Production of a metallurgical coke substitute from biochar depolymerised by wet oxidation

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ABSTRACT

Coke production relies on the availability, cost and quality of coking coal. Depleting coking coal resources and environmental pressure force the metallurgical industry to search for alternative methods to produce coke. Waste spent coffee grounds (biomass) treated via hydrothermal liquefaction (HTL) is an energy-efficient method to produce biochar.

In this study the use of HTL biochar as feedstock for the production of a coke substitute was investigated. Wet oxidation treatment of the prepared biochar samples was done with different wet oxidant hydrogen peroxide concentrations (5, 15, 30 vol.%). The biochar was treated for different time durations (0.5, 1, 2, 6 and 24 hours) and at different temperatures (room temperature and 80°C). Characteristics for the prepared biochar samples were compared to characteristics for coking coal and values found in literature to evaluate whether a coke pre-cursor was produced. The various samples were characterised and pyrolysed at 1100°C (10°C/min) under N_2 for 2 hours to obtain a coke substitute. The prepared coke substitute samples were also subjected to gasification reactions in a CO_2 atmosphere to determine the reactivity of the produced coke substitute samples. The results from the prepared samples were compared to that of a coke sample obtained from industry.

Characterisation of the various samples before and after thermal treatment was done using Fourier-transform infrared spectroscopy (FTIR), free swelling index, ultimate and proximate analysis, gross calorific value and compressive strength determination. Gasification reactivity of waste biochar samples was determined by a Thermogravimetric Analyzer (TGA) at 900°C under CO_2.

The investigated characteristics of the produced coke substitute obtained from the pyrolysed biochar treated for 24 hours with 30 vol.% H_2O_2 at room temperature, showed the most promising results when compared to blast furnace coke as a coke pre-cursor. The 24-hour room temperature pellet had a significantly higher compressive strength value of 3.22 MPa (per unit area) compared to a coke sample obtained from industry that had a value of 1.02 MPa (per unit area).

The results concluded that the average initial reactivity, reactivity at 50% conversion and average final reactivity of the prepared samples were mostly equal to the coke sample obtained from industry. The reactivity of the coke sample at 50% conversion was 4.7×10^3 min^{-1} with the closest reactivity calculated for the 2-hour room temperature wet oxidation treated sample with a value of 4.6×10^3 min^{-1}. Thus, the coke substitute produced from the waste ground coffee biochar subjected to a wet oxidation treatment method using hydrogen peroxide solutions may be utilised as a coke substitute.

Keywords: spent coffee grounds, biochar, wet oxidation, coke production, biomass, hydrothermal liquefaction, biochar reactivity.

OPSOMMING

Die produksie van coke is afhanklik van die beskikbaarheid, koste en kwaliteit van coke steenkool. Uitputting van coke steenkoolbronne en omgewingsdruk dwing die metallurgiese industrie om na alternatiewe metodes te soek om coke te produseer. Afval gebruikte koffiebone (biomassa) wat behandel word met hidrotermiese vloeibaarheid (HTL), is 'n energie-doeltreffende metode om biochar te produseer.

In hierdie studie is die gebruik van HTL-biochar vir die produksie van 'n coke-plaasvervanger ondersoek. Nat oksidasiebehandeling van die voorbereide biochar monsters is gedoen met verskillende nat oksidant waterstofperoksied konsentrasies (5, 15, 30 vol.%). Die biochar is behandel vir verskillende tydsdure (0.5, 1, 2, 6 en 24 uur) en by verskillende temperature (kamertemperatuur en 80°C). ‘Die waardes verkry vir die monsters is vergelyk met die waardes vir coke steenkool en literatuurwaardes om te evalueer of 'n coke van goeie gehalte vervaardig is. Die verskillende monsters is gekarakteriseer en vir 2 ure by 1100°C (10°C / min) onder N_2 gepyroliseer om 'n coke plaasvervanger te verkry. Die voorbereide coke-plaasvervanger monsters is ook aan vergassingsreaksies in 'n CO_2-atmosfeer onderwerp om die reaktiwiteit van die geproduseerde coke-plaasvervanger monsters te bepaal. Die resultate van die voorbereide monsters is vergelyk met dié van 'n coke monster wat uit die industrie verkry is.

Karakterisering van die verskillende monsters voor en na termiese behandeling is gedoen met behulp van FTIR, vrye swellingindeks, ‘ultimate’ en ‘proximate’ analises, bruto verbrandingswaarde en bepaling van die druksterkte. Vergassingsreaktiwiteit van afval biochar monsters is bepaal deur 'n Termogravometriese Analiseerder (TGA) by 900°C onder CO_2.

Die eienskappe van die geproduseerde coke-plaasvervanger wat verkry is uit die gepyrolyseerde biochar wat vir 24 uur behandel is met 30 vol.% H_2O_2 by kamertemperatuur, het die belowendste resultate getoon in vergelyking met industriële coke. Die 24-uur kamertemperatuurpille het 'n beduidende hoër druksterktewaarde van 3.22 MPa verkry in vergelyking met die industriële coke monster wat ‘n druksterkte van 1.02 MPa gehad het.

Die resultate het getoon dat die gemiddelde aanvanklike reaktiwiteit, reaktiwiteit by 50% omskakeling en die gemiddelde finale reaktiwiteit van die voorbereide monsters meestal gelyk was aan die coke monster wat uit die industrie verkry is. Die reaktiwiteit van die coke monster by 50% omskakeling was 4.7 x 10^3 min^{-1}, met die naaste reaktiwiteit wat bereken is vir die 2-uur kamertemperatuur-behandelde monster (4.6 x 10^3 min^{-1}). Dus kan die coke-plaasvervanger wat vervaardig word uit die afval gemaalde biochar wat aan 'n nat oksidasie-behandelingsmetode onderworpe is, gebruik word as 'n coke-plaasvervanger.

Sleutelwoorde: gebruikte koffiebone, biochar, nat oksidasie, coke produksie, biomassa, hidrotermiese vloeibaarheid, biochar reaktiwiteit.

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CHAPTER 1 INTRODUCTION

In this chapter, a brief overview of the investigation will be given. The problem statement; aims and objectives; and scope of the study are stated.

1.1 Background and motivation

The metallurgical industry generates a large amount of carbon dioxide (CO_2) due to their use of fossil fuels as a fuel source or as a reductant (Montiano *et al.*, 2014). One of the fuel sources and reductants used during metallurgical processes, such as the production of pig iron, is metallurgical coke (Adrados *et al.*, 2015). An observed decline in metallurgical coke production is caused by a decrease in the production capacity of existing coke producing plants (Díez *et al.*, 2002). The renovation of these plants will require huge investments (Díez *et al.*, 2002). This, as well as depleting coking coal resources, contributes to the increase in the cost of metallurgical coke. The high cost of metallurgical coke has led to the use of less expensive feedstocks, like coal blends, for the production of coke (Díez *et al.*, 2002). Other inexpensive feedstocks for the production of metallurgical coke or metallurgical coke substitutes include the use of biomass and waste materials. The utilisation of these alternative sources to produce metallurgical coke or metallurgical coke substitutes may significantly reduce the CO_2 net emissions (Kokonya *et al.*, 2013).

The focus has shifted in recent years to investigate the use of biomass as an alternative or addition to fossil fuels, due to its CO_2 neutrality (Mafu *et al.*, 2017). South Africa produces large amounts of biomass from municipal wastes, the sugar industry and the paper industry (Mafu *et al.*, 2016). Biomass is a hydrocarbon material with an elemental composition of carbon, nitrogen, oxygen, sulphur and hydrogen (Yaman, 2004). Energy can be extracted from the biomass by using thermal processes. These thermal processes include direct combustion, gasification, pyrolysis and liquefaction (Toor *et al.*, 2011). Direct combustion is not favoured due to the high moisture content of biomass that influences the stability of the combustion process (Yaman, 2004). Hydrothermal liquefaction (HTL) involves the use of the biomass feedstock with an added solvent and/or a catalyst (Von Wielligh *et al.*, 2018). The main advantage of the HTL process is that the biomass feedstock can be used as is, without drying. Another advantage of this process is that the temperature ranges between 250°C and 350°C, which is considerably lower than pyrolysis conditions, which usually occur above 400°C (Von Wielligh *et al.*, 2018). This process also produces a relatively stable bio-oil (Toor *et al.*, 2011). Since the process produces stable bio-oils, it is usually used for converting carbonaceous materials into liquefied products (Toor *et al.*, 2011), making the solid biochar a waste by-product of the process.

The use of waste products such as biochar, biomass and low-rank coals as raw material for the production of coke is being investigated. Previous studies by Madabhushi (2013), showed promise when converting brown coal into coke using a thermal process. However, due to the low coke reactivity and strength, the process was judged to be unsuccessful (Madabhushi, 2013). Other production methods include the addition of a binder to a low-rank coal and using different curing temperatures (Cengizler & Kemal, 2006). These methods often included the use of expensive moulds in order to produce the coke. Authors such as Montiano *et al.* (2014), investigated the addition of biomass to coal to prepare coke; however, no interaction was observed between the coal and biomass and the conclusion was that the addition of biomass should be kept to a minimum (Montiano *et al.*, 2014).

The utilisation of an aqueous oxidant to pre-treat the biochar before coke production was proposed by Miura *et al.* (1996). The pre-treatment was found to oxidatively depolymerise brown coals and recover small-molecule fatty acids (Miura *et al.*, 1996). Miura *et al.* (1996) used wet oxidation methods for producing valuable chemicals from brown coals and showed that brown coals can be oxidatively depolymerised by the aqueous oxidant, hydrogen peroxide. Ashida *et al.* (2017) investigated this method to produce a metallurgical coke from brown coal. Since low-rank coals do not have thermoplastic qualities between 400°C and 550°C as expected for coking coal, the addition of an aqueous oxidant was thought to assist in the thermoplastic nature of the coals by causing degradation reactions (Ashida *et al.*, 2017). Ashida *et al.* (2017) proposed that wet oxidation can be used as a pre-treatment to produce coke from low-rank coals. This study describes the combination of wet oxidation and an inexpensive biomass feedstock to produce a coke substitute.

1.2 Problem statement

The rapid decrease of high-grade coking coal reserves and increasing production prices create the need to develop new technologies to produce metallurgical coke from low-cost materials (Ashida *et al.*, 2017). Since South Africa produces an abundance of waste biomass, the opportunity arises to use the biomass as a precursor to producing biochar. Biochar, however, does not meet all the requirements necessary for coke production. These requirements include safe oven pushing performance, thermoplasticity between 400°C and 550°C and chemical qualities like low ash and low sulphur content (Ashida *et al.*, 2017; Díez *et al.*, 2002). It is postulated that pre-treatment of biochar by using a wet oxidation method may depolymerise the char upon thermal treatment to give it the thermoplasticity required to produce coke (Ashida *et al.*, 2017). The addition of an aqueous oxidant, hydrogen peroxide, may also assist in increasing the tensile strength of the coke due to possible formation of cross-linking reactions between oxygen-containing functional groups and hydrogen (Ashida *et al.*, 2017). The wet oxidation of biochar, produced from biomass, may assist to improve the chemical and mechanical properties of the biochar to produce a higher quality coke substitute.

1.3 Aim and objectives

The aim of this study is to investigate the effects of a wet oxidation treatment method on an obtained biochar sample in order to prepare the biochar as a raw material for coke production. The synthesised coke substitute should have the appropriate mechanical strength and reactivity for use in blast furnaces.

Accomplishment of the following objectives are needed to achieve this aim:

- Obtain a biochar sample produced via hydrothermal liquefaction of spent coffee grounds;
- Characterise the biochar sample using ultimate analysis, proximate analysis, Fourier-transform infrared spectroscopy (FTIR), calorific value, compressive strength and CO_2 reactivity;
- Treat the produced biochar by using a wet oxidation method with hydrogen peroxide at various temperatures and time durations;
- Characterise the obtained products using ultimate analysis, proximate analysis, FTIR, calorific value, compressive strength, CO_2 reactivity and free-swelling index tests;
- Produce the coke substitute from the treated biochar samples by using thermal processing; and
- Characterise the coke substitute products using ultimate analysis, proximate analysis, FTIR, calorific value, compressive strength and CO_2 reactivity tests.
- Compare the various measured coke characteristics of the prepared coke substitute samples with a metallurgical coke sample obtained from industry.

1.4 Scope of the study

The experimental procedures, the outline of the study and techniques are summarised in Figure 1-1.

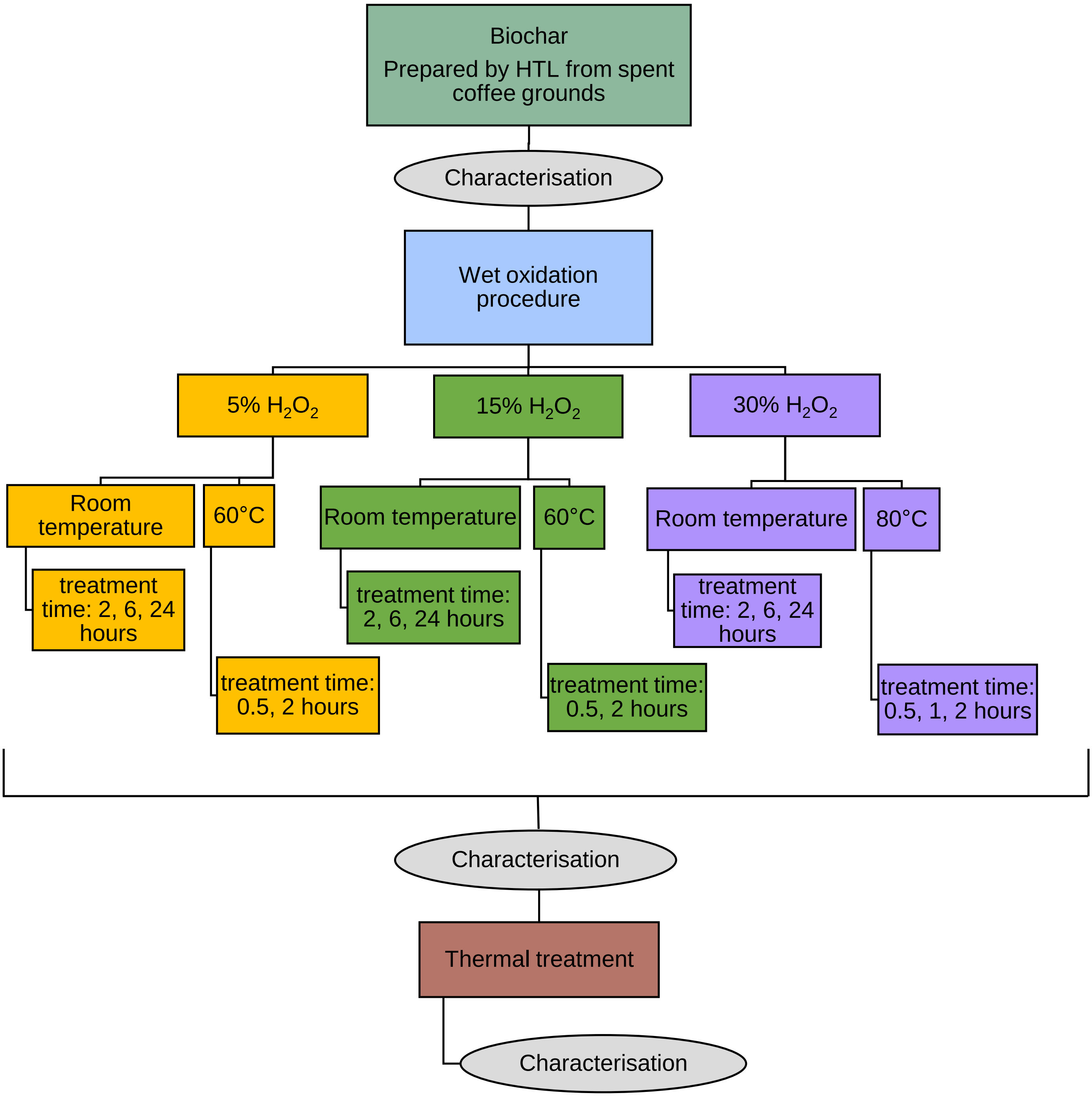

Figure 1-1: **Flowchart of the scope of the study.**

1.5 Study outline

The dissertation will be written according to the following order. The first chapter includes the background information as well as the aim and objectives regarding the use of a wet oxidation treated biochar sample as a source to produce a metallurgical coke substitute. Chapter 2 contains a literature review of previous studies and uses for biochar, the recent methods to produce metallurgical coke as well as treatment methods, such as wet oxidation. Chapter 3 includes a description of the oxidative treatment process of the biochar, biochar coke precursor and produced coke substitute. Characterisation of the biochar and produced precursor products is described. Chapter 4 include evaluation of the thermal processing of the coke substitute that is produced from the biochar and comparison to an industrial coke sample. Chapter 5 contains the final conclusions with recommendations for future studies.

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CHAPTER 2 LITERATURE REVIEW

An overview of coke, coke producing methods, coke uses, and coke characterisation methods will be given in this chapter; followed by a short review of alternative processes for the production of coke and coke substitutes. Biomass and biochar will also be discussed as an alternative to producing coke or coke substitutes.

2.1 Coke

Metallurgical coke is defined as a macroporous carbon material of high strength that is produced by the carbonisation of coal or coal blends at temperatures between 700°C and 1100°C (Díez *et al.*, 2002). Coke is a carbon-rich material that has passed through an intermediate fluid state during production (Schobert, 2013). The fluid state can be achieved through the carbonisation of feedstocks (Schobert, 2013). Carbonisation is usually thermally driven and requires temperatures exceeding 500°C (Schobert, 2013). The products formed by carbonisation is a carbon-rich solid, bio-oils and hydrogen-rich gases (Schobert, 2013). High-temperature carbonisation (between 700 and 900°C) maximises the yield of the solid carbon-rich product (Schobert, 2013). The result is a porous and hard coke that is used in furnaces (Schobert, 2013). The porous and hard coke produces a smokeless solid fuel with lower sulphur content, less volatiles and cleaner-burning qualities when used in blast furnaces (Schobert, 2013). Coke is made and used for various furnace types and applications that will be discussed later in the chapter, however, the use and production of coke for blast furnaces is the main interest in this study.

2.2 Coke production

Coke is traditionally prepared by using coking coal as feedstock. The coal is characterised by parameters such as low ash, sulphur and volatile matter contents, plastic properties and coking pressure (Barriocanal *et al.*, 2003). The coking pressure is the internal gas pressure generated by the coal during coke production (Nomura *et al.*, 2010). These parameters of the coal should be within fixed limits to produce a high-quality coke. To stay within these limits, apart from using the limited supply of high cost good coking coals, blending of coal is used to create a starting material that has acceptable properties (Barriocanal *et al.*, 2003; Díez *et al.*, 2002).

Coke is currently produced in slot type furnaces from the carbonisation of coal or coal blends (Díaz-Faes *et al.*, 2007). The coal or coal blends usually consist of bituminous coal with a small amount of inertinite coal and anthracite or coal fines (Díaz-Faes *et al.*, 2007). The feedstock undergoes slow heating in an inert atmosphere to soften and solidify it after undergoing a plastic stage (Díaz-Faes *et al.*, 2007). The different plastic stages of the coking process consist of pre-plastic, plastic and post-plastic stages (Díaz-Faes *et al.*, 2007). The pre-plastic stage occurs up to 350°C during which water, light hydrocarbons and carbon dioxide are released (Díaz-Faes *et al.*, 2007). Thereafter, the plastic stage (between 350 and 500°C) releases volatile matter and molecular disruption takes place resulting in a remaining structure that has fluidity properties. In the final stage, condensation takes place eliminating the hydrogen and leaving the final product with an ordered structure (Díaz-Faes *et al.*, 2007).

Coke producing practices demand that the feedstock is low in cost, can produce a high-quality coke and has safe oven pushing performances (Díez *et al.*, 2002). The cost to produce coke has increased significantly due to depleting coking coal reserves and the high financial investment needed for the renovation of existing coke plants (Díez *et al.*, 2002). The high cost of coke has led to the investigation of methods to reduce the cost of conventional coke utilisation in blast furnaces by using coke substitutes or alternative sources for coke production. One of the ways to reduce the amount of coke used is to introduce pulverised coal injection (PCI) by injecting pulverised coal as an extra reducing agent through the tuyeres in blast furnaces (see Figure 2-2: tuyeres are in the same section as the blowpipe) (Lundgren *et al.*, 2009). However, by using an additional reducing agent such as PCI, the quality of the coke is forced to be of a higher grade. High quality coke is required since there is an increase in residence time in the blast furnaces when PCI is used during the production of pig iron (Lundgren *et al.*, 2009).

Coke producing technologies such as that of Ignasiak (1981), includes a patented method to produce metallurgical coke from oxidised, high-volatile and caking coal. They investigated coal oxidation performed in a heated oxygen-containing atmosphere (<350°C). It was postulated that by mixing the oxidised coal with non-oxidised coal and carbonising it, it will produce a more homogeneous coke (Ignasiak, 1981). They concluded that the exposure of coal to elevated temperatures in an oxygen-containing atmosphere can improve the mechanical strength of the coke, keeping in mind that there is an optimum range of oxidation level (Ignasiak, 1981).

An additional process to produce coke is by the production of formcoke. Formcoke involves the briquetting of a wide range of coals, biomass and/or raw coals as raw material, in addition with a binder, to produce a product similar to metallurgical coke (Madabhushi, 2013; Plancher *et al.*, 2002). The main requirements for formcoke is a high calorific value, a high fixed carbon content, chemical content requirements and a high compressive strength before and after reaction (Plancher *et al.*, 2002). Other processes to produce formcoke from low-grade coal was investigated by briquetting brown coal with pitch as a binder and curing it at different temperatures in air (Cengizler & Kemal, 2006).

An alternative method to produce coke is through the conversion of brown coals to coke. This method was investigated by Madabhushi (2013), but due to low coke strength and reactivity further investigation was needed.

Other research includes the use of biomass as an additive to traditional coal blending techniques. Montiano *et al.* (2014) found that the addition of biomass (sawdust) to coking coal should be kept to a minimum since it adversely influences the fluidity as well as the heating matrix results since no interaction occurs between the coal and the sawdust.

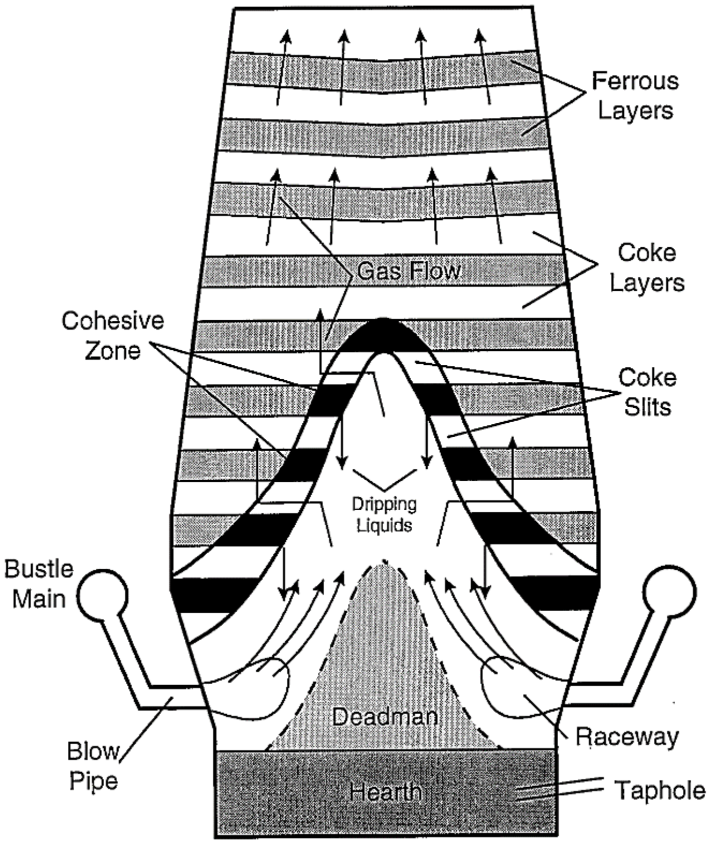

Figure 2-1: Schematic presentation of an Iron blast furnace (Iwamasa *et al*., 1997).

2.3 Coke uses

One of the main uses of coke is during the production of pig iron. Pig iron is a crude material of high-quality steel. During pig iron production the coke is fed into a blast furnace with the iron ore (see Figure 2-2) where it plays three major roles (Díaz-Faes *et al.*, 2007; Hilding *et al.*, 2005). The coke acts as (i) a fuel, (ii) a permeable support and (iii) as a reducing agent (Díaz-Faes *et al.*, 2007; Díez *et al.*, 2002; Hilding *et al.*, 2005; Wang *et al.*, 2016). Of these roles, the role of fuel and chemical reducing agent can be replaced by other resources such as oil, plastic, coal and gas (Díez *et al.*, 2002). The role coke has as a permeable support, however, cannot be replaced in the blast furnace (Díez *et al.*, 2002). Therefore, it is important that the coke is of a high grade since the coke is subjected to thermal, chemical and mechanical degradation in blast furnaces (Díez *et al.*, 2002). The furnaces used in current ferroalloy producing methods also include submerged arc furnaces (SAF) that can be open, semi-closed, closed, as well as direct current (DC) furnaces (Naiker, 2007; Nelson, 2016; Beukes, 2017). Certain specifications are of great importance and must be met for the coke to be used during the production of the specific ferroalloy in the specific furnace or blast furnace.

SAF usually utilise lumpy reductants within a certain particle size distribution, since the coke layer also serves as permeable support (Nelson, 2016). DC furnaces, on the other hand, do not have a preferred reductant particle size since the reductants form part of the slag. The many advantages of DC furnaces as compared with AC furnaces, such as the ability to use any reductant particle size, must be balanced out by the challenging aspects of DC furnaces (Nelson, 2016). These challenges include complex power supply units, the unstable nature of 1- or 2-electrode arc furnaces and intricate cooling design requirements of the furnace (Nelson, 2016). These electrodes are susceptible to complex compressive, time-dependent tensile and thermal stresses (Nelson, 2016). Figure 2-3 shows an example of a closed submerged electric arc furnace with graphite or anthracite and pitch electrodes for chromite smelting (Naiker, 2007). The use and requirements for the use of coke in blast furnaces is discussed in further detail.

The specifications of the coke used in the different furnaces include a controlled and low amount of ash, sulphur, phosphorus and moisture. For the use of coke in the blast furnace, the ash content should be low, otherwise, it may influence the performance of blast furnaces adversely since it is incombustible and could contain contaminants such as sulphur (Ishii, 2000).

The moisture affects the thermal value of the coal negatively and the sulphur causes emitted sulphur oxides which leads to issues such as corrosion problems (Ishii, 2000). Other contaminants include sodium and chlorine which causes fouling in blast furnaces (Ishii, 2000). The ability of the coke to resist degradation in thermal and chemical environments in blast furnaces needs to be evaluated (Díez *et al.*, 2002). The quality parameters should also include lump size, size distribution, mechanical strength, as well as chemical and mechanical stability (Díez *et al.*, 2002).

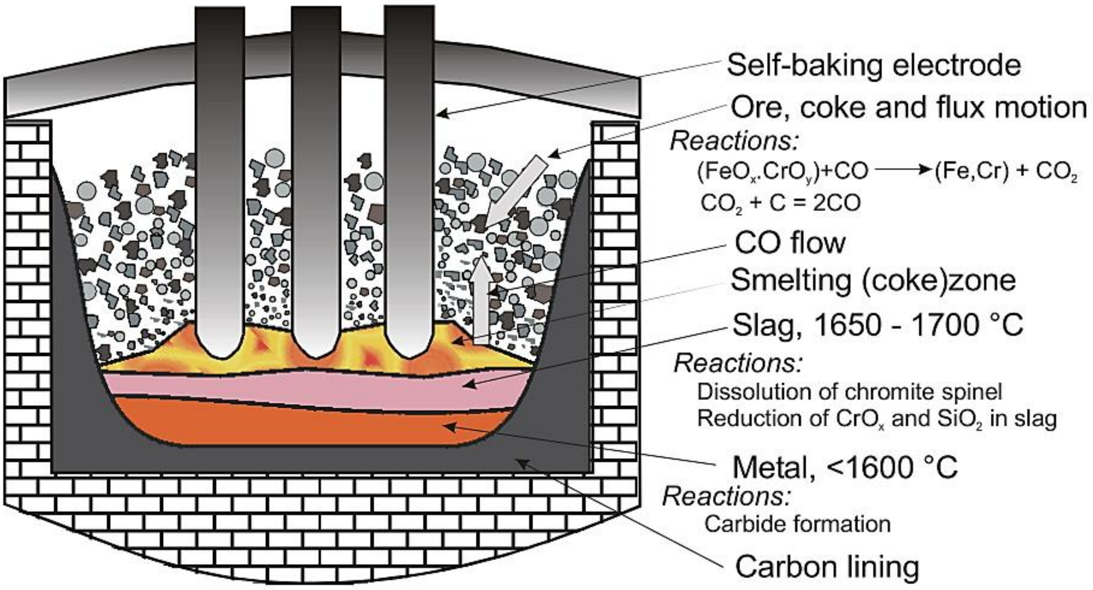

Figure 2-2: Illustration of a submerged arc furnace for chromite smelting (Naiker, 2007).

As the coke descends in the blast furnace during the production of pig iron, it is subjected to gasification and indirect reactions with FeO (Wang *et al.*, 2016). The gasification reactions of the coke lead to a porous fragile coke layer (Ishii, 2000). To prevent the degradation of the coke layer, sometimes a more reactive coke is proposed causing the gasification reactions to be limited to only the surface layer of the coke structure, leaving the stability of the coke structure intact (Ishii, 2000). The higher the reactivity of the coke, the quicker the coke combusts and gasifies (Ishii, 2000). If a too reactive coke is used, the degradation of the coke layer will continue to occur due to an increase in porosity of the coke structure (Ishii, 2000). A porosity of more than 52% will lead to significant degradation of the coke structure (Ishii, 2000).

The residence time of coke in blast furnaces is also increased with iron making trends such as PCI (Díez *et al.*, 2002). It is therefore important to optimise the critical quality parameters of coke to reach higher productivities when an alternative higher level of fuel injections is operative (Díez *et al.*, 2002). The partial replacement of coke by other technologies, like PCI, is needed for blast furnace operation to decrease operational cost and the demand of coke (Ishii, 2000). Changes in the blast furnace occur as the rate of the PCI is increased. These changes include an increase in the permeability resistance in the furnace, heat loss and insufficient oxygen supply leading to the accumulation of unburnt char (Ishii, 2000). All these changes lead to a reduction in the gasification and combustion rates of the coal or coke (Ishii, 2000). Coal particles in an oxygen-enriched environment, during PCI, release volatile matter, combust and pyrolyse (Ishii, 2000). When oxygen levels are low, the combustion flame expands and the heat dissipates resulting in a lower combustion rate (Ishii, 2000). Carbon solution is decreased with an increase in PCI rate. This is overcome by increasing the heat flux ratio through oxygen enrichment (Ishii, 2000).

PCI is one of the possible applications of biochar coke substitutes and is advantageous since it reduces the amount of metallurgical coke needed. It also increases the generation of hydrogen gas which improves the reduction of iron (Adrados *et al.*, 2015), which in turn improves the quality of the iron produced (Borrego *et al.*, 2008).

2.4 Coke characterisation

Various models are used in the coke producing industry to predict the quality of coke for blast furnaces. The models take the different properties of the feed materials into consideration to prepare the preferred coke specifically for the consumer. Since coke is produced on a large scale the need exists to characterise and predict the properties of coal as raw material to avoid the high costs of large-scale testing (Díaz-Faes *et al.*, 2007).

The main quality indices for coke in blast furnaces includes mechanical strength and reactivity towards CO_2 (Cimadevilla *et al.*, 2005a). To determine the coke quality, the Coke Strength after Reaction (CSR) index is normally used. This is determined by measuring the coke mechanical strength after the coke has reacted with CO_2 for 2 hours at 1100°C (Díaz-Faes *et al.*, 2007). Coke’s reactivity towards CO_2 depends on the ash and maceral composition as well as the thermoplastic properties (Díaz-Faes *et al.*, 2007). Another test that is widely used is the Coke Reactivity Index (CRI). This index takes the physical properties such as the cold mechanical strength, resistance to degradation and fragmentation by fissuring, cohesion and abrasion into account (Álvarez *et al.*, 2007).

The coke producing technology currently available has to make a trade-off between structure and quality parameters such as chemical composition and thermal stabilities (Díez *et al.*, 2002). The coke strength is usually reduced to provide the coke with a better reactivity (Ishii, 2000). A poor-quality coke has high reactivity and high degradability. A coke with high degradability alters the coke consumption in blast furnaces since the gas flow is inadequate to maintain the needed integrity (Rodero *et al.*, 2015). An increase in coke degradability impairs the efficiency of the blast furnace since the permeability is reduced and blocking of the tuyeres with the residues occurs (Díez *et al.*, 2002). A good quality coke has a high CSR index and a low CRI value (Díez *et al.*, 2002). Various authors found correlations between CSR and CRI, as well as the Spanish National

Coal Institute reactivity test (INCAR: ECE) methods (Díez *et al.*, 2002; Menendez *et al.*, 1999). Other authors used mathematical models to predict coke quality (Zhang *et al.*, 2004).

Coke reactivity is defined as the mass loss produced at high temperatures when the coke is reacting with oxidising agents under specific conditions (Rodero *et al.*, 2015). The CO_2 reactivity (carboxy reactivity) is regulated by the Boudouard reaction equilibrium:

$$C(s) + CO_2\,(g) \leftrightharpoons 2CO(g)\ \ \Delta H^\circ = 163\ kJ \tag{1}$$

As coke temperature increases in furnaces, the Boudouard's equilibrium shifts to the right to increase the coke consumption (Rodero *et al.*, 2015). It is therefore beneficial if the coke has a low reactivity towards CO_2 in blast furnaces.

Impurities in coke have an adverse effect on the performance of the coke and need to be kept as low as possible. These impurities include moisture, volatile matter, sulphur, ash, phosphorous, and alkali contents (Díez *et al.*, 2002). Diez *et al.* (2002), stated the following required chemical properties of blast furnace coke. The moisture content of coke influences the coke reactivity rate and must fall within 1 to 6 wt.% for maximum moisture content (Díez *et al.*, 2002). The sulphur and ash contents decrease the coke productivity in furnaces and should be between 0.5 and 0.9 wt.% dry-based (db) and 8 and 12 wt.%. db, respectively. Volatile matter causes problems during the cleaning of furnaces and should be less than 1 wt.% db. Alkali metal compounds should be less than 0.3 wt.% db and phosphorous between 0.02 and 0.06 wt.% db.

In order to maintain good permeable support, the physical properties of coke must include a narrow particle size distribution and a resistance to breakage and abrasion (Díez *et al.*, 2002). Empirical methods to determine resistance to degradation include shatter tests, revolving drum tests and a combination of breakage and abrasion tests (Díez *et al.*, 2002). Porosity is not considered an essential factor in coking properties; however, some authors differ on this subject (Loison *et al.*, 2014).

Coke is also characterised according to ultimate analysis, proximate analysis, dilatometry, free-swelling indices and agglutination indices (Loison *et al.*, 2014). Petrography is also used to quantify and characterise coke by looking at the microstructure and microtexture. The different carbon forms present in coke form part of the microtexture (Lomas *et al.*, 2017). Metallurgical coke has a mosaic-like optical texture due to the anisotropic carbon in the material (Marsh *et al.*, 1982). Coke is also composed of inerts, isotropic carbon and flow-type anisotropic carbon (Marsh *et al.*, 1982). The feed material determines the fluidity, size and shape of the produced coke's anisotropy (Marsh *et al.*, 1982). The produced coke's performance depends on each component's optical texture. The randomly orientated mosaics form part of a matrix to produce a coke that is more resistant to crack propagation than isotropic carbon (Marsh *et al.*, 1982). In blast furnaces, anisotropic carbon has better resistance to gasification when compared to isotropic carbon and plays a role in the rate of solution loss in blast furnaces (Marsh *et al.*, 1982). Anisotropic carbon can maintain a high coke strength (Marsh *et al.*, 1982). Co-carbonations are postulated to be a manner to produce a coke that has a mosaic optical structure (Marsh *et al.*, 1982).

2.5 Utilisation of biomass waste

The main driving force behind the use of biomass as a source of energy is the possibility to reduce CO_2 emissions. Biomass wastes include residues from the forestry and paper industry, crop residues and municipal waste (Kwapinski *et al.*, 2010; Mafu *et al.*, 2016). These materials are high in carbohydrates and lignin content, which are perfect for biorefining (Kwapinski *et al.*, 2010). Without biorefining, these materials would have been landfilled and may have produced methane emissions (Kwapinski *et al.*, 2010).

The conversion of biomass to biofuels is done according to four mechanisms, i.e. thermochemical, biochemical, agrochemical and direct combustion (Piyo, 2014). Thermochemical mechanisms include pyrolysis, gasification and direct liquefaction (Piyo, 2014; Toor *et al.*, 2014).

Pyrolysis thermal energy is used to break apart molecules, in a similar way to carbonisation, to convert raw materials into carbon-rich materials through thermal treatment (Adrados *et al.*, 2015; Schobert, 2013). The pyrolysis of biomass produces bio-oil, synthetic gas and biochar (Kwapinski *et al.*, 2010; Piyo, 2014). Pyrolysis is conducted in an inert atmosphere at temperatures ranging from 300°C to 600°C (Piyo, 2014). Pyrolysis occurs according to three stages. The first stage occurs below 200°C where the main volatile products are released, i.e. water, carbon monoxide, carbon dioxide and hydrogen sulfide (Schobert, 2013). The second stage occurs between 350°C and 550°C. During this stage, the light hydrocarbon gases and organic compounds are released and condense to form coal tar (Schobert, 2013). The last and final stage (>550°C) produces a high carbon content solid and gaseous by-product due to the breaking apart of larger molecules (Schobert, 2013). The pyrolysis conditions of biomass influence char development (Mafu *et al.*, 2017). By increasing the pyrolysis temperature, char development takes place by the elimination of aliphatic groups as the aromaticity increases, which is progressed by aromatic ring condensation (Kwapinski *et al.*, 2010; Mafu *et al.*, 2017). Dry and smaller particle sizes of biomass are preferred since larger particle sizes will use more energy during pyrolysis (Kwapinski *et al.*, 2010).

Liquefaction processes depend on the chemical composition of the cellulose, hemicellulose and lignin of the raw materials, as well as the temperature, solvent and catalyst used in the process

(Piyo, 2014). Hydrothermal liquefaction (HTL) processes negate the need to dry the preferred feedstock since water is added to the HTL process (Piyo, 2014). Figure 2-4 shows the hydrothermal liquefaction reactor setup at North-West University. Biomass has a high moisture content making the HTL method an energy-efficient process (Piyo, 2014). Large amounts of sludge waste are produced per year and can be converted into pure products efficiently and effectively by HTL (Piyo, 2014). HTL is done by operating at temperatures between 200°C and 370°C and at pressures greater than 220 bar (Piyo, 2014). The HTL process is used to produce stable bio-oils from carbonaceous solid feedstocks (Toor *et al.*, 2014). The solid biochar is produced as a by-product of the stable bio-oil (Toor *et al.*, 2014). Biochar is obtained at approximately 200°C and 1 MPa where carbonisation occurs and biochar are formed (Piyo, 2014).

Figure 2-3: **Hydrothermal liquefaction reactor pilot plant at the North-West University.**

Thermochemical mechanisms are essential in converting waste biomass into energy sources such as biochar. Biochar is chemically and biologically more stable than the original biomass waste it is converted from (Piyo, 2014). Biochar is used in the social and agricultural sectors as a source of fuel for cooking and heating, as well as a soil amendment for water and mineral retention (Glaser *et al.*, 2001; Piyo, 2014). The use of biochar, compared to biomass, is beneficial since the biochar has a higher calorific value than biomass, produces less ash than the biomass and also produce a smokeless fuel since most of the volatiles are driven off during the conversion process (Glaser *et al.*, 2001).

Various studies have been done on the effect of biomass addition to coals to be used as PCI. Du *et al.* (2014) found promising results when coal is partially replaced by biomass for PCI to still keep reasonable burnout in blast furnaces. The co-gasification of biomass and coal is a topic of interest for many authors. Das *et al.* (2014) found that the blending of biomass with non-coking coal, could produce a coke with promising swelling numbers, chemical analyses and shatter tests.

2.5.1 Spent coffee grounds as biomass waste feedstock for hydrothermal liquefaction

Coffee is the second largest commodity after petroleum and is grown in 80 countries (Campos-Vega *et al.*, 2015). In 2017, about 9.51 million tons of spent coffee grounds (SCG) were discarded into landfill (Von Wielligh *et al.*, 2018). Approximately 50% of the total input feedstock of coffee for the production of soluble coffee grounds are seen as a residue (Tsai *et al.*, 2012). This leads to a disposal problem of SCG. SCG have no significant market other than for its use as soil amendment, a precursor for activated carbon production and as a sorbent for metal ions removal (Campos-Vega *et al.*, 2015). SCG does not compete as a food source (Von Wielligh *et al.*, 2018).

Spent coffee waste contains organic compounds such as fatty acids, lignin, hemicellulose, cellulose and polysaccharides (Pujol *et al.*, 2013). Lignin has a greater heating value than hemicellulose and cellulose (Toor *et al.*, 2014). Biomass rich in lignin are suitable for thermochemical processes due to their higher solid yield after pyrolysis (Mafu *et al.*, 2016)

Due to the high-water content of SCG, pyrolysis is not an ideal method to treat it; however, it is ideal for HTL since water is added during the liquefaction process (Von Wielligh *et al.*, 2018). The biomass hydrolyses into smaller pieces, polymerises again and produces HTL products (Von Wielligh *et al.*, 2018). Another advantage of HTL is that the operating temperature is between 200°C and 370°C, which is much lower than pyrolysis conditions, which usually occurs above 400°C (Piyo, 2014; Von Wielligh *et al.*, 2018). The biochar product prepared from SCG shows a similar composition to that of lignite coal (Von Wielligh *et al.*, 2018). One of the drawbacks of lignite coal is that it shows no agglomeration and swelling (Loison *et al.*, 2014), which is necessary when producing coke.

Previous studies investigated the use of SCG as fuel by treating the SCG through pyrolysis. A calorific value of 31.9 MJ/kg was obtained at optimal conditions (Tsai *et al.*, 2012). However, very high nitrogen content was present in the prepared biochar leading to the possible formation of NO or NO_2, which is not beneficial for the environment (Tsai *et al.*, 2012). The biochar prepared in this manner showed promising results for use in the industrial sector but only if a more environmentally friendly manner of production could be used (Tsai *et al.*, 2012).

2.6 Utilisation of biochar

Sustainable development is about striving for the efficient and optimal use of energy sources (Mangena & Du Cann, 2007). One of these energy sources is biochar. Char is a carbon-rich product that does not go through an intermediate fluid state during production (Kwapinski *et al.*, 2010; Schobert, 2013). The use of biomass-derived feedstocks as alternative energy sources could significantly reduce CO_2 net emissions compared to fossil fuels (Adrados *et al.*, 2015).

The utilisation of pyrolytic chars depends on the chemical and structural properties of the char, as well as the pyrolysis conditions (Mafu *et al.*, 2017). If the pyrolysis temperature is high, the elemental composition changes. This leads to higher fixed carbon and elemental carbon contents, lower elemental oxygen and lower volatile matter contents (Mafu *et al.*, 2017).

Most of the published work regarding the use of biochar in an integrated system to produce coke focuses on bio-oils and/or the use of catalysts. The bio-oil can be used as a feedstock for producing valuable chemicals and the biochar can be used as a carbon source (Adrados *et al.*, 2015). Studies show that to obtain coke from biochar is not an easy process since the conditions to obtain a good quality product are very sensitive (Adrados *et al.*, 2015). These process conditions include the heating rate of pyrolysis of the biochar. Moderate temperature and fast pyrolysis provide the optimum conditions to maximise the yield of liquids but are not beneficial to the quality of biochar (Adrados *et al.*, 2015). Biochar yield and quality is at a maximum at a slow heating rate and high operational temperatures (Adrados *et al.*, 2015; Kwapinski *et al.*, 2010; Mafu *et al.*, 2017).

It is known that the addition of biomass to the coal matrix for coke production reduces the maximum fluidity (Kokonya *et al.*, 2013; Montiano *et al.*, 2014). Some authors found that co-pyrolysis or co-combustion brings no interaction between the coal and biochar matrix (Montiano *et al.*, 2014).

2.7 Oxidation method for coke production

Coal oxidises naturally in air. Coal reacts with oxygen to produce water and dehydrogenated coal (Loison *et al.*, 2014). The oxidation of coal is accelerated by increased temperature and an increase in the number of hydroxyl groups (OH) in the coal, which serve as attachment points for oxygen (Loison *et al.*, 2014). The oxidation of coal in air is barely visible and does not alter the calorific value of the coal (Loison *et al.*, 2014). Extensive research is being done to determine the effect of weathering on coal and on its structural and chemical characteristics (Cimadevilla *et al.*, 2005a). Air oxidation adversely influences the thermoplastic properties of coal which in turn affects the coke produced from the coal (Cimadevilla *et al.*, 2005a). The plasticity of coal decreases upon oxidation of coal (Loison *et al.*, 2014). Usually, moisture and atmospheric conditions influence the physical and chemical properties of coking coal adversely; however, such conditions can reduce smoke formation during combustion of briquettes (Loison *et al.*, 2014; Mangena & Du Cann, 2007).

Previous studies on the use of a wet oxidant, hydrogen peroxide, on coal indicated that pyritic sulphur is removed from the coal (Mukherjee *et al.*, 2001). The wet oxidation treatment also decreased the ash content significantly (Mukherjee *et al.*, 2001). Further degradation of organic material occurs with longer wet oxidation treatment times (Mukherjee *et al.*, 2001). Another author used peroxide to remove inorganic sulphur completely and observed a reduction in ash content of the coal (Vasilakos & Clinton, 1984).

The wet oxidation method can be used to improve the highest possible effective use of low-cost materials. Low-cost materials include the use of lignite, brown coals and biochar. Low-rank coals and lignite are abundant resources and are used in various power generation processes (Miura *et al.*, 1996). However, they have some disadvantages including high moisture content and low calorific values (Miura *et al.*, 1996). Miura *et al.* (1996) found that liquid phase oxidation of these resources could be a way to utilise them for the production of fatty acids. Other authors have tried to use hydrogen peroxide as an oxidising agent but focused on the structure of the coal and not the physical changes thereof (Miura *et al.*, 1996). Ashida *et al.* (2017) found that the oxidation of brown coal resulted in the highest tensile strength when treated at 60°C for 2 hours using 30% hydrogen peroxide.

Similar experimental work with hydrogen peroxide was done by Sun *et al.* (2014) and Plancher *et al.* (2002), in order to improve the compressive strength of lignite briquettes with or without the use of a binder. Plancher *et al.* (2002) investigated the use of hydrogen peroxide when used with a binder (coal tar) to improve coke briquette strength and concluded that the hydrogen peroxide treatment is difficult to control even though it showed promising results (Plancher *et al.*, 2002). Sun *et al.* (2014) found that an increase in compressive strength was observed in oxidised coal due to the increase in hydrogen bond association which increases the oxygen-containing functional groups. This was confirmed by using FTIR analysis.

2.8 Summary of chapter

The production of coke using traditional, experimental and novel techniques has been discussed. A lot of research has been done on traditional and experimental techniques of producing coke as the cost of coke is increasing due to the depletion of coking coals. The metallurgical industry is facing increasing pressure to reduce CO_2 emissions which is shifting the focus of research towards more energy-efficient methods to produce coke. A great part of the literature focuses on reducing the use of fossil fuels in metallurgical processes by partially replacing fossil fuels with biomass or biochar. Previous authors found promising results when combining biomass, biochar or brown coals as raw materials with coking coal to produce coke. New technologies, such as HTL, create more effective and efficient ways to utilise waste biomass. Although the effect of oxidation on coal is known, the effect of oxidation on biomass or biochar still needs to be researched. Some authors investigated the effect of oxidation on coke feedstock, but research still needs to be done to determine if biochar can be used without coal, binders and moulds to prepare coke or coke substitutes.

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CHAPTER 3 CHEMICAL AND PHYSICAL CHARACTERISATION OF SPENT COFFEE GROUND BIOCHAR TREATED BY A WET OXIDATION METHOD FOR THE PRODUCTION OF A COKE SUBSTITUTE

3.1 Introduction

Coal or coal blends are used for the production of coke through carbonisation at temperatures of up to 1100°C (Díez *et al.*, 2002). Coke is utilised mainly to produce ferroalloys in blast furnaces. Blast furnace coke plays a significant role as permeable support, which cannot be substituted by other substances (Díaz-Faes *et al.*, 2007; Díez *et al.*, 2002).

Coke is subjected to thermal and mechanical degradation in blast furnaces (Díez *et al.*, 2002). Blast furnace coke has certain critical coke qualities that must be adhered to, which include the resistance of coke to thermal and chemical degradation (Díez *et al.*, 2002). These coke quality requirements must be met to provide sufficient permeable coke support and safe furnace performance (Díez *et al.*, 2002). The coke producing industry usually needs to make a trade-off between the coke structure and the chemical composition or thermal stabilities (Díez *et al.*, 2002). The critical qualities of the coke depend on the specific blast furnace, electric furnace type or operational conditions and characteristics demanded from the coke. The quality parameters widely used in the coke producing industry to characterise blast furnace coke is the Coke Strength after Reactivity (CSR) index and the Coke Reactivity Index (CRI) (Álvarez *et al.*, 2007; Díez *et al.*, 2002; Lundgren *et al.*, 2009; Menendez *et al.*, 1999). These tests take the coke's reactivity towards CO_2 into account, as well as the coke's post-reaction mechanical strength (Álvarez *et al.*, 2007). Other characterisation techniques to determine the quality of the coke include proximate and ultimate analyses, free swelling index and agglutination indices (Loison *et al.*, 2014). The different analysis data need to be within certain limits for the safe and efficient performance of blast furnaces (Díez *et al.*, 2002).

The need for improved coke quality, economic pressure and depleting coking coal resources force the metallurgical industry to look for alternative coke producing methods such as coal blending (Díez *et al.*, 2002). Other methods include the use of the pulverised coal injection (PCI) method to produce pig iron. The use of PCI forces the industry to use a higher quality coke with better permeability and higher strength since the use of fine reductants increases the residence time and coke degradation rate in blast furnaces (Díez *et al.*, 2002). Other alternative methods include the use of renewable resources such as biomass and biochar. Waste biomass is produced from the agricultural, municipal, forestry and paper industries (Kwapinski *et al.*, 2010). Spent coffee grounds (SCG) is one such waste biomass material. Approximately 9.51 million tons of SCG was discarded into landfill in 2017 (Von Wielligh *et al.*, 2018). SCG does not have a significant market value other than for its use as a soil amendment (Glaser *et al.*, 2001), metal ions remover (Fosso-Kankeu *et al.*, 2019) and as a precursor for activated carbon (Campos-Vega *et al.*, 2015).

Energy can be extracted from SCG utilising gasification, pyrolysis and direct liquefaction (Piyo, 2014; Toor *et al.*, 2014). Liquefaction of raw materials by using hydrothermal liquefaction (HTL) negates the need to dry the feedstocks because water is added to the process, making the HTL process an energy-efficient mechanism to extract energy (in the form of chemical compounds) from raw materials (Piyo, 2014). An HTL reactor operates between 200°C and 370°C, much lower than pyrolysis temperatures, which usually occurs between 300°C and 600°C (Piyo, 2014). The HTL process converts carbonaceous solids to stable bio-oils with biochar as a by-product and in most cases a waste product (Toor *et al.*, 2014).

Various authors have investigated the use of biochar or biomass in integrated systems to produce coke or coke substitutes. Wijayanta *et al.* (2014) investigated the utilisation of pulverised oak char as a substitute for use in PCI and found promising results with a similar temperature profile compared to the pulverised coal used in blast furnaces. The addition of sawdust to coal blends to produce coke was investigated by Montiano *et al.* (2014). It was concluded that the fluidity was decreased significantly and that no interaction between the coal and sawdust was observed (Montiano *et al.*, 2014). Das *et al.* (2002) found that adding biomass to non-coking coals could give the coal the swelling, elemental composition and strength needed to produce coke. The addition of biomass to coking coals can also reduce CO_2 emissions as biomass is regarded as CO_2 neutral (Kokonya *et al.*, 2013). Coking coal blended with biomass has different influences on the critical coke quality parameters and led the investigation to different techniques, such as oxidation, to produce a coke substitute.

The coking industry frequently encounters oxidation of coking coals by air. Coal and coke samples are oxidised to some degree during the testing and fine crushing of the samples. The particle size of the coal affects the oxidation thereof since the oxygen may diffuse into the interior of the coal particle (Loison *et al.*, 2014). Oxidation of coking coal is accelerated by an increase in temperature (Loison *et al.*, 2014). The lower the rank of coal the faster the oxidation occurs. The presence of oxygen in the coal accelerates the oxidation process, which can be attributed to the presence of hydroxyl groups serving as attachment points for oxygen (Loison *et al.*, 2014). Although the effects of the oxidation are not visible and do not alter the calorific value of the coal, the coking properties are affected adversely (Loison *et al.*, 2014). Previous studies on the oxidation of coal with an aqueous oxidant have focused mainly on the elucidation of the structure of coal and the solubility of low-rank coals (Loison *et al.*, 2014).

Experimental work focusing on the use of a wet oxidant, such as hydrogen peroxide, to improve the compressive strength of low-cost materials was conducted. Sun *et al.* (2014) and Plancher *et al.* (2002) investigated the effect that wet oxidation has on the compressive strength of the oxidised coal and observed an increase in compressive strength after the wet oxidation treatment, with or without the addition of a binder to the hydrogen peroxide treatment.

The use of a wet oxidation treatment to produce a metallurgical coke substitute from inexpensive waste raw materials with sufficient mechanical strength and chemical properties without the use of a binder is investigated and reported on in this part of the dissertation.

3.2 Materials and methods

3.2.1 Materials

SCG was gathered from a local coffee shop in the Potchefstroom area, in South Africa. The SCG was used as feedstock to produce biochar. Biochar was prepared by HTL from the SCG. The SCG biochar was generated with the North-West University's continuous hydrothermal liquefaction pilot plant (as indicated in section 3.2.2) and used on an as-received basis as prepared by the faculty of engineering. This biochar was used as biochar source throughout this study. Hydrogen peroxide was obtained from Thembane Chemicals, in South Africa. Hydrogen peroxide at 30% concentration (100 Vol) was used throughout this study. Nitrogen (high purity: 99.999%) from AFROX, South Africa was used during pyrolysis of the treated biochar to obtain an inert atmosphere. Coke produced by a local coke supplier and producer was obtained to serve as a reference when comparing the properties of the prepared coke substitute to coke used in blast furnaces. The sample preparation and characterisation techniques, i.e. ultimate analysis, proximate analysis and the gross calorific value, were done according to coal standard methods as described by Mafu *et al.* (2018) and Acar *et al.* (2012). The different ISO procedures used are based on the ISO 13909-4: 2001 method for sample preparation. Proximate analysis was based on the ISO 11722: 1999, ISO 1171: 2010, ISO 562: 2010 and ISO 562: 2010 methods. The ultimate analysis was based on the ISO 12902 CHN instrumental method.

3.2.2 Sample preparation and characterisation

The process of HTL of the SCG is described by Von Wielligh *et al.* (2018) and Fosso-Kankeu *et al.* (2019). The SCG slurry was fed into the HTL reactor at 3 vol%. Reverse-osmosis water was used to prevent damage to the reactor by normal tap water, which is high in chlorine. The slurry was left overnight, where after it was sealed and pressurised. The temperature was increased to 305°C. The slurry spent 10 minutes in the reactor vessel at the reaction temperature. The slurry was then left to cool and depressurise. The aqueous oil was separated from the solid biochar by pressure filtration. The biochar was then obtained and dried at 80°C for 24 hours to remove solvents and moisture present in the biochar. Thereafter, the biochar was crushed using a mortar and pestle and sieved to < 300 µm using a Labotec sieve. The sieved and dried biochar was used for wet oxidation treatments. Crushing and sieving of the biochar was done before each experiment to minimise the effect of additional oxidation in air. The biochar was characterised before and after the different experiments to determine the effect the wet oxidation treatment had on the biochar. The biochar was characterised according to ultimate and proximate analyses, calorific value, free-swelling index (FSI), compressive strength and Fourier-transform infrared spectroscopy (FTIR).

3.2.3 Wet oxidation treatment experiments at room and elevated temperatures

Oxidation experiments were carried out by combining 5 g prepared SCG biochar with 50 ml of 5%, 15% and 30% (all vol%) hydrogen peroxide (H_2O_2) solutions. The slurry was stirred for different treatment times and at different temperatures. Initial experiments were conducted to determine which concentration of the H_2O_2 solution will cause sufficient oxidation of the biochar slurry. These experiments were conducted at room temperature for 2, 6 and 24 hours and at an elevated temperature of 60°C for 0.5, 1 and 2 hours, as well as at 80°C for 0.5, 1 and 2 hours. The produced biochar samples were washed with deionised water and dried overnight at 80°C. The samples were then sieved using a Labotec 300 µm sieve.

The wet oxidation experiments were conducted using water baths and refluxers to prevent evaporation of the H_2O_2 that occur during prolonged treatment times and at elevated temperatures. The respective samples were washed with deionised water, filtered and dried at 80°C for 24 hours after the mentioned treatment time, temperature and concentration of H_2O_2 solution. The processes were repeated until enough sample was prepared for thermal treatment and characterisation.

3.2.4 Characterisation of biochar samples

Characterisation of the different samples before wet oxidation, after wet oxidation and after thermal treatment was done to determine the effect of wet oxidation on the physical and chemical properties of the biochar and produced coke substitute samples. To elucidate the chemical and elemental composition, proximate and ultimate analyses were performed on the samples as described by Loison *et al.* (2014) and Díez *et al.* (2002). FTIR was done using a BRUKER VERTEX 70 FTIR spectrometer in a single step measurement from 4000 cm^{-1} to 400 cm^{-1}. The gross calorific values were determined, as described in the literature (Acar & Ayanoglu, 2012), to indicate whether the heating value of the produced coke substitute and pre-cursor was sufficient when compared to untreated samples.

The swelling and coking propensity of coking coal is seen as one of the main requirements for producing a high-quality coke (Loison *et al.*, 2014). The crucible swelling numbers of the prepared biochar samples were measured as described in the literature (ISO 501:2012) (Loison *et al.*, 2014). The crucible swelling number or FSI was used to determine the effect the oxidation has on the plastic and fluidity properties of the biochar, as well as an indication of the caking properties of the raw material (Loison *et al.*, 2014). The FSI values were determined using a Meker-Fisher burner and by ramping the temperature of a finely crushed 1 g sample in a crucible and lid from room temperature up to 820°C within 2.5 minutes as described in literature (Loison *et al.*, 2014). The residue left in the crucible was compared to a series of standards (Loison *et al.*, 2014). The H_2O_2 concentration with the most promising results was used for further investigation and characterisation.

3.2.5 Pelletisation of biochar

Pellets were generated by using an LRXplus strength tester, operating with a 5 kN load cell. Each pellet consisted of 0.5 g biochar. The dried biochar was placed in a Specac PT 10 mm die set and compressed at a 15 mm/min rate until a 1.5 kN load was achieved. The load was kept on the die set for 30 seconds to ensure sufficient compression. The pellets were carefully removed to ensure the pellets remained intact.

The coke sample obtained from industry was reduced in size by drilling a 10mm diameter cylinder through the coke lump by means of a hollow diamond drill bit. Manual sanding was used to reduce the height of the coke cylinder into a pellet with similar dimensions to the prepared coke substitute pellets (10mm x 10mm).

3.2.6 Thermal treatment and pellet curing

After the wet oxidation treatment and pelletisation, the samples were subjected to thermal treatment to produce a coke or coke substitute. The pellets were thermally treated (pyrolysed) in an electric tube furnace (Lenton Elite thermal system furnace with a programmable controller). The pellets were loaded into the furnace, flushed with pure nitrogen and heated at 10°C per minute to 1100°C. The pellets were kept isothermally at this temperature for 2 hours. Nitrogen flow rate remained at 600 ml per hour throughout the treatment. The pellets were left in the furnace until cooled to room temperature before they were removed from the inert environment.

3.2.7 Compressive strength

The compressive strength was determined by diametric compressive strength determination tests of the produced thermally treated pellets using an LRXplus strength tester. The breakage of the pellets was recorded in kN. The area of each pellet was measured to convert the compressive strength to MPa. The average compressive strength and standard deviations of at least 8 pellets were determined for each sample. Outliers were eliminated by using the Q-test (95% confidence level) (Crouch *et al.*, 2013).

3.3 Results and discussion

3.3.1 Determination of optimum H_2O_2 concentration

The oxidising and corrosive nature of H_2O_2, as well as the additional costs of using a high concentration of H_2O_2, led the researcher to use the lowest possible H_2O_2 concentration. Diluted H_2O_2 (5%, 15% and 30%) was used for wet oxidation experiments. FSI values gave an indication of the plasticity and caking propensity of the biochar (Loison *et al.*, 2014). The FSI values of the 5% and 15% wet oxidation samples all had a swelling crucible number of 1. From these results, the lower concentrations (5% and 15%) of H_2O_2 showed little to no effect regarding the FSI values and thus the swelling or caking propensity of the chars. The higher concentration H_2O_2 (30%) showed an increase in crucible swelling number and these are listed in Table 3-1. It was therefore determined that 30 vol.% H_2O_2 would be used for the further investigation. In the literature, 30% H_2O_2 is usually used for oxidation experiments on coal (Ashida *et al.*, 2017; Miura *et al.*, 1996).

Table 3-1: FSI values of the 30% treated biochar samples at room temperature and at 80°C for 0.5, 1, 2, 6 and 24 hours with untreated biochar as reference (The first number in the sample identification indicates the time at the specified temperature; the temperature is indicated as RT for room temperature and 80 for 80 ºC).

	FSI
Sample Identification	**Crucible swelling number (1-9)**
Biochar (untreated)	1.0
2RT	1.0
6RT	1.5
24RT	2.0
0.5.80	1.5
1.80	1.0
2.80	1.0

Swelling is seen as the consequence and cause of caking (Loison *et al.*, 2014). The crucible swelling numbers showing oxidation at room temperature between 6 and 24 hours or for short periods (0.5 hours) at elevated temperatures (80°C), indicate that an optimum range of plasticity is obtained by depolymerisation and cross-linking reactions from the use of the wet oxidant H_2O_2 (Ashida *et al.*, 2017). A low and high degree of wet oxidation showed no effect on the crucible swelling number compared to the untreated biochar. Plancher *et al.* (2002), stated that the effect H_2O_2 has on raw materials is often difficult to control as it has an optimum oxidation level at a specific temperature and time duration for the best results to improve swelling indices and compressive strengths.

The thermally treated wet oxidised pellets showed no change in appearance and swelling after determining the FSI value. The same was observed from the coke sample obtained from industry.

3.3.2 Chemical characteristics

Various samples prepared by wet oxidation were compared to untreated biochar samples as well as a sample of coking coal. Thermally treated wet oxidation treated pellets were compared to a blast furnace coke sample.

3.3.2.1 Ultimate analyses

Ultimate analysis data of different samples before and after thermal treatment are summarised in Table 3-2. Different wet oxidation treatment times are listed as 0.5, 1, 2, 6 and 24 hours. Temperatures used are indicated as RT for room temperature and 80 for treatment at 80°C. The values for the untreated biochar samples before and after thermal treatment are also listed in Table 3-2 to serve as a reference.

Cimadevilla *et al.* (2005) found that the oxidation of samples showed a decrease in the volatile matter, a decrease in carbon content and an incremental increase in oxygen. Similar results were obtained by the wet oxidation of the biochar samples before thermal treatment. Sulphur contents of less than 1 wt.% (dry basis) is usually required from coking coal for the production of metallurgical coke (Díaz-Faes *et al.*, 2007; Díez *et al.*, 2002). The sulphur contents of the biochar samples after wet oxidation were < 1%, which falls within the industry requirement. The samples before and after thermal treatment (pyrolysis) showed a reduction in sulphur, hydrogen, oxygen and nitrogen contents.

Table 3-2: Ultimate analysis data for room temperature and 80°C treated wet oxidised biochar, treated for different time durations, before and after thermal treatment (pyrolysis) (the first number in the sample identification indicates the time at the specified temperature; the temperature is indicated as RT for room temperature and 80 for 80 ºC).

Ultimate analysis data for room temperature treated biochar (wt.%)

	Sample Identification	Sulphur (air-dried)	Carbon (air-dried)	Hydrogen (air-dried)	Nitrogen (air-dried)	Oxygen (air-dried)	O/C (x 10)	H/C (x 10)
Before thermal treatment	Biochar (untreated)	0.3	74.5	6.2	2.8	16.2	2.2	0.8
	2RT	0.2	72.1	6.1	2.8	18.8	2.6	0.8
	6RT	0.2	71.9	6.1	2.8	19.0	2.6	0.8
	24RT	0.2	69.4	5.9	2.6	21.8	3.1	0.9
	0.5.80	0.2	65.0	5.8	2.2	26.7	4.1	0.9
	1.80	0.2	64.3	5.9	2.0	27.7	4.3	0.9
	2.80	n.d.	65.2	6.6	n.d.	25.5	3.9	1.0
After thermal treatment	Biochar (untreated)	0.2	94.5	0.6	1.3	3.4	0.4	0.1
	2RT	0.1	95.8	0.4	2.0	1.7	0.2	0.0
	6RT	0.1	96.5	0.4	2.1	0.9	0.1	0.0
	24RT	0.1	94.8	0.6	1.5	3.0	0.3	0.1
	0.5.80	0.1	95.9	0.5	1.3	2.2	0.2	0.1
	1.80	0.1	96.4	0.6	1.2	1.6	0.2	0.1
	2.80	0.1	97.2	0.8	1.4	0.5	0.1	0.1

3.3.2.2 Proximate analyses

The proximate analysis data of the different samples before and after thermal treatment are listed in Table 3-3. Sample identification is similar to that for ultimate analysis. The values for the untreated biochar samples before and after thermal treatment are also listed in Table 3-3 to serve as a reference.

In order to produce blast furnace coke, the coking coal feedstock needs to adhere to certain properties. Comparing the properties of the coking coal used to produce blast furnace coke with the prepared biochar samples indicates whether the chemical properties are sufficient to prepare a coke substitute. The ash yield of coking coals is usually less than 10 wt.% (dry basis) (Díaz-Faes *et al.*, 2007). The ash yield (dry basis) of the different samples in Table 3.3 indicates an acceptable range of less than 10 wt.% (dry basis) in samples prepared by the wet oxidation treatment of biochar at room temperatures for a long period of time (24 hours) or at short treatment times of up to 0.5 hours at elevated temperatures of 80°C.

The fixed carbon content is a coke production cost factor since it increases blast furnace temperature (Von Wielligh *et al.*, 2018). South African coking coal usually has a fixed carbon content between 50 and 60 wt.% (air-dried basis). The produced biochar samples (before thermal treatment) has a fixed carbon content between 20 and 40 wt.% (air-dried basis). The fixed carbon contents decrease with increasing wet oxidation treatment time and temperature compared to the untreated biochar sample. Room temperature treated biochar samples showed higher levels of fixed carbon contents than elevated temperature treated samples (80°C). Thermal treatment (pyrolysis) of the samples increased the fixed carbon content, as expected.

The coking coal needed to produce blast furnace coke requires a moisture content between 1 and 6 wt.% as handling problems become a concern with too high or low moisture contents (Díez *et al.*, 2002). The produced biochar samples including the untreated biochar fall within this limit for moisture content.

The ash yield of blast furnace coke should be low since extra energy is required to melt the ash in blast furnaces, which results in a decrease in productivity of the furnace (Díez *et al.*, 2002). The ash yield (dry basis) of the thermally treated biochar samples ranges between 15 and 41.5 wt. %. Díez *et al.* (2002), stated that a coke ash content higher than 10 wt.% can be used in blast furnaces if the ash chemistry is acceptable.

The coke producing industry further requires a low volatile matter content of less than 1.0 wt.% (dry basis) of the produced coke (Díez *et al.*, 2002). The volatile matter contents (dry basis and air-dried basis) of the prepared coke samples increase with an increase in treatment time and temperature but decrease substantially after thermal treatment (pyrolysis) of the oxidised samples to be less than 2.5 wt.%.

The moisture content of coke should be approximately 4 wt.% (Díez *et al.*, 2002). The thermally treated biochar samples (coke substitute samples) all fall within this range. These thermally treated biochar samples have moisture contents of less than 2.2 wt.% (air-dried basis).

Table 3-3: Proximate analysis data for room temperature (RT) and 80°C treated (80) wet oxidised biochar, treated for different time durations, before and after thermal treatment.

Proximate analysis results (wt.%)

	Sample Identification	**Moisture (air-dried)**	**Ash (air-dried)**	**Ash (dry basis)**	**Volatile (air-dried)**	**Volatile (dry basis)**	**Fixed Carbon (air-dried)**
Before thermal treatment	Biochar (untreated)	2.0	7.8	8.0	50.3	51.2	39.9
	2RT	2.9	7.0	7.2	52.1	53.6	38.0
	6RT	3.2	7.1	7.3	52.5	54.2	37.2
	24RT	4.4	6.5	6.8	54.4	56.8	34.7
	0.5.80	3.7	7.9	8.2	57.0	59.2	31.4
	1.80	4.0	10.2	10.6	57.9	60.2	27.9
	2.80	3.7	14.2	14.7	59.3	61.6	22.8
After thermal treatment	Biochar (untreated)	1.0	15.0	15.1	1.9	1.9	82.1
	2RT	2.2	14.3	14.6	2.0	2.0	81.5
	6RT	2.2	14.0	14.3	1.7	1.7	82.1
	24RT	1.0	15.6	15.7	2.3	2.3	81.1
	0.5.80	1.2	17.6	17.8	2.0	2.0	79.2
	1.80	0.8	24.8	24.9	1.5	1.5	72.9
	2.80	0.6	41.3	41.5	1.4	1.4	56.7

3.3.2.3 Gross calorific value

The calorific value, even though it is not seen as a main coke quality specification, can be used as an indication of the change the wet oxidation treatment had on the biochar when compared with untreated biochar samples. South African coking coal usually has a gross calorific value of approximately 30 MJ/kg. The calorific value of untreated biochar samples, as well as the oxidised samples, are listed in Table 3-4. Literature states that oxidation does not alter the calorific value of coal samples (Loison *et al.*, 2014). The samples oxidised at room temperature do not show as high a decrease in the calorific value than for the 80°C treated biochar samples. This may be an indication that depolymerisation has occurred to a greater extent at higher temperature wet oxidation than at room temperature wet oxidation treatment processes. Thermal treatment (pyrolysis) of the biochar samples slightly increased the calorific values in comparison to the un-pyrolysed samples.

Table 3-4: **Gross calorific value (CV) data of untreated biochar samples, the room temperature oxidised samples (RT) and 80°C treated samples (80) at different time durations (0.5, 1, 2, 4, 6 and 24 hours) before and after thermal treatment.**

Gross calorific value (MJ/kg)		
	Sample Identification	Gross CV (air-dried)
Before thermal treatment	Biochar (untreated)	27.6
	2RT	26.8
	6RT	26.3
	24RT	25.1
	0.5.80	23.6
	1.80	22.7
	2.80	22.3
After thermal treatment	Biochar (untreated)	28.1
	2RT	27.7
	6RT	28.0
	24RT	27.7
	0.5.80	27.0
	1.80	25.5
	2.80	19.2

3.3.2.4 FTIR

Figure 3-1 shows the FTIR spectra of the untreated biochar sample and the oxidised samples before thermal treatment.

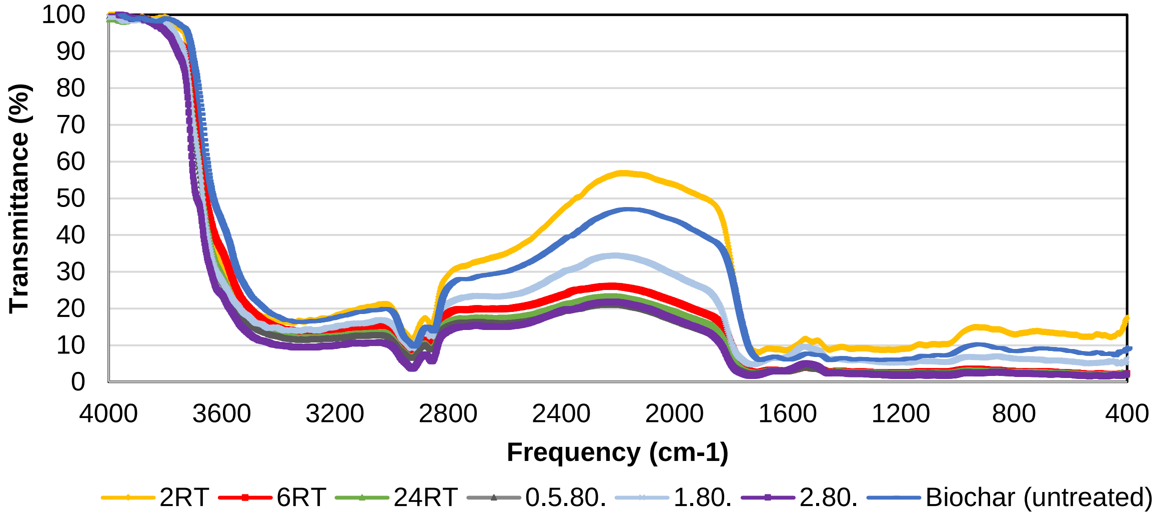

Figure 3-1: **FTIR spectra of the wet oxidation treated biochar samples (The first number in the legend indicates the time at the specified temperature; the temperature is indicated as RT for room temperature and 80 for 80 ºC).**

The broad band between 3200 and 3400 cm^{-1} indicated the vibration modes attributed to the O-H functional group. N-H groups present in this area may have a minor contribution (Li *et al.*, 2014). Methylene and methyl groups (C-H stretch) were present in the 2845 to 2970 cm^{-1} area for all the biochar samples. In this area, the two sharp peaks are attributed to the presence of lipids and caffeine present in roasted coffee (Li *et al.*, 2014). The caffeine is usually indicated by bands at 1655 and 1700 cm^{-1} (Li *et al.*, 2014). The C=C-C bond (aromatic ring structure) has a strong stretching vibration in the 1450 to 1510 cm^{-1} area. Aromaticity can be confirmed with peaks at 670 to 900 cm^{-1} where C-H groups additionally have an out-of-plane bend. The transmittance indicated that common functional groups were present in all the samples. No substantial changes were observed for the functional group distribution in the samples.

The thermally treated oxidised biochar samples (see Annexure A, Figure A-1) showed no significant peaks or absorption indicating that the heating process degraded the organic compounds from the biochar (Li *et al.*, 2014).

3.3.3 Physical characteristics

3.3.3.1 Compressive strength of biochar pellets before thermal treatment

The mechanical strengths of biochar pellets before thermal treatment were determined. The effect the thermal treatment had on the hardening of the biochar pellets was investigated. The pellets were left to air-dry overnight at ambient temperature. Thereafter, the pellets were subjected to compressive strength tests to determine their mechanical strength. The pellets were extremely friable, and no data could be recorded regarding the compressive strength for the untreated and wet oxidation treated biochar samples.

3.3.3.2 Compressive strength values of thermally treated pellets

The compressive strength values of the thermally treated biochar and some of the wet oxidation treated biochar samples are shown in Figure 3-2. The compressive strengths of the prepared samples were compared to a coke sample (indicated as “Coke Industry” in Figure 3-2) obtained from a local coke producer.

The pyrolysed untreated biochar showed a very low compressive strength. An increase in wet oxidation treatment time and temperature showed an increase in the compressive strength of the thermally treated oxidised biochar samples. The biochar samples oxidised for 24 hours at room temperature (24RT) showed the highest compressive strength value. The treated biochar showed significantly higher results compared to the coke obtained from industry and untreated biochar. Sun *et al*. (2014) observed similar results stating that oxidation treatment increased the compressive strength of biochar.

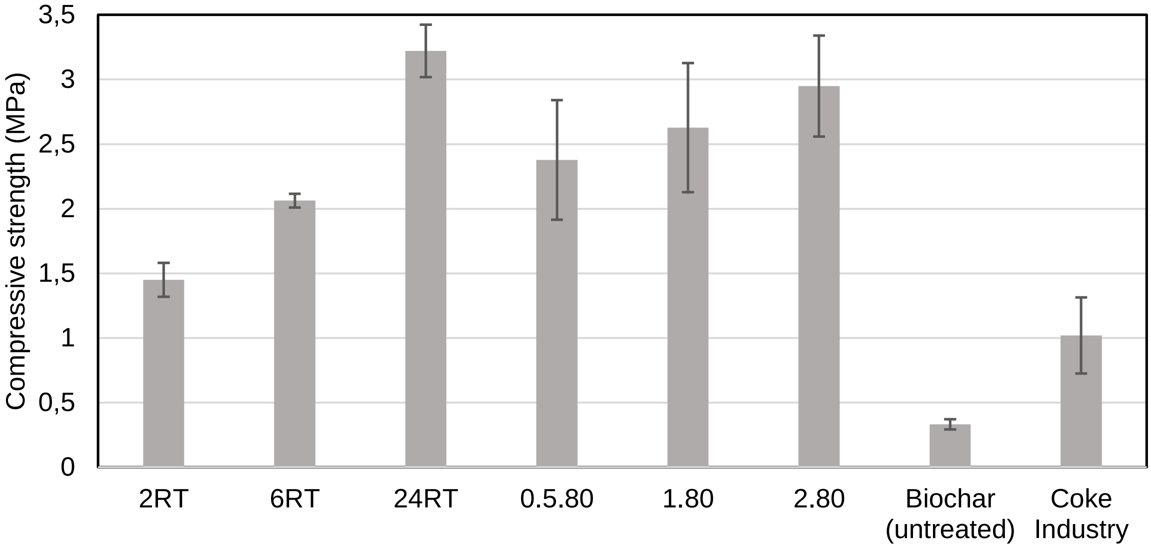

Figure 3-2: **Compressive strength values of the different thermally treated oxidised samples (RT or 80), thermally treated (not wet oxidation treated) biochar (Biochar (untreated)) and a coke sample obtained from industry (Coke Industry).**

3.3.4 Conclusions

The production of a high-quality coke substitute is dependent on various chemical and physical requirements set by the metallurgical industry. Biochar was prepared by HTL from spent coffee grounds and was subjected to a wet oxidation treatment process using H_2O_2.

The physical and chemical characterisation of the wet oxidation treated biochar samples were compared to findings reported in literature and to coking coal samples and it was concluded that:

- The preferred H_2O_2 concentration used to obtain biochar samples to produce a coke substitute is 30 vol.%.
- FSI values of biochar prepared with 30% H_2O_2 increased when the biochar is treated for long time durations (6-24 hours) at room temperature or for short time durations (0.5 hours) at elevated temperatures of 80°C. The FSI values were increased to 2.0 for the 24-hour room temperature treated sample and to 1.5 for the 6-hour room temperature treated sample and 0.5-hour 80°C treated sample.
- The sulphur contents of all the oxidised biochar samples were within the industry limits at less than 1% when oxidised at room temperature (2-24 hours) or elevated temperatures for short time durations (0.5 hours).

- Fixed carbon contents of the oxidised biochar samples were just below industry requirements of between 50 and 60 wt.%, with values obtained between 20 and 40 wt.% (air-dried).
- The moisture contents of the wet oxidation treated samples (< 4.4 wt.% air-dried) were all within the industry parameters which should be between 1 and 6 wt.%.
- Similar functional groups were present for the samples treated by the wet oxidation method compared to the untreated biochar. The thermally treated samples showed a degradation of the organic compounds.
- The strength of the prepared biochar pellets before thermal treatment had no appreciable strength. By comparing the not thermally treated pellet strength of the wet oxidation treated biochar pellets to that of the untreated biochar similar results were obtained.
- Gross calorific value of the wet oxidation treated samples (< 26.8 MJ/kg) all fell below the preferred blast furnace coking coal value of approximately 30MJ/kg.

After comparing the chemical and physical characterisation of the produced coke substitute, a coke sample obtained from industry and findings in literature it was concluded that:

- Ash yields of the prepared coke samples (thermally treated wet oxidation treated biochar samples) need to be further investigated to determine whether the ash chemistry of these samples is acceptable for use in blast furnaces. Ash yields of less than 14.7 wt.% (dry basis) were obtained.
- A substantial decrease in volatile matter content was visible after the wet oxidised samples were thermally treated; however, the volatile matter content of less than 2.3 wt.% (dry basis) was higher than the industry requirement of less than 1 wt.% (dry basis).
- The moisture contents (< 2.2 wt.% air-dried) of the produced coke substitute samples were within the limits expected from blast furnace coke (approximately 4 wt.%).
- Compressive strength values of the produced pellets were substantially higher – with values of up to 3.220 Mpa – than the coke sample (1.020 MPa) obtained from industry. The compressive strength of the room temperature treatment of the biochar samples increased with an increase in treatment time. Elevated temperature treated wet oxidised samples showed a decrease in compressive strength with an increase in wet oxidation treatment time compared to the room temperature treated samples.
- The compressive strength results of the 2-hour treated samples at room temperature and at 80°C showed that an increase in treatment temperature, at a similar time duration, produced pellets with higher compressive strength at elevated temperatures.

A coke substitute can be produced by a 24-hour wet oxidation treatment with 30 vol.% H_2O_2 at room temperature to produce a chemically and physically stable product, which adheres to the investigated industry requirements. The produced coke substitute from this biochar sample also has the potential to be used as a fine reductant, such as for PCI in blast furnaces during the production of pig iron.

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CHAPTER 4 GASIFICATION REACTIVITIES OF THERMALLY TREATED SPENT COFFEE GROUNDS BIOCHAR PRE-TREATED BY WET OXIDATION

4.1 Introduction

The coke industry uses mechanical degradability and chemical reactivity to determine the quality of coke for specific uses in electric or blast furnaces (Rodero *et al.*, 2015). The reaction between coke and CO_2 is based on the Boudouard equilibrium which states (Rodero *et al.*, 2015):

$$C(s) + CO_2(g) \leftrightharpoons 2CO(g) \quad (1)$$

A coke of low degradability and low CO_2 reactivity will provide adequate coke consumption in furnaces, without waste excess CO produced (Hilding *et al.*, 2005; Rodero *et al.*, 2015). Low reactivity towards CO_2 is preferred since an increase in furnace temperature will cause Equation 1 to shift to the right and increase coke consumption. The reactivity of the coke sample is measured by the endothermic gasification reaction given in Equation 1 (Menendez *et al.*, 1999).

Various authors have investigated the reactivity of coke towards CO_2. The reactivity of coke towards CO_2 is indicated as the main quality parameter and the ECE-INCAR, NSC, IRSID-CERCHAR, ECE and various other tests were developed accordingly (Álvarez *et al.*, 2007; Díaz-Faes *et al.*, 2007; Díez *et al.*, 2002; Huo *et al.*, 2014; Loison *et al.*, 2014; Menendez *et al.*, 1999; Patrick, 1990; Wang *et al.*, 2015; Zhang *et al.*, 2004). These tests require certain particle sizes, a specified mass of the sample, temperature ramp rate, isothermal temperature and time and flow rate of reactive gas to measure the gasification mass loss of the sample to determine the reactivity of the coke sample.

Increasing environmental pressure and cost of coking coal are forcing the coke producing industry to replace coking coals by other starting materials (Hilding *et al.*, 2005). The use of biomass and biochar waste as energy and chemical sources has become important in recent years. Energy-efficient ways to extract chemical energy from these feedstocks are enjoying a lot of attention. One way to extract energy from waste biomass is by hydrothermal liquefaction (HTL). HTL negates the need to dry the feedstock since water is added to the reactor. This process converts the biomass carbonaceous solids into bio-oil and biochar, with biochar being a waste product in many cases (Toor *et al.*, 2014). One of the biomass waste feedstocks that is widely available and does not compete as a food source is spent coffee grounds (SCG). SCG to the magnitude of 9.51 million tons was produced in 2017 where most of it was discarded as landfill (Von Wielligh *et al.*, 2018). Half of the coffee feedstock used to prepare soluble coffee is seen as a residue (Tsai *et* *al.*, 2012). Biochar produced from this waste material (SCG) after HTL is attracting attention as a coke pre-cursor.

Coal weathering is a natural and complex process causing chemical and physical changes in coal structure (Cimadevilla *et al.*, 2005b). One of the main problems the coke producing industry faces is the oxidation of coking coals (Cimadevilla *et al.*, 2005b). The oxidation of coking coals causes changes in the thermoplastic properties of the coals, which subsequently influences the quality of the coke produced from the coking coal (Cimadevilla *et al.*, 2005b). The wet oxidation of coal was studied by Ashida *et al.* (2017) and they found promising results in improving the compressive strength of the biochar to produce a coke substitute.

The chemical and some physical characteristics of the prepared coke substitute samples are similar to an industrial coke sample and were described in chapter 3. The study reported in this chapter focuses on the gasification reactivity of the prepared coke substitute samples produced from wet oxidation treated SCG biochar, the waste material from HTL. The measured reactivities are compared to that of an industrial coke sample.

4.2 Materials and methods

4.2.1 Materials

Spent coffee grounds (SCG) to be used as feedstock to produce biochar by means of hydrothermal liquefaction (HTL) were gathered at a local coffee shop (Potchefstroom, South Africa). An HTL reactor pilot plant at the North-West University was used to convert the SCG into biochar as described in chapter 3. As also described in chapter 3, biochar was treated with a wet oxidation treatment by using hydrogen peroxide (30%, 100 Vol) obtained from Thembane Chemicals, South Africa. Pyrolysis of the biochar was done in an inert atmosphere consisting of nitrogen (high purity: 99.999%) obtained from AFROX, South Africa. Carbon dioxide (technical grade) obtained from AFROX, South Africa, was used for coke reactivity tests (gasification). Coke supplied by a local coke producer served as a reference for the prepared coke substitute samples.

4.2.2 Sample preparation and characterisation

Von Wielligh *et al.* (2018) and Fosso-Kankeu *et al.* (2019) described the hydrothermal liquefaction (HTL) process with SCG as feedstock. Coke substitute samples were prepared through pyrolysis of the wet oxidation treated waste samples, after HTL and wet oxidation treatment of the SCG samples, as described in chapter 3. The wet oxidation treated samples (coke pre-cursor) were subjected to thermal treatment in an N_2 atmosphere to produce a coke substitute (Maree *et al.*, 2019).

Ultimate and proximate analyses, as well as the compressive strengths of the coke samples compared favourably to values reported in literature and with that of industrial coke (Maree *et al.*, 2019).

4.2.3 Reactivity towards CO_2

In order to investigate the reactivity of the produced coke substitute samples, an adaptation of various methods to determine coke's reactivity towards CO_2 was used which had the most similarity with the method of Hilding *et al*. (2005). The coke reactivity experiments were conducted under isothermal conditions in a thermogravimetric analyser (TGA) (SDQT-600) as shown in Figure 4-1. The reactivity of the coke is important as it will be used within blast furnaces to withstand chemical and mechanical degradation. Each coke substitute sample (approximately 13 mg) with a particle size of less than 300 µm was placed inside the TGA by means of a platinum crucible, which was flushed with nitrogen at a flow rate of 100 millilitres per minute. Samples were heated at 50°C per minute to 900°C. Thereafter, the CO_2 reactivity was measured by introducing CO_2 (at 10 millilitres per minute) into the furnace and recording the mass loss. The samples were left isothermally in CO_2 for a minimum of 250 minutes. The equations used to calculate the conversions, gasification rates and reactivities of the biochar samples were obtained from Mafu *et al.* (2018).

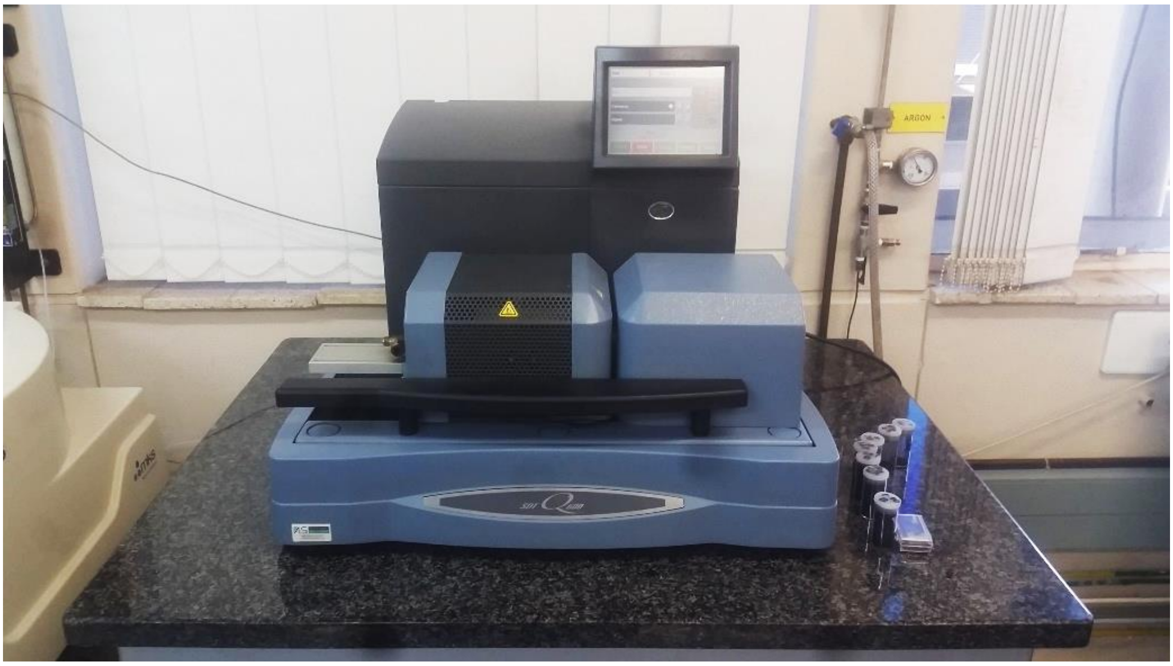

Figure 4-1: TGA used for gasification experiments (SDQT-Q600).

Fractional conversion (X) was determined using Equation 2. Initial char mass is indicated by m_0 and final weight after gasification is referred to as m_f. The char weight at time t is indicated by m_t. Gasification rate of the biochar was determined using Equation 3.

$$X = \frac{m_0 - m_t}{m_0 - m_f} \qquad (2)$$

$$r = \frac{\delta X}{\delta t} \qquad (3)$$

Determinations of the average initial reactivity (R_i), reactivity index at 50% conversion (R_{50}), and average final reactivity (R_f) were done according to Equations 4 to 6.

$$R_i = \frac{\sum_{X=0\%}^{X=10\%} r}{N} \qquad (4)$$

$$R_{50} = \frac{0.5}{\tau_{50}} \qquad (5)$$

$$R_f = \frac{\sum_{X=70\%}^{X=90\%} r}{N} \qquad (6)$$

The number of data points is indicated by N and the time required for the biochar to reach 50% conversion is indicated by τ_{50}. The conversions, gasification rates and reactivities were calculated for all the thermally treated samples and the coke sample obtained from industry.

4.3 Results and discussion

4.3.1 Fractional conversion

Mass loss versus time curves of the various room temperature treated samples, as well as of the untreated biochar and industrial coke sample are given in Figure 4-2. The data in Figure 4-2 was used to determine the fractional conversion curves as illustrated in Figure 4-3.

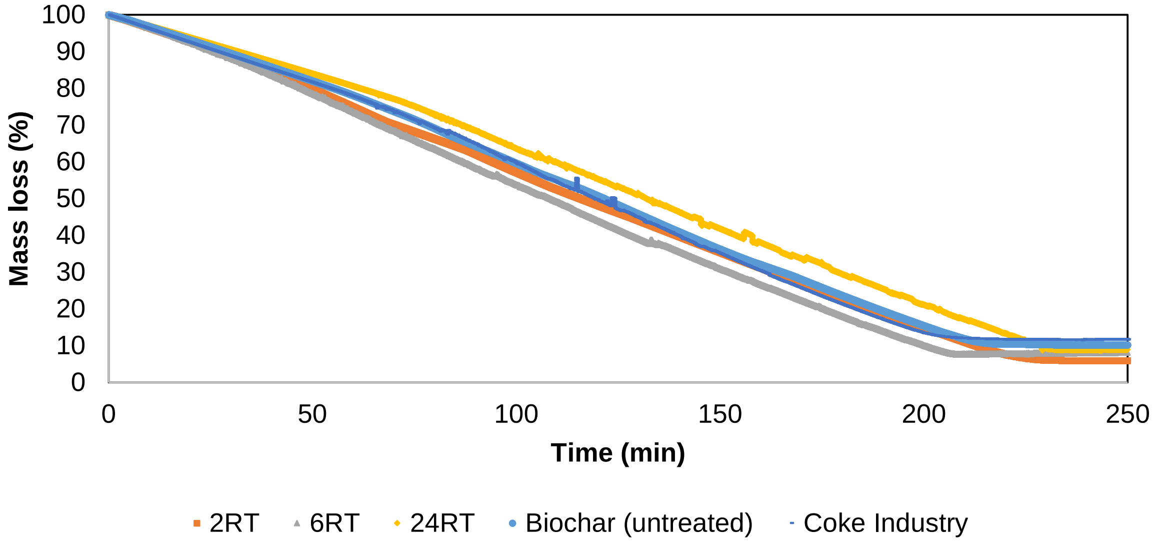

Figure 4-2: Mass loss curve at 900°C in a CO_2 atmosphere of the untreated biochar, of coke obtained from industry and of the room temperature wet oxidation treated biochar samples treated for 2, 6 and 24 hours (The first number in the sample identification indicates the time at the specified temperature with RT as room temperature).

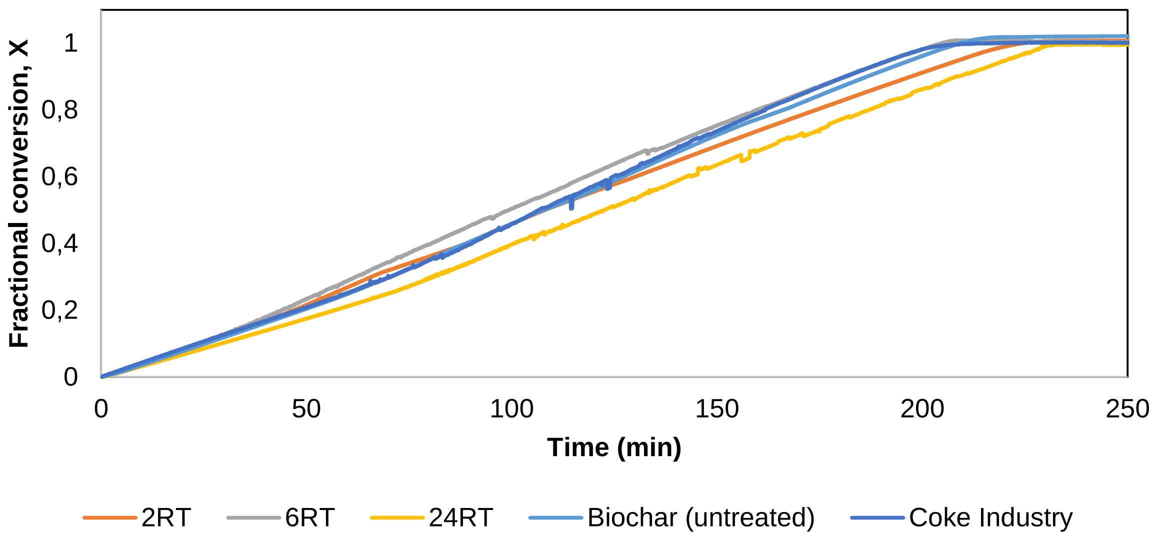

Figure 4-3: Fractional conversions (at 900°C in a CO_2 atmosphere) of the untreated biochar, coke obtained from industry and the room temperature wet oxidation treated biochar samples treated for 2, 6 and 24 hours (The first number in the sample identification indicates the time at the specified temperature; the temperature is indicated as RT for room temperature).

Fractional conversion curves (Figure 4-3) indicate that the conversion of the 6-hour room temperature treated sample occurred at a faster rate.

The room temperature treated samples treated for 2 and 24 hours, were converted at a decreased rate compared to the untreated biochar or coke industry sample. However, similar room temperature treated sample conversion rate curves indicate that the wet oxidation treatment time showed no significant effect on the conversion rate of the various samples using this method.

Figure 4-4 illustrates the mass loss curves versus time of the elevated temperature treated coke substitute samples. The data from Figure 4-4 was used to determine the fractional conversion curves shown in Figure 4-5.

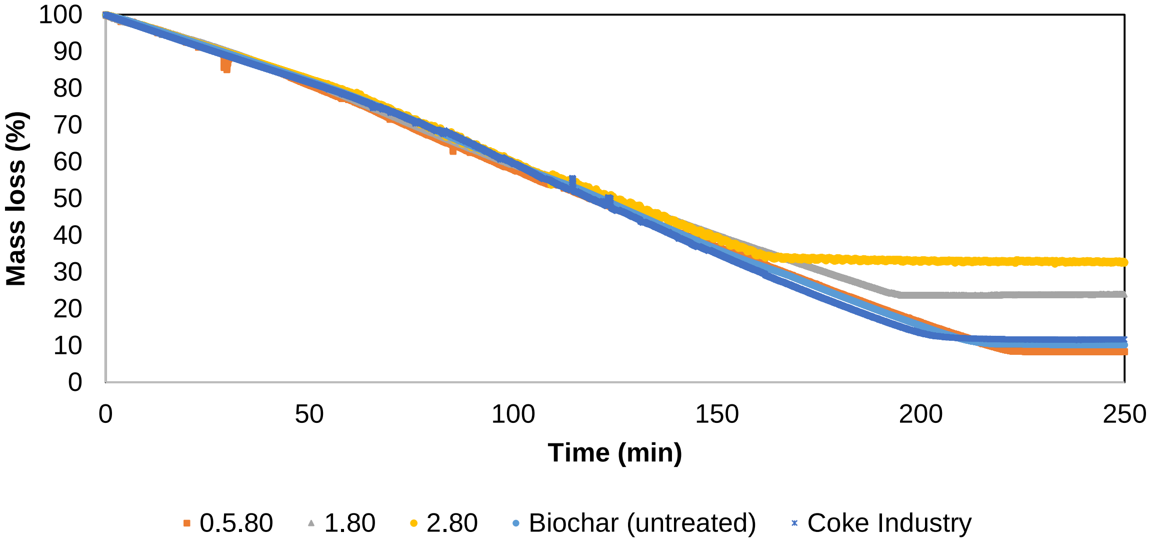

Figure 4-4: **Mass loss curves at 900°C in a CO_2 atmosphere of a coke sample obtained from industry, untreated biochar and wet oxidation treated samples prepared at 80°C for 0.5, 1 and 2 hours (The first number in the sample identification indicates the time at the specified temperature of 80°C).**

Figure 4-5 shows the fractional conversion of the elevated temperature treated (80°C) biochar, as well as the untreated biochar sample and coke sample obtained from industry. Figure 4-5 illustrates that the 2 hour 80°C treated coke substitute had the highest conversion rate, followed by the 1 hour 80°C wet oxidation treated coke substitute sample. The elevated temperature treated samples treated for longer time durations all showed slightly higher conversion rates compared to the biochar and coke sample. The half an hour treated sample showed the lowest conversion rate.

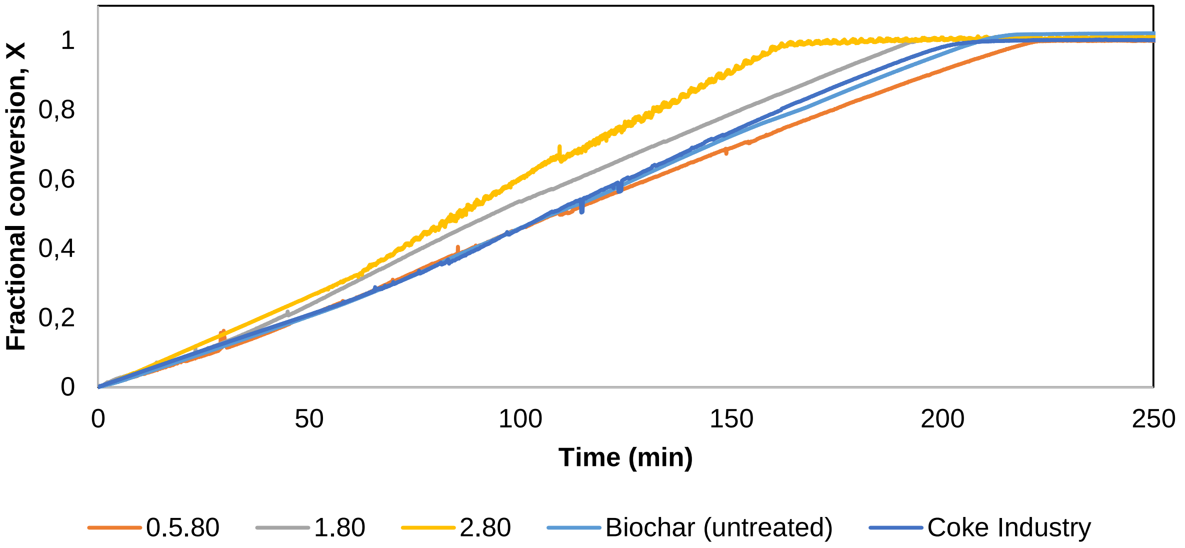

Figure 4-5: **Fractional conversion curves (at 900°C in a CO_2 atmosphere) of a coke sample obtained from industry, untreated biochar and wet oxidation treated samples prepared at 80°C for 0.5, 1 and 2 hours (The first number in the sample identification indicates the time at the specified temperature; the temperature is indicated as 80 for 80 ºC).**

4.3.2 Reactivity

Reactivity for the biochar samples is presented in Table 4-1. The untreated biochar sample was not wet oxidation treated but only thermally treated. This sample will serve as a reference alongside the coke sample obtained from industry (Coke Industry sample).

Table 4-1: **Reactivity for the untreated biochar samples, coke sample from industry, the room temperature treated (RT) and 80°C (80) temperature treated biochar at treatment times of 0.5, 1, 2, 6 and 24 hours.**

Sample Identification	**Reactivity (min^{-1}) ($x10^3$)**		
	$R_{i,ave}$	R_{50}	$R_{f,ave}$
Biochar (untreated)	3.6	4.6	4.8
Coke Industry	4.4	4.7	4.9
2RT	3.7	4.6	4.6
6RT	3.8	5.0	5.0
24RT	3.2	4.1	4.3
0.5.80	3.7	4.5	4.6
1.80	4.7	5.4	5.3
2.80	4.8	5.8	6.0

From the Boudouard's equilibrium reaction (Equation 1), coke consumption increases as the temperature is increased in furnaces shifting the equilibrium to the right (Rodero *et al.*, 2015). It is therefore beneficial for coke to have a low reactivity towards CO_2. Subsequently, the prepared sample's reactivity needs to be equally reactive or less reactive than the coke sample obtained from industry. The average initial reactivity of the prepared samples was all less than the industrial coke sample with the exception of the 2 and 1 hour 80°C treated samples that had higher average initial reactivities. The 1-hour 80°C wet oxidation treated sample (1.80) showed a reactivity value (4.7 $x10^3$ min^{-1}) closest to the initial reactivity of the Coke Industry sample (4.4 $x10^3$ min^{-1}). The 6-hour room temperature treated sample had a reactivity of 3.8 $x10^3$ min^{-1} which was just below the reactivity of the coke sample obtained from industry. Reactivities at 50% conversion (R_{50}), indicated that the Coke Industry sample had a reactivity of 4.7 $x10^3$ min^{-1}. The untreated biochar sample and the 2-hour room temperature treated sample both had a reactivity of 4.6 $x10^3$ min^{-1} which is just below the reactivity of the coke industry sample. The highest 50% conversion reactivity was obtained by the 2 hour 80°C treated sample (5.8 $x10^3$ min^{-1}). Final reactivities indicated that the 6-hour room temperature treated sample had a reactivity of 5.0 $x10^3$ min^{-1} which was closest to the coke sample obtained from industry (4.9 $x10^3$ min^{-1}). The 2 hour and 1 hour, 80°C treated prepared samples had the highest average final reactivities with 6.0 $x10^3$ min^{-1} and 5.3 $x10^3$ min^{-1} values, respectively. The reactivities indicated that a certain range of oxidation treatment is preferable to obtain selective higher reactivities. Longer wet oxidation treated samples (1 to 2 hours) at elevated temperatures (80°C) showed higher reactivities. The room temperature wet oxidation treated samples treated for 6-hour time durations showed promising results of producing a coke substitute with reactivities lower or similar to the coke sample obtained from industry. Elevated temperature (80°C) wet oxidation treatments showed that 1 and 2-hour wet oxidation treatment is sufficient to obtain a very reactive coke substitute.

4.4 Conclusions

The reactivity index of blast furnace coke is a critical coke quality parameter. This index was adjusted to fit the particle size and sample mass of the prepared samples to determine the reactivity of untreated biochar (not wet oxidation treated), coke substitute samples and a coke sample obtained from industry. The prepared coke substitute samples were compared to the heat-treated biochar sample and coke from industry and it is concluded that:

- The fractional conversion of the room temperature treated coke substitute samples indicated that equal or lower conversion rates were achieved when compared to the coke industry sample.

- The elevated temperature treated biochar samples showed higher conversion rates compared to the coke sample from the industry, with the exception of the half an hour 80°C treated sample.
- The average initial reactivities of the prepared samples were all lower than that of the coke sample obtained from industry with the exception of the 1 and 2 hour, 80°C treated coke substitute samples that had higher reactivites. The coke sample from industry had a reactivity of 4.4 x 10^3 min^{-1}. The coke substitute sample that had the closest reactivity was the 1-hour 80°C wet oxidation treated sample with a reactivity of 4.7 x10^3 min^{-1}.
- Reactivity at 50% conversion showed that the 2-hour 80°C treated sample had the highest reactivity of 5.8 x 10^3 min^{-1}. The coke sample from industry showed 50% conversion reactivity of 4.7 x 10^3 min^{-1}. The 2-hour room temperature treated sample had the closest reactivity to the industrial coke sample with a reactivity of 4.6 x10^3 min^{-1}, similar to the untreated biochar sample.
- Average final reactivities indicated that coke had a reactivity of 4.9 x 10^3 min^{-1}, which was lower than that of the 6-hour room temperature treated sample (5.0 x10^3 min^{-1}), as well as the 1 and 2 hour 80°C treated samples (5.3 x 10^3 min^{-1} and 6.0 x 10^3 min^{-1}, respectively). The other prepared samples all had lower reactivities than the coke samples. The prepared coke substitute samples closest to the coke sample from industry were the 6-hour room temperature wet oxidation treated sample and the untreated biochar sample (4.8 x 10^3 min^{-1}).

The coke substitutes produced from SCG biochar (HTL waste product) by heat treatment after wet oxidation have similar reactivities as a coke sample obtained from industry. The preferred wet oxidation treatment time and temperature rely on the preferred reactivity of the coke. A longer wet oxidation treatment of 1 and 2 hours at elevated temperatures showed higher overall reactivities. Room temperature wet oxidation treated samples, treated for 6 hours, showed similar reactivities than the values of the industrial coke sample. The most promising results, closest to the industrial coke sample, were obtained from the 6-hour room temperature wet oxidation treated sample. The wet oxidation treatment of the waste after HTL of the SCG, using H_2O_2 as oxidant, resulted in a biochar that may be utilised for the production of a coke substitute.

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CHAPTER 5 CONCLUSIONS

5.1 Introduction

This chapter summarises the conclusions made throughout this study regarding the production of a coke substitute by using the waste biochar produced during HTL of spent coffee grounds and wet oxidation treatment of the biochar before heat treatment. This chapter also indicates the contribution this study makes to the existing knowledge field and concludes with future work to be done and recommendations.

"The aim of this study is to investigate the effects of a wet oxidation treatment method on an obtained biochar sample in order to prepare the biochar as a raw material for coke production. The synthesised coke substitute should have appropriate mechanical strength and reactivity."

-Aim as stated in Chapter 1.3

As coking coal prices soar and coking coal reserves are depleting, a new technology needs to be developed to produce coke from inexpensive feed materials. The investigated feed material, biochar, is a waste by-product produced from the HTL of SCG. The two main quality parameters to determine coke quality are coke's ability to resist degradation and reactivity towards CO_2 in blast furnaces. The produced substitute coke samples' mechanical strengths were tested as an indication of their degradability. The samples' coke reactivities were determined by an adapted version of existing standard methods (ECE-INCAR). Other quality parameters used to characterise coke were also measured for the samples and the chemical composition of the coke and biochar samples were determined. These tests included FTIR, ultimate and proximate analyses and gross calorific value. The fluidity and plastic properties of coking coal are also important coking factors and the Free Swelling Indices (FSI) were determined to indicate if the prepared biochar samples had efficient plastic and coking properties. These characterisation techniques are based on the study objectives and will be discussed in the conclusions.

5.2 Conclusions in terms of the coke pre-cursor samples

Various methods were used to indicate whether an appropriate coke pre-cursor was produced by comparing the prepared samples to the findings reported in literature for coking coals. It is concluded that:

- A biochar sample was obtained by hydrothermal liquefaction (HTL) of spent coffee grounds (SCG).

- Wet oxidation treatment of the waste SCG was effective at a high concentration of 30 vol.% H_2O_2.
- FSI values of the wet oxidised pellets indicated that room temperature wet oxidation treatment was preferred for time durations between 6 and 24 hours or at elevated temperatures of 80°C for a short period of time of approximately 0.5 hours. These treatments increased the swelling index number of the biochar by 0.5 to 1 crucible swelling numbers.
- Compressive strength of the coke pre-cursor before thermal treatment showed no appreciable values.
- Sulphur contents of the produced coke pre-cursor indicated that the samples that were wet oxidation treated at room temperature between 2 and 24 hours and at elevated temperature at 80°C for 0.5 hours, fell within the industry limit of less than 1 wt.%.
- Industry requirements further expect a fixed carbon content of approximately 50 to 60 wt.%; however, the produced coke pre-cursor biochar had a fixed carbon content of between 20 and 40 wt.% (air-dried).
- Volatile matter of the coke pre-cursor was 2.3 wt.% (dry basis) which was higher than the industry requirement of less than 1 wt.% (dry basis).
- Moisture contents of the prepared precursor samples fell within the industry limits (1-6 wt.%) with moisture contents of less than 4.4 wt.% (air-dried).
- FTIR indicated that similar functional groups were present in the wet oxidation treated samples compared to the untreated biochar. Thermal treatment of the samples indicated degradation of some organic compounds.
- The gross calorific value of the SCG coke precursor samples fell below the industry requirements for coking coal (30 MJ/kg) with calorific values of less than 26.8 MJ/kg.

5.3 Conclusions in terms of the coke substitute samples

Various methods were used to indicate whether a coke substitute could be produced with sufficient properties to serve as an industrial coke substitute. The results indicated that:

- The calorific values of the coke substitute samples were between 19.2 and 28.0 MJ/kg, which were within coke parameters, where coke usually has a gross calorific value of approximately 26 MJ/kg.
- Prepared coke substitute samples had ash yields of less than 14.7 wt.% (dry basis). Further investigation into the chemical composition of the ash is needed to determine whether the coke substitute can be used in blast furnaces.
- Moisture contents were within the limits of industrial coke samples (approximately 4 wt.%) with values of less than 2.2 wt.% (air-dried).

- The compressive strengths of the produced coke substitute samples were substantially higher (up to 3.220 MPa) than the compressive strength values of the coke sample obtained from the industry with a value of 1.020 MPa. Room temperature wet oxidation treated samples showed the highest compressive strengths, and also an increase in strength with increased treatment time.
- Comparing similar time duration wet oxidation treatments (2 hours) at different temperatures (room temperature and 80°C), indicated that the 80°C treated pellet had a compressive strength value of 2.950 MPa and the room temperature treated pellets had a compressive strength value of 1.450 MPa. The elevated temperature treated pellet showed a higher compressive strength value compared to the room temperature treated pellet. Both the room temperature and 80°C treated pellets were wet oxidation treated for the same time duration of 2 hours.
- The gasification conversion rates of the coke substitute samples prepared from the room temperature wet oxidation treated samples, were equal or lower than that of the coke sample obtained from industry.
- The coke substitute samples prepared from the 80°C wet oxidation treated biochar samples, showed higher gasification conversion rates when compared to coke from industry.
- The average initial reactivities of the coke substitute samples were lower than that of the coke sample obtained from industry with the exception of the 1 and 2 hour 80°C wet oxidation treated sample. The coke sample obtained from industry had an initial reactivity of 4.4 x 10^3 min^{-1}. The 6-hour room temperature treated sample showed a reactivity lower than the coke sample obtained from industry with a value of 3.8 x 10^3 min^{-1}.
- The 50% conversion reactivities indicated that the 2-hour 80°C treated sample had the highest reactivity (5.8 x 10^3 min^{-1}). The coke sample obtained from industry had a 50% conversion reactivity of 4.7 x 10^3 min^{-1}. Similar reactivity was observed for the 2-hour room temperature treated coke substitute sample (4.6 x 10^3 min^{-1}).
- The industrially obtained coke sample's average final reactivity was 4.9 x 10^3 min^{-1}. Reactivities closest to the industrial coke samples were achieved by the 6-hour room temperature wet oxidation treated sample (5.0 x 10^3 min^{-1}) and the untreated biochar sample (4.8 x 10^3 min^{-1}).

5.4 Concluding final remarks

Based on the comparison between the coke pre-cursor and coking coal, as well as the comparison between the prepared coke samples and a coke sample obtained from industry it is concluded that:

- The results indicated that a coke substitute can be produced from the biochar waste material after HTL of SCG. The wet oxidation treatment of the SCG biochar followed by thermal treatment of the samples showed promising results for producing a coke substitute.
- The 24-hour wet oxidation treatment with 30 vol.% H_2O_2 at room temperature produced a coke substitute sample with chemical and mechanical properties similar to that required by the industry.
- Further investigation showed that a coke substitute with a reactivity similar to a coke sample obtained from industry was produced by using room temperature (for 6 hours) wet oxidation treatment of the SCG biochar as a precursor sample. Eighty degrees Celsius (80°C) wet oxidation treatments of 1 to 2 hours showed higher reactivities than the coke sample obtained from industry.
- The produced coke substitute sample has the potential to be used as a fine reductant (similar to pulverised coal used in PCI) or coke substitute in blast furnaces during the production of pig iron.
- The produced coke substitute can reduce the use of coking coal or coke by the addition of the coke substitutes in blast furnaces.
- The cost to produce coke or coke substitutes has the potential to be decreased since a waste product is used to produce a coke substitute.
- CO_2 net emissions would be decreased during the production of coke because the waste biochar used, has a carbon neutral nature.

Referring to the aims stated in Chapter 1, the reactivity and mechanical strength were of importance. It can be concluded that a mechanically strong and reactive coke can be produced from SCG by means of HTL, wet oxidation treatment and thermal treatment.

5.5 Contribution to existing knowledge field

The contribution of this study is based on the re-use of a waste material to replace an expensive material, coke. Coke resources are depleting, and the cost thereof are increasing. Therefore, the production of a coke substitute by using a waste product (SCG) to produce a biochar, by using an energy efficient method (HTL), which can be used in place of coke is of great importance to science and society. The produced coke substitute is part of the search for greener alternatives to fossil fuels. The use of the coke substitute can also reduce CO_2 emissions due to its carbon neutral biomass. The use of an inexpensive waste material to produce a coke substitute is regarded as a valuable contribution.

Existing coke quality parameters and quality index parameters were reviewed and summarised. A full account was given of the use of biomass or inexpensive feedstocks to produce a coke by means of oxidation. The chemical and physical characterisation of the prepared waste biochar samples and coke pre-cursors provided insight on the structure and characteristics of these materials.

5.6 Future work and recommendations

The work done on the preparation of a coke substitute revealed aspects that need to be studied further to understand the effect wet oxidation has on the preparation of a coke substitute. Therefore, continued investigation and recommendations are important in further elucidating the structure of the prepared coke and its applications to the industry. The future work and recommendations include:

- Determination of the CSI and CSR index values of the SCG coke substitute since these standard testing methods are widely used to determine the precise reactivity and mechanical strength of the sample.
- Investigation of the use of other waste biomass resources that can be subjected to HTL, wet oxidation treatment and thermal treatment to determine whether coke substitutes can be produced from these substances. Blending of the various waste biomass samples also needs to be considered to reduce waste.
- Determination of the behavior of the coke substitute under chemical and mechanical degradation reactions.
- Detailed analysis of the structure of the prepared coke substitute to further understand the effect wet oxidation has on the biochar.
- Investigation of alternative oxidation methods by means of extensive aerial oxidation or the use of other wet oxidants to determine whether alternative oxidation is also efficient for producing a coke substitute.
- Investigate the feasibility to prepare the coke substitute pellets on a larger scale in an inert environment.
- Do an economic study to determine if the proposed process is feasible.

ANNEXURE A

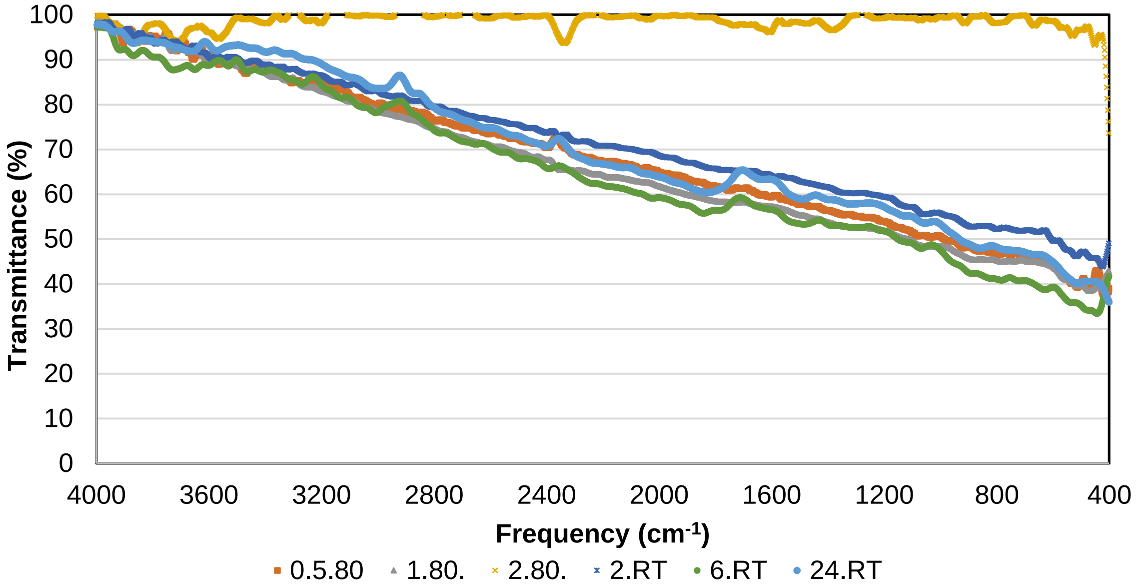

Figure A-1: FTIR data for pyrolysed biochar samples treated at 80°C and room temperature for 0.5, 1, 2, 6 and 24 hours (the first number in the sample identification indicates the time at the specified temperature; the temperature is indicated as RT for room temperature and 80 for 80ºC).