 Biochar quality requirements

Regarding metallurgical processes most suitable raw material is wood-based biomass. Woody materials have more homogeneous composition than herbaceous biomass. Stem wood-based materials tend to have low ash and sulphur content at attainable level. Also, harmful elements on iron and metal industry like K, Na and P are often at a low level. Biomass use in metallurgy without upgrading it is not useful. Raw biomass requires upgrading because properties such as high moisture content, low heating value, low fixed carbon, grindability or unwanted inorganic elements (e.g. Na, K, S, Cl, P) are not at a feasible level to use as a reducing agent in metallurgy. Pyrolysis as thermochemical conversion method will convert biomass into biochar, which has much of the wanted reducing agent properties for example lower oxygen content in char leads to an increase in heating value. (Suopajärvi et al. 2018, 387; Suopajärvi et al. 2013, 515)

Important parameters for reducing agent injected to BF are ignition, reactivity chemical composition, and physical properties (e.g. particle size) (Suopajärvi et al. 2017, 721). Chemical properties of biochar are crucial for the BF process behaviour. (Suopajärvi et al. 2013, 516) In table the 9 are properties of two most used fossil-based reducing agents. Especially PC values can be used in comparison of wanted biochar properties.

TABLE 9. Typical properties of blast furnace reducing agents and biochar from birch chips and lignin in slow pyrolysis of 500°C (Babich et al. 2016, 19; Toloue Farrokh et al. 2020, 4; Toloue Farrokh et al. 2018 116; Geerdes 2015, 46)



Characteristics	Coke	Pulverized coal (PC)	Birch biochar 500 °C	Lignin biochar 500 °C
Elemental analysis (wt. %)				
C	87–92	80–85	89.9	85.9
H	~ 0.4	3.5–5	3.07	3.56
N	~ 0.4	~ 1.5	0.54	1.23
O	~ 0.5	3–8	5.3	8.6
S	0.6–0.8	0.4	0.014	0.121
Proximate analysis (wt. %)				
C_{fix}	87–92	60–80	87.8	83
VM	0.2–0.5	10–38	11	18.0
Ash	8–11	5–12	1.2	0.7
Water uptake (%)	-	0–1	5.58	~ 12
Higher heating value *[MJ/kg)*	~ 30	~ 30	33.9	33.1
H/C ratio	~ 0.004	0.04–0.06	0.03	0.04
O/C ratio	~ 0.006	0.03–0.1	0.06	0.1

Combustibility of a solid fuel can be evaluated from a measure of higher heating value (HHV). Raw biomass tends to have small HHV (<20 MJ/kg), which will not guarantee auto-thermal combustion (Yousaf et al. 2017, 147). Higher pyrolysis temperature increases biochar HHV due to the formation and elimination of high energy bonds. Energy bonds mean the energy required to break one mole of bond. (Yang et al. 2016, 201). Heating values of birch BC and lignin BC are even higher than pulverized coal or coke (table 10), which indicates their good combustibility.

Applicable solid fuel for blast furnace injection has low O/C and H/C ratio, which will decrease smoke and water vapor formation and energy losses experienced during combustion. Pyrolysis at higher temperatures (>500°C) creates biochar with O/C and H/C ratios like pulverized coal (PC). (Toloue Farrokh et al. 2019, 17) Li et al. 2016 studied biochar made from pristine pine and results indicate that pyrolysis temperature should be above 500°C. O/C ratios of biochar in pyrolysis temperature 500 °C was 0.12 and in 600°C was 0.04. O/C ratio 0.12 is high compared to pulverized coal.

Bulk density increases significantly after grinding (from ~300 kg/m^2 to 600–700 kg/m^2) but still it is ~20 % lower than PC (~800 kg/m^3). Lower bulk density of both biochar can cause insufficient mass flow rates to blast furnace (BF). Bulk density can be affected by higher pyrolysis temperature. Results indicate that biochar is possible to blend with fossil coals for the use in BF injection. Toloue Farrokh et al. 2020, 5)

In char pyrolyzed at 500°C structure is porous and brittle, which indicates good grindability. Char pyrolyzed in 650°C showed reverse behavior in grindability (chars in table 5). As decomposition and devolatilization occurs between 300–500°C, in above that carbonization and bond forming is main reaction resulting in structurally ordered biochar that will not ground easily. Large share of small particles is visible in pulverized biochar pyrolyzed in 500°C and 650°C, which indicates improved grindability compared to particles of biochar pyrolyzed in 300°C, which were acicular in shape indicating poor grindability. (Toloue Farrokh et al. 2020, 5–7)

Moisture absorption in biochar is higher than pulverized coal (PC). The porous structure of biochar increases its high water uptake. Moisture uptake is important for proper char handling and storage solutions. PC´s moisture uptake is 0–1 %

and it can be stored outside due to that. Biochar water uptake is considerably higher and causes limitations to its handling. (Toloue Farrokh et al. 2020, 6)

Biochar are more active compared to fossil coals with the same volatile content. Biomass chars have higher surface area and isotropic disordered physical properties of the material. This creates higher reactivity towards CO_2, which is beneficial in preventing soot formation in BF process. Injection of biochar will decrease slag formation and result in higher production rate, which is based on lower sulphur, ash content and higher content of CaO compared to PC. As slag amount decreases due to basicity of ash it will decrease lime or limestone addition to the BF that is used to control slag. (Suopajärvi et al. 2018, 393; Suopajärvi et al. 2013, 516–517)

Slow pyrolysis biochar has the following advantages in blast furnace use: high heating value, high biochar burnout ratio, low ash content, low S content, high replacement rate of fossil fuels and increased productivity. Disadvantage is how the sufficient mass flow injection is achieved. (Suopajärvi et al. 2013, 524) Suopajärvi et al. (2013) suggest that fast pyrolysis biochar might also have good combustion characteristic.

Harmful elements that enter the process from blast furnace reducing agents are zinc (Zn), potassium (K), sodium (Na), phosphorus (P) and most harmful sulphur (S). Sulphur content is damaging in hot metal and should be removed already in the BF. In metallurgy the amount of ash and content of it are important factors in reducing agents. Pulverized coals tend to have higher content of SiO_2 and Al_2O_3 and woody biochar contain elements that increase basicity e.g. Ca and Mg, which is favourable. The number of alkalis and P in biochar should be as low as possible. Low heating value, high share of oxygen and volatiles, low share of fixed carbon in the biochar will inhibit its use for BF injection. (Toloue Farrokh et al. 2018, 116) Conclusion is that depending on the biochar C content it exceeds PC as a reducing agent in BF injection. (Suopajärvi et al. 2018, 394)

Permeability and lower bulk density of pulverized biochar should be considered when designing efficient pneumatic conveying systems from silos to tuyeres. Low density biochar requires larger storage facilities than pulverized coal. Also, dry storage is required due to high moisture uptake of biochar. Decentralized production is possible, or pyrolysis unit would be possible to integrate in an integrated steel plant. Biochar production is possible to integrate with energy production and steel plants waste heat can be utilised for biomass drying or pyrolysis. (Suopajärvi et al. 2018, 398; Suopajärvi et al. 2017, 728)

Potential markets are available for the use of biochar in steel and iron industry especially as a reducing agent in blast furnace. SSAB Raahe mill conducted trials where 10 % replacement rate of pulverized coal (PC) was successful. Also, lab-scale trials concluded that 20 % of PC can be replaced by slow pyrolysis biochar without any modifications to the process. If Raahe mill replaces 10 % of PC with biochar it would require biochar production of 35 000 tonnes/year. Currently supplier of that scale in Finland is not realistic. Also, hydrogen is currently under research as a substitute of coke. (SSAB, 2019)

3.2 Catalysis in biomass refinery

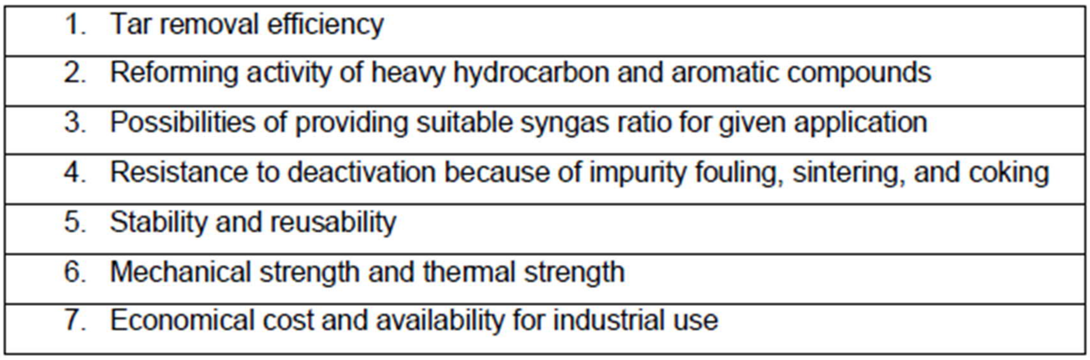
Biochar-based catalyst in biomass refining is thought to be suitable and possibly create more integrated process. It is due to biochar being a by-product or a product of biomass refinery it can improve the economics of its own production process. Biochar different physicochemical properties e.g. surface area, pores, surface functionality, mechanical strength and inorganic species are the reason for its catalytic use. Its basic properties together with great tailoring possibilities makes it an alternative for other commercial catalysts. It is also, considered as environmentally friendly and low-cost choice. (Kumar et al. 2020, 1–2)

Thermochemical conversion (valorization) of biomass includes biomass convert by pyrolysis (and gasification) into syngas to produce high valuable molecules (fine chemicals, biofuels etc.). During the process tar is produced as a by-product and different catalytic methods for exploiting it as valuable products or additional syngas are being developed. (Jeguirim & Limousy 2019, 318, 325) Catalytic valorization of lignocellulosic biomass has great potential and it is actively researched. Focus in the next chapter will be only on the biochar use as a catalyst on thermochemical processes of biomass. Biochar catalyst or biochar supported catalyst can be used to in syngas upgrading, tar removal and bio-oil reforming. Biochar as a catalyst used for these purposes usually requires further modification but can be used as in some cases. (Li et al. 2017, 70)

3.2.1 Thermochemical conversion of biomass

Fast pyrolysis bio-oils usually have low stability because acidity, high content of oxygenated functional groups and various impurities. Bio-oil composition is a mixture of 30–40 wt.% of organic components that are rich in oxygen, tars including naphthalene, toluene and benzene and water around 25 wt.%. Wanted bio-oil products are e.g. alcohols, hydrocarbon and phenols and unwanted compounds include acids, PAHs, and carbonyls (esters, aldehydes, ketones). Bio-oil needs to be upgraded so it can be utilised as a fuel. Modification of bio-oil requires e.g. removing of oxygen in different forms (CO, CO_2, H_2O) and it can be removed with the use of catalyst. In table the 10 are typical criteria for selection of catalyst in thermochemical conversion process. (Ohra-aho et al. 2020, 2; Abou Rjeily et al. 2021, 4)

TABLE 10. Criteria for selection of catalyst (Guan et al. 2016 455–456)



1. Tar removal efficiency
2. Reforming activity of heavy hydrocarbon and aromatic compounds
3. Possibilities of providing suitable syngas ratio for given application
4. Resistance to deactivation because of impurity fouling, sintering, and coking
5. Stability and reusability
6. Mechanical strength and thermal strength
7. Economical cost and availability for industrial use

Catalytic pyrolysis provides conversion of biomass into hydrocarbons and high-added value molecules with only a one step process. It is in situ upgrading because the catalyst is added to the feedstock before the process. In continuous process at large scale, e.g. in circulating fluidized bed reactor accumulation of char in the reaction is possible, and this will cause ash buildup over the catalyst surface. Ex situ catalytic pyrolysis consists of separate reactors that are in series as two-stage reactors. Gases are produced in the first reactor and operated into the second one where gases are in contact with catalyst. It creates more controlled and stable process and e.g. fixed bed can be used as a secondary reactor so there are no limits catalyst life. Main disadvantage is the increase in costs due to the second reactor. (Abou Rjeily et al. 2021, 5–6)

Ohra-aho et al. (2020, 10) found that use of wood-based biochar as catalytic post-treatment changes the content of pine biomass pyrolysis gases compared to non-catalytic treatment during pyrolysis. Advantageous for bio-oil stability was that biochar catalyst decreased the bio-oil compounds having carbonyl groups. Also, biochar has high adaptation rate of polysaccharide-derived products into carbon dioxide, which indicates oxidation of carbohydrate compounds that are related to decline of lignin mixture that will boost their stability. (Ohra-aho et al. 2020, 10)

Biochar can be used as unexpensive catalyst for converting tar components into H_2, CO and CH_4 and reducing tar mixtures while converting, corresponding to the syngas yield. Biomass tar is a complex mixture of several organic compounds and can condense on the process equipment and affect negatively to process stability and safety. Also, aromatic compounds in tars such as PAHs and benzene are toxic and harmful to environment. Tar removal from syngas is essential in pyrolysis and gasification process. (Guo et al. 2018, 81)

Tar is removed in the process either in situ tar reduction (primary reduction), which avoids the formation of tar or post tar reduction (secondary reduction), which cleans the product gas of tar that is already produced. In situ reduction operating conditions or equipment design can be altered or by addition of catalyst beforehand. Traditional catalysts used in tar reduction are dolomite, olivine, alkali, nickel, and char. Dolomite is a rock-forming mineral that composes of calcium magnesium carbonate ($CaMg(CO_3)_2$) (Islam 2020, 3). Olivine is also, a rock forming mineral that composes from Mg or Fe and SiO_4 (Morin et al. 2017, 2). Catalytic post reduction of tar is done by cracking. Catalytic cracking is commercially available method and is also done with previously mentioned catalyst. It basically means that the dirty gas passes through catalysts and chemical reaction occurs. (Basu et al. 2018, 195; Abou Rjeily et al. 2021, 30)

Ni-based catalyst is most used in tar steam reforming due to its activity and high efficiency. It can suffer from fast deactivation because carbon (coke) formed over their surface. To increase coke resistance and increase even more catalytic performance utilisation of bimetallic catalysts such as Ni-Co, Ni-Fe or Fe-Co can be option, which will improve the coverage of oxygen compounds. Ni can be introduced to the catalyst surface for example, Ni-based biochar or Ni-based dolomite. (Basu et al. 2018, 195; Abou Rjeily et al. 2021, 30)

3.2.2 Biochar quality requirements

Biochar physicochemical properties include acid density (especially $–SO_3H$), surface area, pore volume and size, surface oxygen functional groups and metal dispersion and speciation. These properties are important to the performance of biochar-based catalyst. Controlling these properties is essential (figure 10). Biochar surface functionality and porosity is affected by various chemical or physical methods through in situ tuning and postactivation. Usually without modification biochar catalytic properties are not good These methods are common and often used and are discussed in the chapter 4. (Xiong et al. 2017, 256; Liu et al. 12276)

Raw biochar (without upgrading) can be used due to mineral content of biochar for catalytic cracking or reforming of hydrocarbon conversion of pyrolytic gases to hydrogen and hydrocarbons production. Heteroatoms N, O, P, and S content increases biochar catalytic performance e.g. through electron transfer on the carbon surface. (Xiong et al. 2017, 256; Kumar et al. 2020, 6) Surface functionalities are functionalities that can make the biochar surface acid, basic or neutral. Heteroatoms can be inherited or introduced to the biochar surface as biomass precursor or as posttreatment to the char. (Jeguirim & Limousy 2019, 293)

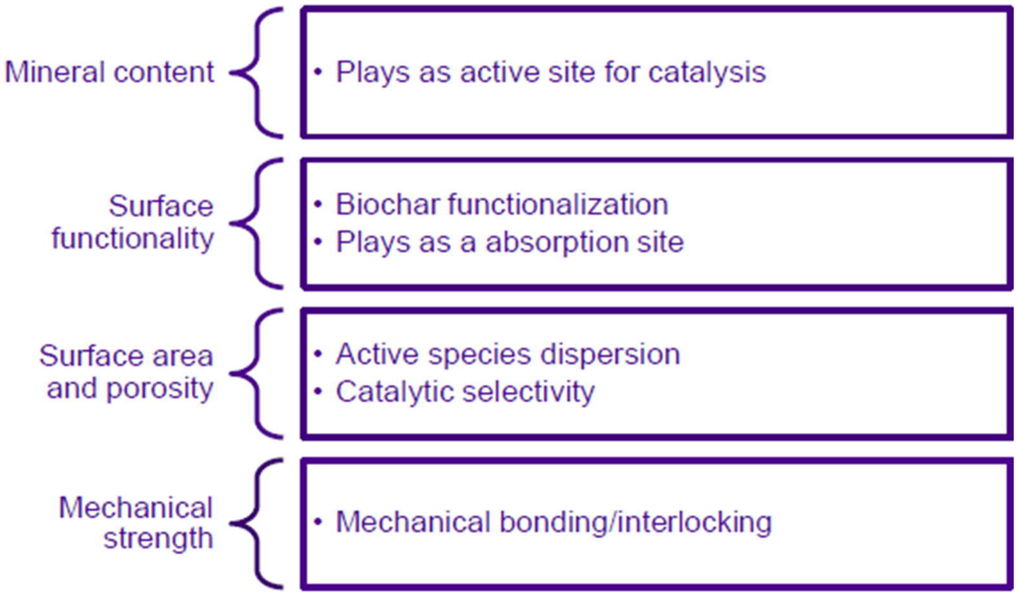


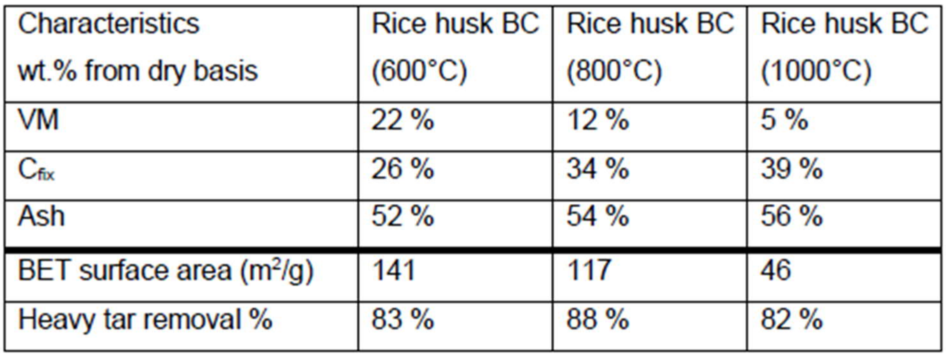
FIGURE 10. Biochar properties with leading catalytic activity. (Kumar et al. 2020, 6, modified)

Ash content of the feedstock affects not only biochar properties but its catalytic performance. As mentioned before high mineral content of biochar is beneficial for the use as a catalyst, but also a disadvantage as it can block the pores. High concentration of Si can affect the metal impregnation (upgrading method) effectiveness negatively (Xiong et al. 2017, 256). Conclusion is that inherited mineral content of biochar does not guarantee catalytic activity. (Kumar et al. 2020, 6; Ohra-aho et al. 2020, 4)

Textural properties including porosity are important for biochar reactivity. High porosity and share of micropores is beneficial for biochar as a catalyst. Often catalysts are fragile, and mechanical strength is important factor or otherwise biochar-based catalyst cannot be used in e.g. fluidized bed reactors. (Jeguirim & Limousy 2019, 297)

Rice husk biochar (BC) is pyrolyzed at different temperatures and then studied how biochar removes tar from pyrolysis gas (table 11). Rice husk BC (600°C) has relatively low fixed carbon content and rice husk BC (1000°C) has low surface area, which explains why the rice husk BC (800°C) has the highest tar removal efficiency 88 %. Biochar were not upgraded before tar removal (Paethanom & Yoshikawa 2012, 4949) Guo et al. (2018, 1) studied also rice husk chars supported by metallic catalyst for in situ tar cracking/syngas upgrading and tar conversion efficiency was over 90 %. Biochar catalyst remained high activity for tar removal after three rounds.

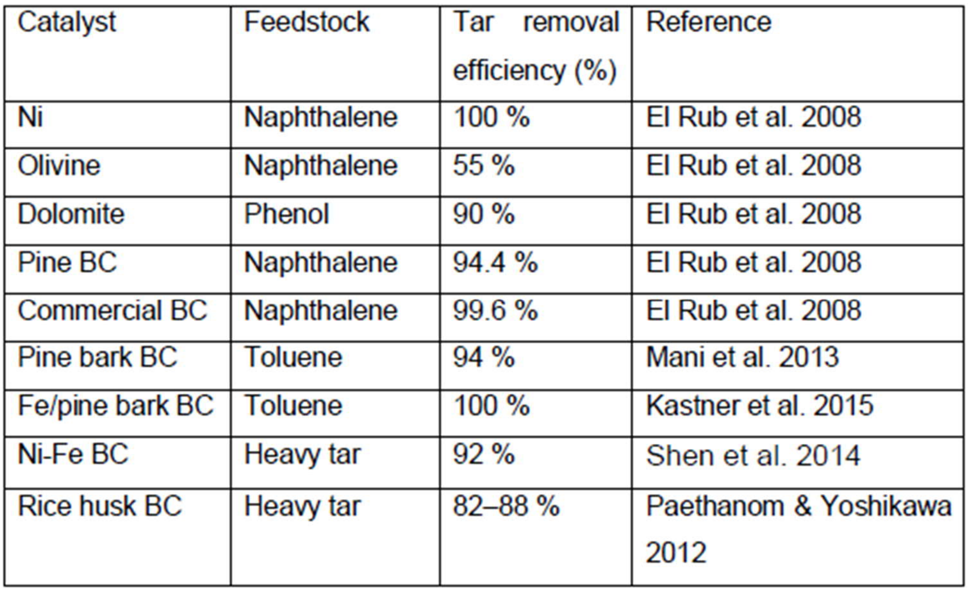
TABLE 11. Characterization of rice husk biochar produced by pyrolysis (Paethanom & Yoshikawa 2012, 4949)



Characteristics wt.% from dry basis	Rice husk BC (600°C)	Rice husk BC (800°C)	Rice husk BC (1000°C)
VM	22 %	12 %	5 %
C_{fix}	26 %	34 %	39 %
Ash	52 %	54 %	56 %
BET surface area (m^2/g)	141	117	46
Heavy tar removal %	83 %	88 %	82 %

Biochar based catalyst can exhibit better performance than commercial catalysts (see table 12). Biochar based catalyst can perform ineffectually at low temperatures. Large scale production with constant biochar properties is also challenging. Catalyst surface can suffer from coking, which is in the most cases the primary reason for catalyst deactivation. Scale-up issues regarding larger scale reactor to be considered are gas flow rate, temperature and pressure variations, catalyst deactivation, contaminants e.g. HCl, HCN, NO_x, SO_x and fly ash in the gas line. (Guan et al. 2016. 458; (Kumar et al. 2020, 9) To use biochar produced in gasification process in tar removal would require design modifications to the gasifier, e.g. passage of pyrolysis product through the biochar or separation of pyrolysis and char gasification zone. (Basu et al. 2018, 2014)

TABLE 12. Tar removal efficiency of different catalysts. BC is an abbreviation of biochar.



Catalyst	Feedstock	Tar removal efficiency (%)	Reference
Ni	Naphthalene	100 %	El Rub et al. 2008
Olivine	Naphthalene	55 %	El Rub et al. 2008
Dolomite	Phenol	90 %	El Rub et al. 2008
Pine BC	Naphthalene	94.4 %	El Rub et al. 2008
Commercial BC	Naphthalene	99.6 %	El Rub et al. 2008
Pine bark BC	Toluene	94 %	Mani et al. 2013
Fe/pine bark BC	Toluene	100 %	Kastner et al. 2015
Ni-Fe BC	Heavy tar	92 %	Shen et al. 2014
Rice husk BC	Heavy tar	82–88 %	Paethanom & Yoshikawa 2012

4 UPGRADING BIOCHAR PROPERTIES

4.1 Use in blast furnace injection

Biochar use in BF injection does not require any extensive upgrading. Biomass should be dried before pyrolysis to moisture content ~10 % for avoiding thermal ballast and effects on the biochar yield. (Suopajärvi et al. 2018, 387) Grinding and conveying properties of biochar are crucial in BF injection. Grindability of biochar is improved by pyrolysis temperature and residence time rather than in any typical chemical/physical upgrading methods. (Suopajärvi et al. 2017 721)

4.2 Use as a catalyst

Activation process is required if biochar is used as a catalyst due to limited surface area, porosity, and surface functional groups. (Cao et al. 2017, 48803). Surface chemistry of biochar can be upgraded by oxidation and sulfonation. Biochar porosity is influenced by chemical treatment, gas activation or metal impregnation (Jeguirim & Limousy 2019, 296–297).

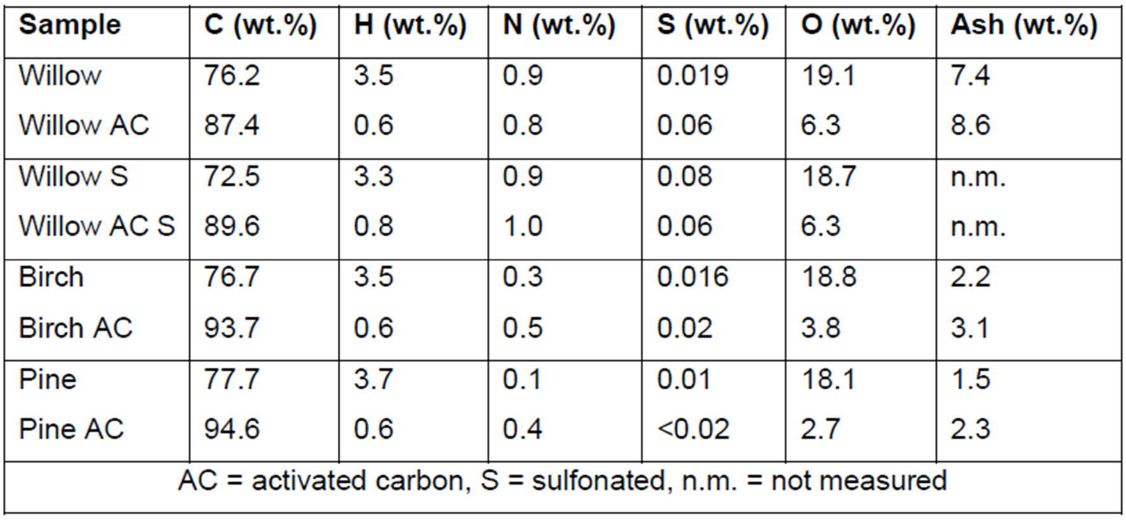
Straightforward and commercially used method for biomass modification is metal impregnation. In pyrolysis or gasification Ni (form nitrate) or iron is usually used as the catalytic active phase. Metal can be added before or after biochar synthesis by impregnation, sol-gel or mixing methods. Most used method is Ni impregnation as a post treatment to biochar. Method is extremely interesting for various catalytic applications e.g. tar reforming, phenol removal and Fischer-Tropsch synthesis. (Jeguirim & Limousy 2019, 313)

Biochar-metal catalysts are pre-loaded with metal precursors (e.g. Ni^{2} , Cu^{2+}, Mg^{2+}, or Fe^{3+}) on the feedstock before or on the biochar after pyrolysis. Biomass is impregnated with aqueous solution of different metal precursors, which are then absorbed to the surface. Metal-impregnated biomass after pyrolysis converts metal precursors to their oxides (e.g. NiO, CuO, MgO or Fe_2O_3) and as a biochar supported metal catalysts. Biochar porous structure could disperse metal, but also entrap reactants, which will result in great catalytic activity of biochar-metal catalyst. (Sun et al. 2020, 9, Cao et al. 2017, 48802)

Physical gas activation after biochar preparation can be done e.g. with steam or CO_2 activation or with a mixture of them. Steam activation usually increases biochar surface area (BET) and pore volume. Steam activation decreases the amount of acidic surface groups, which is related to the decrease of O and H content. Steam effects biochar pore volume and it increases the micropore volume. (Jeguirim & Limousy 2019, 309) This can be seen in the tables 13 and 14. As mentioned previously different lignocellulosic decomposition temperatures and extremely high pyrolysis temperatures, which will impact more greatly to surface area than post modification methods. Factors that are important in steam modification include temperature, time, and steam (Yaashikaa et al. 2019, 5).

Birch, pine and unbarked willow derived biochar were collected from fast pyrolysis in a bench scale BFB pyrolyzer. Biochar were first activated by steam and purified by hydrochloric acid and unwashed or chemically activated willow biochar by sulfonation. Acid washing is preferred treatment for biochar catalyst because it removes minerals (e.g. K, Ca, P, Si, Na, Mg, Fe, Zn), but also increases carbon content by removing H and O (tar compounds) from biochar. Sulfonation is a productive way to create acid catalyst and catalyst support (Jeguirim & Limousy 2019, 296). Based on high O and N content of willow biochar it is chosen for the sulfonation treatment, and as a result it enhanced the number of active acidic sites of it. (Ohra-aho et al. 2020,1–2)

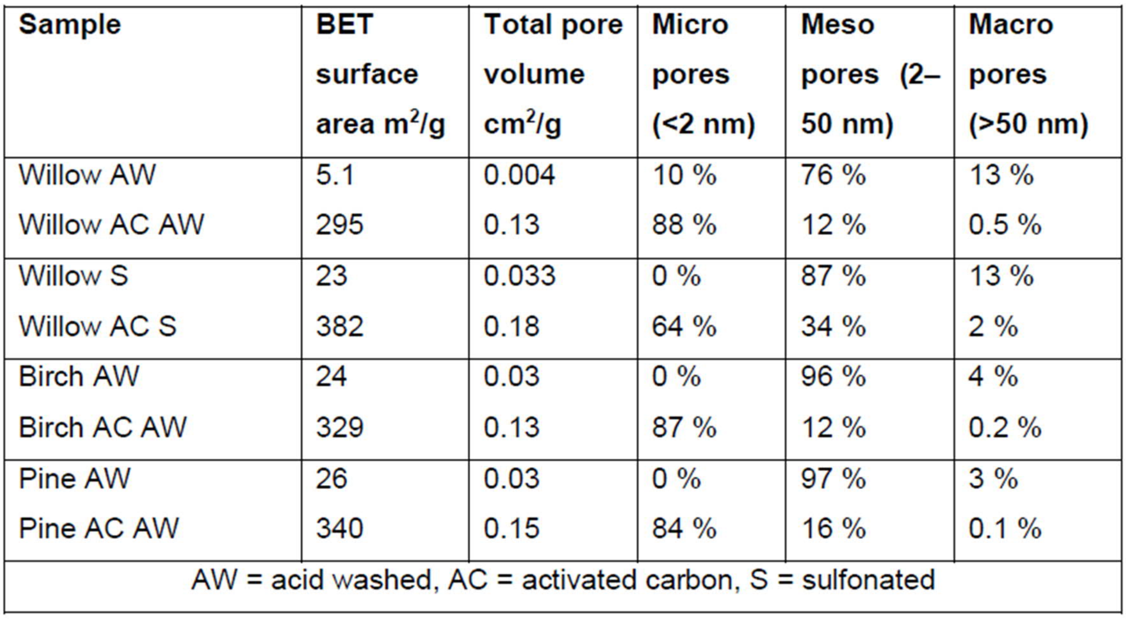
TABLE 13. The elemental analysis and ash of unwashed biochar (Ohra-aho et al. 2020, 4)



Sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	Ash (wt.%)
Willow	76.2	3.5	0.9	0.019	19.1	7.4
Willow AC	87.4	0.6	0.8	0.06	6.3	8.6
Willow S	72.5	3.3	0.9	0.08	18.7	n.m.
Willow AC S	89.6	0.8	1.0	0.06	6.3	n.m.
Birch	76.7	3.5	0.3	0.016	18.8	2.2
Birch AC	93.7	0.6	0.5	0.02	3.8	3.1
Pine	77.7	3.7	0.1	0.01	18.1	1.5
Pine AC	94.6	0.6	0.4	<0.02	2.7	2.3

AC = activated carbon, S = sulfonated, n.m. = not measured

TABLE 14. Characteristics of modified biochar (Ohra-aho et al. 2020, 6)



Sample	BET surface area m^2/g	Total pore volume cm^2/g	Micro pores (<2 nm)	Meso pores (2–50 nm)	Macro pores (>50 nm)
Willow AW	5.1	0.004	10 %	76 %	13 %
Willow AC AW	295	0.13	88 %	12 %	0.5 %
Willow S	23	0.033	0 %	87 %	13 %
Willow AC S	382	0.18	64 %	34 %	2 %
Birch AW	24	0.03	0 %	96 %	4 %
Birch AC AW	329	0.13	87 %	12 %	0.2 %
Pine AW	26	0.03	0 %	97 %	3 %
Pine AC AW	340	0.15	84 %	16 %	0.1 %

AW = acid washed, AC = activated carbon, S = sulfonated

Ohra-aho et al. (2020, 9) found that unwashed AC willow biochar has the greatest impact on post treatment of pyrolysis vapor composition. Acid washing changes the reactivity of willow BC and activated willow BC. Also, after acid washing was done the activation method had greater impact than the biomass type. Willow had highest share of ash and minerals (table 3) and still it performed catalytically best. In these studies, high mineral content was favourable.

Biochar chemical post treatment is easier to perform because smaller volumes and less minerals and therefore it is preferred as a process to improve textural properties of biochar. Acidic post treatments are usually used to upgrade biochar surface acidity and often it does not affect positively to textural properties at the same time. (Jeguirim & Limousy 2019, 300)

Phenol content of bio-oil is positively correlated with catalyst surface area and aromatics content showed negative correlation of the catalyst surface area. Also, bio-oil O-containing compounds and acetic acid reduced significantly (table 16). After using activated biochar catalysts surface areas decreased an average 5–10 %, which indicates its reusability. The table 15 shows that biochar surface area can be over thousand m^2/g with upgrading methods. Chemical activation of biochar with KOH is effective in tar reforming and bio-oil upgrading. (Yang et al. 2020,1)

TABLE 15. Bamboo derived biochar from pyrolysis (600°C) as catalyst and its effect on bio-oil (Yang et al. 2020,6)

Content (%)	No catalyst	BC-CH_3COOK	BC-$KHCO_3$	BC-K_2CO_3	BC-KOH
Phenols	47 %	56 %	57 %	58 %	67 %
Aromatics	9 %	24 %	22 %	19 %	15 %
O-species	23 %	14 %	14 %	15 %	13 %
Acetic acid	21 %	6 %	6 %	7 %	5 %
BET surface area m^2/g	-	803	830	970	1280

Chemical activation methods involve several process steps and activation agents like H_2SO_4, $ZnCl_2$, KOH or NaOH. Often its advantages are large pore size, low temperature (400–900°C), and high surface area. Its disadvantage is multi step process and for example, use of KOH or NaOH as a biochar activator has strong corrosive effect on machinery, which will limit the large-scale industrial production. (Zhang et al. 2021, 602) Physical activation process is a single step and economic process. Activating agents are O_2/air, steam, CO_2, water gas but then again, its disadvantages are high temperature (700–1000°C), small pore size and low surface area. (Kumar et al. 2020, 3).

5 DISCUSSION

Biochar tailor ability seems to be its advantage and a disadvantage. Biochar properties can be affected drastically by pyrolysis conditions such as temperature, heating rate, residence time or pressure, by feedstock or by different pre- or post-treatment methods. Tailor ability of biochar creates hundreds of utilisation possibilities, but severe research is required for finding the right adjustments for wanted biochar properties.

Summary of potential utilisation of biochar in blast furnace injection or as a catalyst are presented in the table 16. Biochar-based catalyst in the field of biorefinery offers a more sustainable option and more integrated process than currently. Target is to use a product of the process and this way also improve the economics of the whole process. Biochar catalyst performance is comparable to a commercial catalyst used. On the other hand, scaling up catalytic pyrolysis will most likely create modification needs to the pyrolysis process equipment. Biochar based reducing agent in BF injection is extremely comparable to pulverized coal and provides massive reductions in CO_2 emissions of steel plant. Markets already exist for biochar in metallurgy and large scale trials are conducted, only an industrial scale production of biochar is missing.

Biochar markets already exist but the end uses are mainly related to agricultural uses of biochar. Also, commercial slow pyrolysis plants exist around the world and markets are expected to grow yearly. Slow pyrolysis pyrolyzer can be scalable and should be kept in mind as an option for producing mainly biochar rather than it just being a by-product from fast pyrolysis. Use of fast pyrolysis as a production method for biochar introduces energy efficiency and better control of pollutants to the production process.

Scaling up biochar production is required. In general, possible limitations for biochar production on an industrial scale are competing end-users, collection and transportation of feedstock materials and ready biochar, but also uniform production of biochar is a challenge in large scale. Production of biochar is highly purpose driven, which makes investing in it risky for companies.

Thesis evaluated different quality requirements for biochar and how the properties can be affected. When exploring new utilisation possibilities of biochar in the future it requires always a specific and extensive research. Trials and research are required due to biochar quality being so sensitive to many different parameters. Further studies are required for designing of active and selective biochar catalyst and how to maintain certain biochar properties in a large scale production of biochar.

TABLE 16. Summary of biochar in blast furnace injection and as a catalyst.

	Biochar injection to blast furnace	Biochar as a catalyst in thermochemical conversion of biomass
Biochar requirements	- High heating value and char burnout ratio - Low ash and sulphur content - Low O/C and H/C ratio	- Large surface area, high porosity, high share of micropores - Mineral content (N, O, P, S) - Acidity
Advantages in utilisation	- Comparable to PC - High replacement ratio of fossil fuels - Increased productivity - Reduce of emissions	- Low-cost catalyst - Comparable to commercial catalysts - Can be applied to pyrolysis and gasification process - Creates more integrated and sustainable process - Reusability
Disadvantages in utilisation	- Sufficient mass flow in injection - Larger and dry storage for BC	- Often BC requires upgrading - Coke resistance of any catalyst - Design modifications to the process
Advantages in technology	- Pyrolysis is uncomplicated - Product yields can be optimized as wanted (oil, gas, char) - Integration to energy production and/or to steel plant possible -	- Pyrolysis in uncomplicated - Product yields can be optimized as wanted (oil, gas, char)
Disadvantages in technology	- Typically, small-scale BC production - High production costs - Purpose driven synthesis	- In industrial scale catalytic pyrolysis probably requires two separate reactors - Purpose driven synthesis

REFERENCES

Abou Rjeily, M., Gennequin, C., Pron, H., Abi-Aad, E. and Randrianalisoa, J.H. 2021. Pyrolysis-catalytic upgrading of bio-oil and pyrolysis-catalytic steam reforming of biogas: a review. Environmental chemistry letters.

Abu El-Rub, Z., Bramer, E.A. and Brem, G. 2008. Experimental comparison of biomass chars with other catalysts for tar reduction. Fuel (Guildford). 87(10–11). 2243–2252.

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., VithanageI, M., Lee, S.S. and Ok, Y.S. 2014. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere (Oxford). Chemosphere, 99. 19–33.

Babich, A. & Senk, D. 2013. Biomass use in the steel industry: Back to the future? Stahl und Eisen. 133. 57–67.

Babich, A., Senk, D., Knepper, M. and Benkert, S. 2016. Conversion of injected waste plastics in blast furnace. Ironmaking & Steelmaking, 43(1). 11–21.

Basu, P. 2018. Biomass gasification, pyrolysis, and torrefaction: practical design and theory. Third edition. London, England: Academic Press.

Bolan, N.S., Thangarajan, R., Seshadri, B., Jena, U., Das, K.C., Wang, H. and Naidu, R. 2013. Landfills as a biorefinery to produce biomass and capture biogas. Bioresource technology. Bioresour Technol, 135. 578–587.

Cao, X., Sun, S. and Sun, R. 2017. Application of biochar-based catalysts in biomass upgrading: a review. RSC advances, 7(77). 48793–4885.

Chemerys, V. and Balternaite, E. 2018. A review of lignocellulosic biochar modification towards enhanced biochar selectivity and adsorption capacity of potentially toxic elements. Ukrainian journal of ecology, 8(1). 21–32.

Da, Z., Niu, X., Li, X., Zhang, W., He, Y., Pan, J., Qiu, F. and Yan, Y. 2017. From Moldy Orange Waste to Natural Reductant and Catalyst Support: Active Palladium/Biomass-Derived Carbonaceous Hybrids for Promoted Methanol Electro-Oxidation. ChemElectroChem, 4(6). 1372–1377.

Demirbas, A. 2001. Carbonization ranking of selected biomass for charcoal, liquid and gaseous products. Energy conversion and management, 42(10). 1229–1238.

Geerdees, M. 2015. Modern blast furnace ironmaking: an introduction. 32015 edn. Amsterdam, Netherlands: IOS Press.

Gholizadeh, M., Li, C., Zhang, S., Wang, Y., Niu, S., Li, Y. and Hu, X. 2020. Progress of the development of reactors for pyrolysis of municipal waste. Sustainable energy & fuels, 4(12). 5885–5915.

Guan, G., Kaewpanha, M., Hao, X. and Abudula, A. 2016. Catalytic steam reforming of biomass tar: Prospects and challenges. Renewable & sustainable energy reviews, 58. 450–461.

Guo, F., Li, X., Liu, Y., Peng, K., Guo, C. and Rao, Z. 2018. Catalytic cracking of biomass pyrolysis tar over char-supported catalysts. Energy conversion and management, 167. 81–90.

Hasanbeigi, A., Arens, M. and Price, L. 2014. Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: A technical review. Renewable & sustainable energy reviews, 33. 645–658.

Hodgson, E., Lewys-James, A., Rao Ravella, S., Thomas-Jones, S., Perkins, W. and Gallagher, J. 2016. Optimisation of slow-pyrolysis process conditions to maximise char yield and heavy metal adsorption of biochar produced from different feedstocks. Bioresource technology; Bioresour Technol, 214. 574–581.

Igalavithana, A.D., Mandal, S., Niazi, N.K., Vithanage, M., Parikh, S.J., Mukome, F.N.D., Rizwan, M., Oleszcuk, P., Al-Wabel, M., Bolan, N., Tsang, D.C.W., Kim, K. and Ok, Y.S. 2017. Advances and future directions of biochar characterization methods and applications. Critical Reviews in Environmental Science and Technology, 47(23). 2275–2330

Islam, M.W. 2020. A review of dolomite catalyst for biomass gasification tar removal. Fuel (Guildford), 267. 117095.

Jeguirim, M. and Limousy, L. 2019. Char and Carbon Materials Derived from Biomass: Production, Characterization and Applications. San Diego: Elsevier.

Jiang, C., B, J., Xiao, X., Zhang, S., Wang, Z., Yan, G., Wu, Y., Wong, C. and He, H. 2020. Converting waste lignin into nano-biochar as a renewable substitute of carbon black for reinforcing styrene-butadiene rubber. Waste management (Elmsford); Waste Manag, 102. 732–742.

Jiang, J., Zhang, L., Wang, X., Holm, N., Rajagopalan, K., Chen, F. and Ma, S. 2013. Highly ordered macroporous woody biochar with ultra-high carbon content as supercapacitor electrodes. Electrochimica Acta, 113. 481–489.

Kan, T., Strezov, V. and Evans, T.J. 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renewable & sustainable energy reviews, 57. 1126–1140.

Kastner, J.R., Mani, S. and Juneja, A. 2015. Catalytic decomposition of tar using iron supported biochar. Fuel Processing Technology, 130. 31–37.

Kim, K.H., Kim, J., Cho, T. and Choi, J.W. 2012. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). Bioresource technology. Bioresour Technol, 118. 158–162.

Kumar, A., Saini, K. and Bhaskar, T. 2020. Advances in design strategies for preparation of biochar based catalytic system for production of high value chemicals. Bioresource technology. Bioresour Technol, 299. 122–564.

Larson, R. and Sandford, J. 2020. Integrating biochar into a manure system. Journal of Nutrient Management. Read on 27.4.2021. https://jofnm.com/article-91-Integrating-biochar-into-a-manure-system.html

Lee, J., Kim, K. and Kwon, E.E. 2017. Biochar as a Catalyst. Renewable & sustainable energy reviews, 77. 70–79.

Leng, L. and Huang, H. 2018. An overview of the effect of pyrolysis process parameters on biochar stability. Bioresource technology. Bioresour Technol, 270, 627–642.

Li, A., Liu, H., Wang, H., Xu, H., Jin, L., Liu, J. and Hu, J. 2016. Effects of temperature and heating rate on the characteristics of molded Bio-Char. Bioresources, 11(2). 3259–3274.

Li, W., Dang, Q., Brown, R.C., Laird, D. and Wright, M.M. 2017. The impacts of biomass properties on pyrolysis yields, economic and environmental performance of the pyrolysis-bioenergy-biochar platform to carbon negative energy. Bioresource technology. Bioresour Technol, 241. 959–968.

Li, X., Shen, Q., Zhang, D., Mei, X., Ran, W., Xu, Y. and Yu, G. 2013. Functional Groups Determine Biochar Properties (pH and EC) as Studied by Two-Dimensional 13C NMR Correlation Spectroscopy. PloS one, 8(6). 4372–4381.

Li, Y., Xing, B., Ding, Y., Han, X. and Wang, S. 2020. A critical review of the production and advanced utilization of biochar via selective pyrolysis of lignocellulosic biomass. Bioresource technology, 312. 123–614.

Liao, W. and Thomas, S. 2019. Biochar Particle Size and Post-Pyrolysis Mechanical Processing Affect Soil pH, Water Retention Capacity, and Plant Performance. Soil systems, 3(1). 14

Liu, W., Jiang, H. and Yu, H. 2015. Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material. Chemical reviews. Chem.Rev, 115(22). 12251–12285.

Liu, Y. and Shein, Y. 2018. Computational Fluid Dynamics Study of Biomass Combustion in a Simulated Ironmaking Blast Furnace: Effect of the Particle Shape. Energy & Fuels. Energy Fuels, 32(4). 4372–4381.

Mani, S., Kastner, J.R. and Juneja, A. 2013. Catalytic decomposition of toluene using a biomass derived catalyst. Fuel Processing Technology, 114. 118–125.

Masek, O., Buss, W., Roy-Poirier, A., Lowe, W., Peters, C., Brownsort, P., Mignard, D., Pritchard, C. and Sohi, S. 2018. Consistency of biochar properties over time and production scales: A characterisation of standard materials. Journal of Analytical and Applied Pyrolysis, 132. 200–210.

Morin, M., Nitsch, X., Pecate, S. and Hemati, M. 2017. Tar conversion over olivine and sand in a fluidized bed reactor using toluene as model compound. Fuel (Guildford), 209. 25-34.

Ohra-aho, T., Lindfors, C., Lehtonen, J., Tamminen, T. and Siipola, V. 2020. Activated Carbons from Fast Pyrolysis Biochar as Novel Catalysts for the Post-Treatment of Pyrolysis Vapors, Studied by Analytical Pyrolysis. C (Basel), 6(65) 65.

Paethanom, A. and Yoshikawa, K. 2012. Influence of pyrolysis temperature on rice husk char characteristics and its tar adsorption capability. Energies (Basel), 5(12). 4941–4951.

Ok, Y.S. 2019. Biochar from biomass and waste: fundamentals and applications. Amsterdam, Netherlands: Elsevier.

Qian, K., Kumar, A., Z, H., Bellmer, D. and Huhnke, R. 2015. Recent advances in utilization of biochar. Renewable & sustainable energy reviews, 42. 1055–1064.

Schmidt HP, Wilson K. 2014. The 55 uses of biochar, the Biochar Journal 2014, Arbaz, Switzerland. ISSN 2297-1114 ‘ Version of 12 th May 2014 Accessed: 11.03.2021.

Shen, Y., Zhao, P., Shao, Q., Takahashi, F. and Yoshikawa, K. 2015. In situ catalytic conversion of tar using rice husk char/ash supported nickel–iron catalysts for biomass pyrolytic gasification combined with the mixing-simulation in fluidized-bed gasifier. Applied Energy, 160. 808–819.

Spokas, K.A. 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon management, 1(2). 289-303.

SSAB. 2019. SSAB:n Raahen tehtaalla testattiin onnistuneesti fossiilisen hiilen korvaamista biohiilellä. Read on 29.03.2021. SSAB:n Raahen tehtaalla testattiin onnistuneesti fossiilisen hiilen korvaamista biohiilellä - SSAB

Sun, X., Atiyeh, H.K., Li, M. and Chen, Y. 2020. Biochar facilitated bioprocessing and biorefinery for productions of biofuel and chemicals: A review. Bioresource technology, 295. 122–252.

Suopajärvi, H., Kemppainen, A., Haapakangas, J. and Fabritius, T. 2017. Extensive review of the opportunities to use biomass-based fuels in iron and steelmaking processes. Journal of Cleaner Production, 148. 709–734.

Suopajärvi, H., Pongracz, E. and Fabritius, T. 2013. The potential of using biomass-based reducing agents in the blast furnace: A review of thermochemical conversion technologies and assessments related to sustainability. Renewable & sustainable energy reviews, 25. 511–528.

Suopajärvi, H., Umeki, K., Mousa, E., Hedayati, A., Romar, H., Kemppainen, A., Wang, C., Phounglamcheik, A., Tuomikoski, S., Norberg, N., Andefors, A., Öhman, M., Lassi, U. and Fabritius, T. 2018. Use of biomass in integrated steelmaking – Status quo, future needs and comparison to other low-CO2 steel production technologies. Applied Energy, 213. 384–407.

Toloue Farrokh, N., Suopajärvi, H., Mattila, O., Sulasalmi, P. and Fabritius, T. 2020. Characteristics of wood-based biochars for pulverized coal injection. Fuel (Guildford), 265. 117017.

Toloue Farrokh, N., Suopajärvi, H., Mattila, O., Umeki, K., Phounglamcheik, A., Romar, H., Sulasalmi, P. and Fabritius, T. 2018. Slow pyrolysis of by-product lignin from wood-based ethanol production– A detailed analysis of the produced chars. Energy (Oxford), 164. 112–123.

Wang, B., Gao, B. and Fang, J. 2017. Recent advances in engineered biochar productions and applications. Critical Reviews in Environmental Science and Technology, 47(22). 2158–2207.

Wang, L., Trininic, M., Skreiberg, Ø, Gronli, M., Considine, R. and Antal, M.J. 2011. Is Elevated Pressure Required To Achieve a High Fixed-Carbon Yield of Charcoal from Biomass? Part 1: Round-Robin Results for Three Different Corncob Materials. Energy & Fuels. Energy Fuels, 25(7). 3251–3265.

Wang, L., Ok, Y.S., Tsang, D.C.W., Alessi, D.S., Rinklebe, J.Ö, Wang, H., Masek, O., Hou, R., O'Connor, D., Hou, D. and Nicholson, F. 2020. New trends in biochar pyrolysis and modification strategies: feedstock, pyrolysis conditions, sustainability concerns and implications for soil amendment. Soil Use and Management, 36(3). 358–386.

Xiong, X., Yu, I.K.M., Cao, L., Tsang, D.C.W., Zhang, S. and Ok, Y.S. 2017. A review of biochar-based catalysts for chemical synthesis, biofuel production, and pollution control. Bioresource technology. Bioresour Technol, 246. 254–270.

Xu, X., Zhao, Y., Sima, J., Zhao, L., Masek, O. and Cao, X. 2017. Indispensable role of biochar-inherent mineral constituents in its environmental applications: A review. Bioresource technology; Bioresour Technol, 241. 887–899.

Yaashikaa, P.R., Senthil Kumar, P., Varjani, S.J. and Saravanan, A. 2019. Advances in production and application of biochar from lignocellulosic feedstocks for remediation of environmental pollutants. Bioresource technology. Bioresour Technol, 292. 122030.

Yang, H., Yan, R., Chen, H., Lee, D.H. and Zheng, C. 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel (Guildford), 86(12). 1781-1788.

Yang, W., Wang, H., Zhang, M., Zhu, J., Zhou, J. and Wu, S. 2016. Fuel properties and combustion kinetics of hydrochar prepared by hydrothermal carbonization of bamboo. Bioresource technology. Bioresour Technol, 205. 199–204.

Yousaf, B., Liu, G., Abbas, Q., Wang, R., Ubaid Ali, M., Ullah, H., Liu, R. and Zhou, C. 2017. Systematic investigation on combustion characteristics and emission-reduction mechanism of potentially toxic elements in biomass- and biochar-coal co-combustion systems. Applied Energy, 208. 142–157.

Zhang, S., Yu, Y., Sheng, K., Liu, J., E, S., Jin, C., Xu, Z. and Zhang, X. 2021. Catalytic valorization of lignocellulosics: from bulk biofuels to value-added chemicals. Biofuels, bioproducts and biorefining, 15(2). 592–608.

Zhang, Z., Zhu, Z., Shen, B. and Liu, L. 2019. Insights into biochar and hydrochar production and applications: A review. Energy (Oxford), 171. 581–598.