



UNIVERSITY OF THE
WITWATERSRAND,
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**The utilisation of *Searsia lancea* Hydrochar produced by
Hydrothermal Carbonisation and as a binder for South
African discard coal fines**

MSc RESEARCH DISSERTATION

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in Engineering (Chemical Engineering) at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

A handwritten signature in black ink, appearing to read 'Ramadimetja Lizah Setsepu', written over a horizontal line.

Ramadimetja Lizah Setsepu

December 2020

ABSTRACT

The provision of energy globally is becoming an absolute imperative in sustaining modern life due to rising population demographics as well as socioeconomic needs in the developing world. The role of waste resources will become imperative in an endeavour to satisfy these demands. Waste resources such as discard coal are ever increasing and growing at an alarming rate in the coal producing countries. Nevertheless, the continued use of coal hangs primarily on the advances in clean-coal technologies (CCT) as an alternative route for the reduction in environmental risk factors such as the emission of greenhouse gases (GHG), coal or refuse dump, acid mine drainage (AMD) etc.

Biomass and waste resources are receiving attention for tackling environmental concerns, energy security and long-term fuel sustainability. Biomass is regarded as the largest and most abundant source of renewable energy and its greenhouse gas emission status is zero to net negative as plants uptake carbon dioxide during their growth. The use of biomass in its raw form is known to lead to different challenges such as high transportation, storage and handling cost, and low conversion ratio of the biomass to high value-based products. To improve on the physiochemical properties of the biomass, pre-treatment methods such as hydrothermal carbonisation (HTC) are useful in transforming it into a product consisting of mainly carbonaceous solid hydrochar with improved physicochemical properties.

This research study focused on producing a renewable solid fuel blend of hydrochar from raw biomass obtained via HTC and South African discard coal fines at different weight ratios. The raw *Searsia lancea* biomass utilized in this study was found to possess a superior fixed carbon content with lower ash content across all plant sections, and higher calorific value than the raw *Tamarix usneoides* also utilized in this study. From the HTC experiments conducted: the blend of *Searsia lancea* S11 and S12, the hydrochar produced under 280 °C and residence time of 90 minutes was found with the highest energy content of 29.71 MJ/kg compared to 16.73 MJ/kg and 17.23 MJ/kg obtained from the discard coal and raw *Searsia lancea*, respectively.

Three properties of the hydrochar were selected and used in developing polynomial regression equations, using central composite design (CCD). The regression equations were designed with response surface methodology (RSM) – which plots 3D surface responses plots of the combined effect of temperature and time. Regression analysis was performed to fit the response functions of mass yield (%), ash content (%) and calorific value (MJ/kg) and to provide a mathematical framework for future analysis of these three responses. The regression equations

developed indicated that the values obtained experimentally agree with the predicted values from the models via correlation coefficients (R^2) which are given as 0.9537, 0.9525, 0.9789 for mass yield, calorific value, and ash content, respectively. The analysis of variance (ANOVA) was performed to demonstrate the suitability of the model developed for each response. It was found that mass yield had temperature (T) as the only significant model term. While, calorific value (T), and time (t), are the significant model terms, and t, Tt, T^2 , t^2 , T^2t , along with Tt^2 were all significant model terms for ash content.

The combustion tests showed that the pellet produced from the 100 wt. % (by weight) hydrochar had the highest reactivity with the lowest ignition temperature and burnout temperature. All the pellets produced from the blend of hydrochar and coal at different weight ratios, and the 100 wt. % hydrochar displayed a similar burning profile to coal but burnt out at lower temperatures to the 100 wt. % discard coal. The concentration of trace elements from the ash generated from these samples were found to meet the disposal standards herein discussed. In addition, of all the samples tested for their mechanical properties, the pellet produced from the blend of 25 wt. % hydrochar + 75 wt. % coal had the highest compressive strength, impact resistance and absorbed the least amount of moisture.

This study has shown that the *Searsia lancea* trees planted as phytoremediation agents for treating AMD from platinum and gold tailings storage facility (TSFs), as well as rehabilitating polluted soils, have demonstrated to be a suitable binder to produce different grades of biocoal pellets.

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A Modimo a ledire ka go loka, ke ya leboga!

DEDICATION

I dedicate this work to firstly my family and my community of Sekgagakgaping, Mokopane, Limpopo. This is only the tip of the iceberg. Watch the space!

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NOMENCLATURE

CV	Calorific value	MJ/kg
t	Residence time	minutes
T	Reaction temperature	°C
R ₀	Severity factor	—

Abbreviations

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
CCD	Central Composite Design
CO ₂	Carbon Dioxide
DOM	Dissolved Organic Matter
GC-MS	Gas Chromatography-Mass Spectroscopy
GHG	Greenhouse Gas
HHV	Higher Heating Value
HTC	Hydrothermal Carbonisation
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ISO	International Organisation for Standardisation
MPa	Mega Pascal
MSW	Municipal solid waste
Mtoe	Million tonnes of oil equivalent
RSM	Response Surface Methodology
R ²	Coefficient of Correlation
SEM	Scanning Electron Microscope
TGA	Thermogravimetric analysis

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

The world population in 2017 was estimated to be around 7.3 billion and this number has been projected to increase to 10.5 billion by the year 2040 (EIA, 2016 and Saba *et al.*, 2017). The increase in the human population will inevitably require an increasing energy output, which will require more fossil fuels and biomass to be added to the world's total energy mix. One of the main challenges facing the world due to increased energy demand and population growth is climate change, which leads to droughts, food shortages, and environmental pollution. Sarfo, (2008) reported that reducing the dependence on fossil fuels would not only curb greenhouse gas emissions, but shield energy security because they are non-renewable and finite. Consequently, the use of renewable energy sources such as biomass and refuse-derived fuel will be inevitable in the near future.

Biomass is known as a lignocellulosic material derived from living or recently living organic materials such as wood and agricultural residues (Kambo and Dutta, 2015). The use of biomass as a solid fuel for co-firing has received great attention from researchers and boiler manufacturers as a CCT option in recent years. It has been found to be a potential alternative renewable energy source for power generation due to its low emission, low ash and total sulphur content among other fuel characteristics (Rousset *et al.*, 2011 and Teixeira *et al.*, 2012). Perlack *et al.* (2011) and Saba *et al.* (2017) reported that biomass is the largest and most abundant source of renewable energy and its greenhouse gas emission status is zero to net negative as these plants' uptake carbon dioxide during their growth.

The biomass sources proposed for this study are *Searsia lancea* (also known as *Rhus lancea*) and *Tamarix usneoides* (commonly called the Salt Cedar). These trees are part of the Mine Woodlands Research Project started in 2002 at AngloGold Ashanti Limited. The trees were planted for phytoremediation of AMD as well as rehabilitating polluted soils (Dye *et al.*, 2008). Most of these trees were planted between 2003 and 2008 on an estimated 320 hectares of land, now all matured they may be cut and utilized as firewood by the community (Dye *et al.*, 2008 and Mosito, 2016). The use of these trees as firewood in their raw form would only contribute to GHG emissions, poor air quality and undermining the potential of these trees as an alternative energy source.

Nevertheless, biomass is not without any challenges, such as low bulk density, low carbon content, high oxygen content, high alkali and alkaline earth metal composition and low energy density (Kambo and Dutta, 2014). Furthermore, it has been stated that these inferior qualities create challenges such as high transportation, storage, and handling costs, and low conversion of the biomass to high value-based products for energy and other carbon-based applications (Kambo and Dutta, 2015). With the application of thermal pre-treatment processes such as HTC coupled with densification, the above-mentioned challenges may be reduced.

The *Searsia lancea* and *Tamarix usneoides* trees are known as metallophyte plants and can withstand extremely elevated heavy metal (HM) concentrations by either hydrological control and phytostabilisation of the HM in the soil or by hyper accumulation and subsequent storage in subcellular compartments (Spruyt *et al.*, 2014). The ability to utilize these trees which were planted for the rehabilitation of AMD water, and turn them into a clean fuel is of key importance to this study.

The most applied thermal pre-treatment methods include slow pyrolysis, gasification, torrefaction, and HTC (commonly referred to as wet torrefaction). The selection of a pre-treatment method has been found to depend largely on the type of feedstock as well as the desired properties of biochar, which ultimately determine the end application of the product (Kambo and Dutta, 2015). Studies have shown that the main products obtained from slow pyrolysis are biochar and gases such as CO, CO₂, CH₄, and H₂ (Mohan *et al.*, 2006; Brownsort, 2009 and Kambo and Dutta, 2015). Slow pyrolysis produces a higher solid yield of biochar (25 - 35%) compared to other forms of pyrolysis, but the biochar from slow pyrolysis has a far lower yield than those obtained through torrefaction and HTC.

Zhang *et al.* (2018) stated that torrefaction is a thermo-chemical process that converts biomass feedstock at temperatures between 200 and 300 °C with little to no oxygen content. Through mild torrefaction, the converted feedstock into a high energy density product possesses improved physicochemical properties and reduced moisture content amongst others (Bergman *et al.*, 2005; Kambo and Dutta, 2014 and Kambo and Dutta 2015). However, the biochar produced is of higher calorific value, but the main limitation for this method is its failure to remove or reduce the alkali and alkali earth metals from the biochar produced (Kludze *et al.*, 2013; Kambo and Dutta, 2014). The same limitation was also noted in the gasification of biomass where the biochar produced had a high concentration of alkali and alkaline earth

metals, and polyaromatic hydrocarbons (PAHs) which are highly toxic (Ippolito *et al.*, 2012). In addition, all the processes discussed above require that feed material to be dried prior to processing.

Given the above challenges associated with the aforementioned methods, this research seeks to produce a renewable solid fuel blend of hydrochar from raw biomass obtained via HTC and South African discard coal fines. Park *et al.* (2018) along with Yeoh *et al.* (2018) reported that HTC has the advantage of directly hydro-treating wet or green biomass material without a need to undergo pre-drying. Kudo *et al.* (2014) further expanded the process by “hydrolytically removing highly volatile cellulosic material, i.e., cellulose and hemicellulose,” thus transforming the biomass into a solid that is effectively lignin. This modification could enhance the plasticizability of the biomass during briquetting to a reasonable extent and promote particles’ coalescence/fusion and densification of the briquettes (Kudo *et al.*, 2014). The HTC process utilized in this study uses subcritical water mainly at temperatures between 200 and 280 °C, and the condition at this stage is high ion constant and low dielectric constant, which makes it more responsive to non-polar solvents (Bandura and Lvov, 2005 and Saba *et al.*, 2017). Hydrochar produced from HTC has been shown to contain less alkali and alkaline earth metals at high temperatures, with similar combustion properties to coal.

The aim of this research is therefore to use HTC under high pressure and temperature to produce alternative solid fuels, known as biocoal (blend of hydrochar and coal fines) pellets. These will serve as a fuel for the local communities (those around the Witwatersrand Basin gold fields Tailings Dams) for cooking, as a substitute fuel, which can be used in extending the life span of the decommissioned power plant for heat generation and electricity, along with other industrial boiler users. The results of this investigation would determine the next phase in the production of these new solid fuel. Once this concept has been proven in the laboratory for these species along with coal fines, the next step would be to pilot a semi-continuous facility in the production of these products.

1.2 RESEARCH PROBLEM STATEMENT

There is an urgent need to invest in renewable energy sources, such as biomass, because of increasing global demand for electricity driven by population growth, as well as stringent carbon policies and the depletion of fossil fuels. The *Searsia lancea* and *Tamarix usneoides* tree species present an opportunity for feedstock to produce hydrochar. For coal power plants to ensure sustainable energy supply, they need to integrate with renewable energy sources. This sustainability problem provides extraordinary potential. Application of HTC followed by the subsequent densification of the HTC treated material will assist in addressing some of the challenges associated with other biomass treatment methods. In addition, the outcome of this research will add to the body of knowledge on energy applications using South African indigenous biomass resources and will contribute towards establishing the suitability of such plants in the field of phytoremediation and to produce hydrochar through HTC.

1.3 HYPOTHESIS

The biocoals to be formed/produced (blend of hydrochar and coal fines) will yield fuel products of high calorific value than the parent materials (discard coal and raw biomass), better physicochemical and mechanical properties.

1.4 RESEARCH QUESTIONS

The following questions were addressed in this research:

- What are the physicochemical characteristics of the raw biomass, coal, hydrochar, and biocoal?
- Will the conversion of *Searsia lancea* and *Tamarix usneoides* using HTC lead to a high-energy solid fuel?
- Will the hydrochar blended with the coal fines improve the physicochemical properties of the biocoal products?
- Will the hydrochar act as a binder when blended with the coal fines to produce pellets?
- Will the HTC process of *Searsia lancea* and *Tamarix usneoides* have an effect on the ash chemistry?
- What dissolved organic matter will be present in the HTC residue/process water?

1.5 RESEARCH AIM AND OBJECTIVE

The aim of this research is to produce a renewable solid fuel blend of hydrochar from raw biomass obtained via HTC and South African discard coal fines.

The specific objectives of this study are:

- To perform a physicochemical characterisation of the raw biomass, coal, hydrochar, and biocoal,
- To convert the *Searsia lancea* and *Tamarix usneoides* trees into high energy hydrochar products,
- To blend the hydrochar with coal fines and subsequently produce biocoal pellets,
- To conduct ash chemistry analysis on raw biomass and biocoal,
- To analyse the process water to check for dissolved organic matter.

1.6 DISSERTATION OUTLINE

Chapter 1 presents the background information and motivation for the research study.

Chapter 2 provides a review of different types of biomass resources, biomass pre-treatment methods, HTC, and pelletisation. In addition, the mechanical properties of pellets were also reviewed.

Chapter 3 describes the materials and methods used in the study. This chapter describes the design of experiments method used in investigating the effects of reaction temperature and residence time on mass yield, calorific value, and ash content. The chapter, likewise, discusses in detail the characterisation techniques and equipment used.

Chapter 4 discussed the raw fuel characteristics, the effects of HTC reaction temperature and residence time on mass yield, calorific value, and ash content. Central composite design (CCD) was used to develop polynomial regression equations, which measures the interactions between the process variables and the identification of significant factors that contribute to the regression model and statistical analysis. The combustion profiles of the hydrochars, as well as the pellets, are discussed. The results of organic and inorganic analysis of the process water results and, finally, the mechanical properties of the hydrochar and biocoal are presented and discussed.

Chapter 5 summarised the conclusion of the study and offered recommendations for future work.

All the references used in this research are included at the end of this dissertation. Further supporting information related to this study is presented in the Appendix section.

CHAPTER 2: LITERATURE REVIEW

2.1. INTRODUCTION

This section provides an in-depth review of the published literature on global and South African findings related to this research study. The study sheds light on two tree species i.e., *Searsia lancea* and *Tamarix usneoides*; previously used as phytoremediation agents for (AMD), and as potential feedstock to produce high-energy binder for coal fine material via HTC. The two trees species were characterised for their physicochemical properties, and then subjected to HTC and finally blended with coal fine material and densified into pellets. The central argument of this study is that *Searsia lancea* and *Tamarix usneoides* can be used to form biocoal with comparable or better qualities than coal and for different end applications. The products produced may be used as an alternative energy source for heating and cooking, as well as pulverized fuel for combustion in an industrial boiler. The works of literature cited in this section support the fact that there is a need to utilize coal fines that are available in South Africa, and worldwide. Many authors also indicate the need to curb the environmental pollution resulting from the coal-mining-combustion life cycle, through the utilization of coal discard dumps. This research was conducted in consideration of the demand for an energy mix that will provide cleaner energy alternatives towards the current overreliance on coal for combustion and domestic application in present South Africa.

2.2. GLOBAL ENERGY CONSUMPTION RATES

The provision of energy globally is becoming an absolute imperative in sustaining modern life due to rising population demographics as well as socio-economic developmental needs in third world countries (Carpenter, 2015). This results in the global increase in energy consumption along with demand. For example, Figure 2-1 illustrates how energy consumption has been rising with each successive year since 2006. Enerdata, (2018) reported that in 2016 the energy consumption in Europe was 1821 Mtoe (million tonnes of oil equivalent), with 1004 Mtoe for CIS, 2473 Mtoe for North America, 840 Mtoe for Latin America, 5585 Mtoe for Asia, 154 Mtoe for the Pacific, 781 Mtoe for Africa and 760 Mtoe for the Middle-East. As depicted in the figure, developing regions such as Africa, the Middle East, and the Pacific are still lagging behind their developed counterparts in terms of provision and accessibility to energy resources.

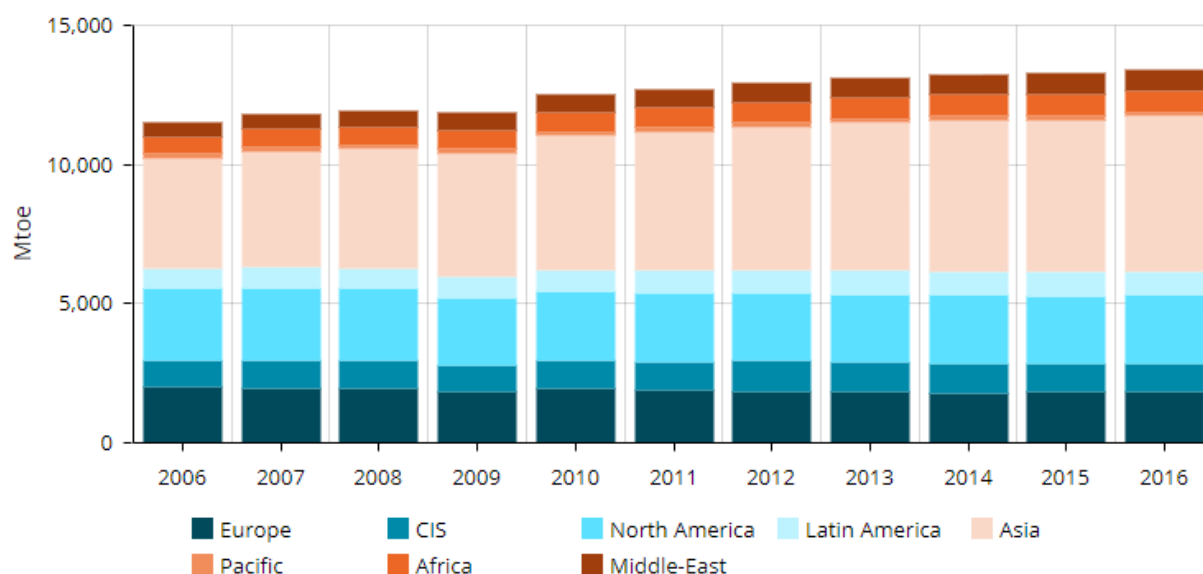


Figure 2-1: Total energy consumption by regions in 2005-2016 (Enerdata, 2018).

According to Silakova, (2018) Figure 2-2 shows that the consumption of fossil fuels in 2015 was 78.4 %, which makes them the most widely, used resources for energy production. The share of the total renewable energy consumption in the same year was 19.3 %, with the traditional biomass contributing about 9.1 % and modern renewable contributing 10.2 %. The renewable energy facet as reported herein consists of utilizing biomass in the traditional sense (heating and power), along with modern renewable and bioenergy sources such as geothermal, solar power, wind, and hydropower (Silakova, 2018). Enerdata, (2018) reported that for the last 10 years, Asia, North America, and Europe have been the leading regions in the world bioenergy production. While the current world-leading countries in the production of renewables for energy production are Norway (97.9 %), New Zealand (84 %), Colombia (82 %) and Brazil (81.2 %) (Enerdata, 2018 and Silakova, 2018). According to the report by Silakova, (2018) biomass presents a valuable source of renewable energy that has the potential to produce heat, electricity, chemicals, and transport fuels. In the developed world, the modern bioenergy sector is progressing with the use of biomass for biofuels (generally transportation fuels), such as ethanol, bio-oil, and biodiesel (REN21, 2017). The developing world, especially Africa still cuts trees for cooking and heating, such applications are not efficient in unlocking the true potential associated with these resources.

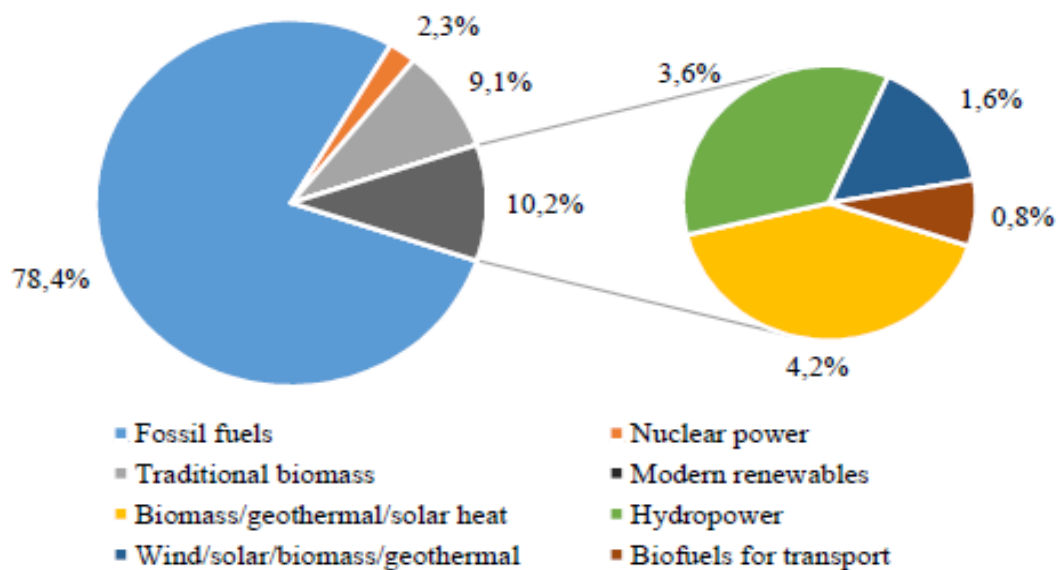


Figure 2-2: Share of energy resources in total energy consumption in 2015 (Silakova, 2018).

2.3. COAL ENERGY IN SOUTH AFRICA

The South African energy landscape is still largely fossil fuel-based. That is, the South African economy still largely depends on coal for power generation and it has been projected in the 2018 Integrated Resource Plan (IRP) draft, that this will continue for the next coming 50 years or so (Department of Energy, 2018). One of the other strains on the supply chain is that South Africa shares and distributes its power supply through the Southern African Power Pool (SAPP) to other neighbouring countries (Aziz and Dittus, 2011). The increase in demand for electricity renders the reliability of the South African electrical grid incompetent at the very least with scheduled load shedding, and blackouts in South Africa and neighbouring countries (Aziz and Dittus, 2011).

This shortfall is expected to continue into the near future, as the SAPP countries do not seem to have any new power generation plans on the horizon according to (Aziz and Dittus, 2011). To mitigate power shortfalls, the South African government plans to add more capacity to the grid and reduce strain on supply by building two additional power plants (Kusile and Medupi). According to Cohen, (2018), Kusile and Medupi power stations were meant to become fully operational in 2015, however, reports of their construction have been plagued by spiralling costs, delays as well as corruption scandals.

Coal remains South Africa's dominant source of energy

Total electricity generated by source, 2016

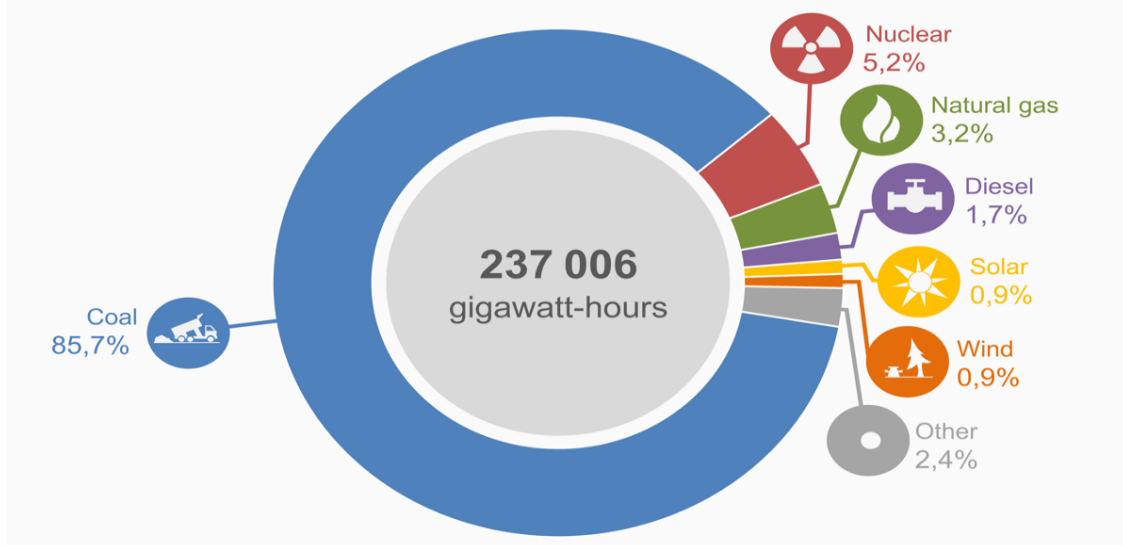


Figure 2-3: Total of electricity generated (Source: (Statistics South Africa, 2016)).

Figure 2-3 provides an insight into the state of electricity generation for the year 2016 in South Africa. From the diagram, it is clear that coal is still the majority energy source at 85.7 % followed by Nuclear at 5.2 % (Statistics South Africa, 2016). The share of the remaining energy sources is natural gas (3.2 %), diesel (1.7 %), solar (0.9 %), wind (0.9 %) and other (2.4 %). In essence, 90.6 % of the energy sources listed above are non-renewable while 7.0 % are renewable sources. For South Africa to curb emissions, it needs to reduce its percentage of non-renewable resources being used as well as incorporate more bioenergy resources. Although there is a need to shift towards cleaner energy, the overwhelming dominance of coal might seem impossible to break. This is because coal is not only a relatively cheap source for energy production, but it is relatively abundant in South Africa (Statistics South Africa, 2016). In addition, coal is also one of the main contributors to South Africa's economic growth, which in 2008 exceeded gold and other resources as a major contributor to SA's gross domestic product (GDP) (Statistics South Africa, 2016). Its mining was responsible for about 1.8 % of total value added to the economy in 2016, higher than gold (1.3 %), but on par with platinum group metals (1.8 %) (Statistics South Africa, 2016). Additionally, South Africa's coal reserves that can be economically recoverable are estimated to be between 15 and 55 billion tonnes and their rank consists of anthracite (2 %), metallurgical coal (2 %), and the remaining 96 % of

reserves are bituminous coal (Ebehard, 2011). Also, the author wrote that the majority of South Africa's mines and reserves are concentrated in the Central Basin which includes the Witbank, Ermelo, and Highveld coalfields.

It is a recognized fact that fossil fuels or hydrocarbons are the largest contributor to environmental contamination, i.e., air, water, and land. These pollutions occurred because of the coal quality used at the power plants and inadequate control of coal combustion processes. The most common issues related to fossil fuel combustions are the release of SO_x and NO_x as well as CO_2 emissions from the power plants. In recent years, South Africa's CO_2 emissions have increased tremendously, and the country has committed to impose CO_2 emission limits, in which it would peak between 2020 and 2025, plateau for approximately a decade and decline in absolute terms thereafter (Department of Energy, 2018). Figure 2-4 depicts the emission reduction path in line with the peak-plateau-decline (PPD) limitations for electricity generation as depicted in the promulgated IRP 2018 (Department of Energy, 2018).

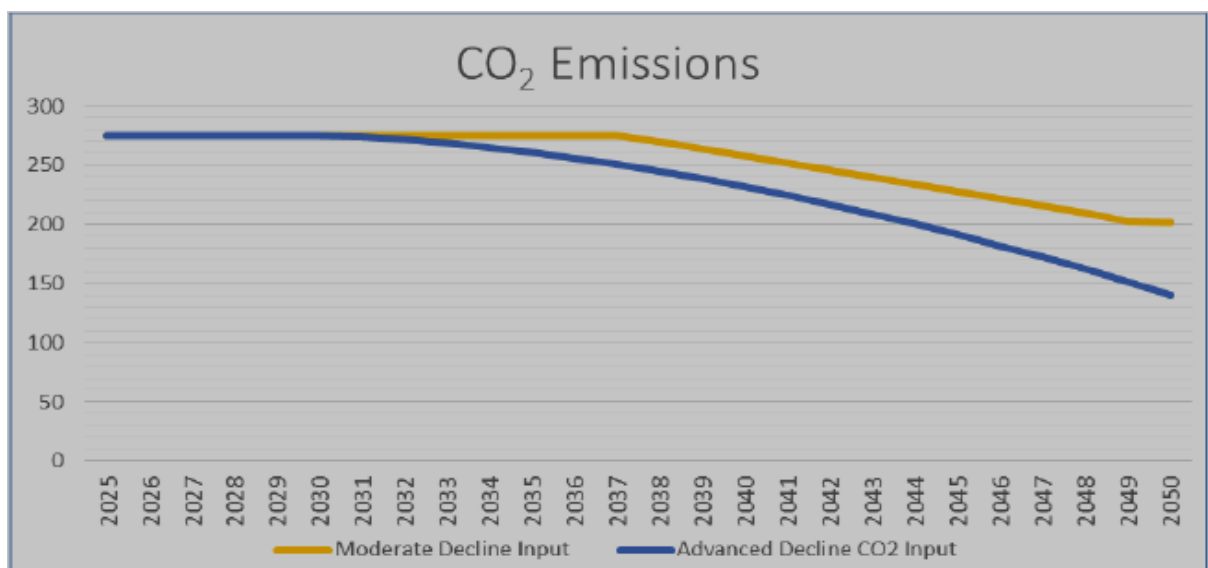


Figure 2-4: Emission Reduction Trajectory (Peak-Plateau-Decline) (Department of Energy, 2018).

It can be concluded that to meet the commitments to reduce emissions in South Africa, bio-energy and clean coal technology methods need to be adopted. Gaqa and Watts, (2018) advised that the future of coal hang primarily on the advances in clean-coal

technologies as a route for the reduction of environmental risk factors such as CO₂ emissions.

2.4. COAL

Coal is currently the primary source of energy for electricity generation in South Africa and is also used in the generation of a significant quantity of the country's liquid fuels (Gaqa and Watts, 2018). South African coal, in general, has a high ash content, which can be up to 65 % from the Waterberg coalfield, and consequently will require further beneficiation to improve its quality such that it can meet export standards (maximum ash content is 15 %) (Eberhard, 2011). The beneficiation process results in two grades of coal, high quality, and middling product. The high-quality coals are known as A grade coal, with ash content of around 15 % and a calorific value of 26 MJ/kg, net as received (Eberhard, 2011). The coal middling, which is more of lower quality (characterised by high ash and sulfur contents); is specifically used for electricity generation by Eskom (Eberhard, 2011). Gaqa and Watts, (2018) on the other hand reported that from the beneficiation of coal in South Africa, about 60 million tons of discard coal are generated annually. A range of other products such as ultra-fines and thermal coal used in the domestic power and synthetic fuel production with higher ash and lower calorific values are also produced (Eberhard, 2011).

The discard generated in the country from the washing plants and the fines generated during mining or screening has been estimated to be approximately 1.5 billion tonnes (Belaïd, 2017). This presents both a challenge and an opportunity in that it is a potential resource for power production through the fluidized bed technology, while it is also an environmental challenge (Eberhard, 2011). Lloyd, (2000) clarifies that discard coal consists of poor quality (high ash and sulphur) and its volatile matter diminishes as stockpiles age. It is noteworthy to mention that the age of the discard coal is important, in that it undergoes weathering over several years, thus making it more difficult to be beneficiated (Belaïd *et al.*, 2013). The accumulation of this resource over the years is due to the lack of interest in finding an alternative approach in combusting this resource or using it for non-energy applications. Hence, this has led to the pollution of hectares of land and also leading to spontaneous combustion and groundwater contamination (Belaïd *et al.*, 2013). One of the significant approaches to utilize this resource is to combust it in a

circulating fluidized bed (CFB), which is a technology that has high tolerance and flexibility regarding fuel of choice. Another approach is to bind this resource, which is mostly of high ash content with biomass (binder) to produce a solid fuel that can be used in an existing PF boiler or CFB boilers.

Belaid *et al.* (2013) conducted a test on the combustion efficiency of high ash South African discard coal. The author does confirm that SA discard coal utilised in his study has the potential to be used for power generation. The calorific value of the coal utilised was 5.04 MJ/kg with an ash content of 73.5 %, which was lower than that used currently at the Lethabo power station ranging from 14 and 16 MJ/kg (Belaid *et al.*, 2013). The authors further reported that the same coal was also tested for its emission trends and it was concluded to yield results well below the minimum emission requirement limits. Figure 2-5 displays both the calorific value and ash content plotted against discard coal tonnages in South Africa. This figure illustrates the potential of discard coals available in the country as an energy source if combusted in a CFB boiler designed in accordance with this coal specification. More so, there are other recent solutions to dealing with discard coal through wet beneficiation, but in this study, we intend to hydrothermally process the biomass then blend it with the discard coal to produce densified biocoal.

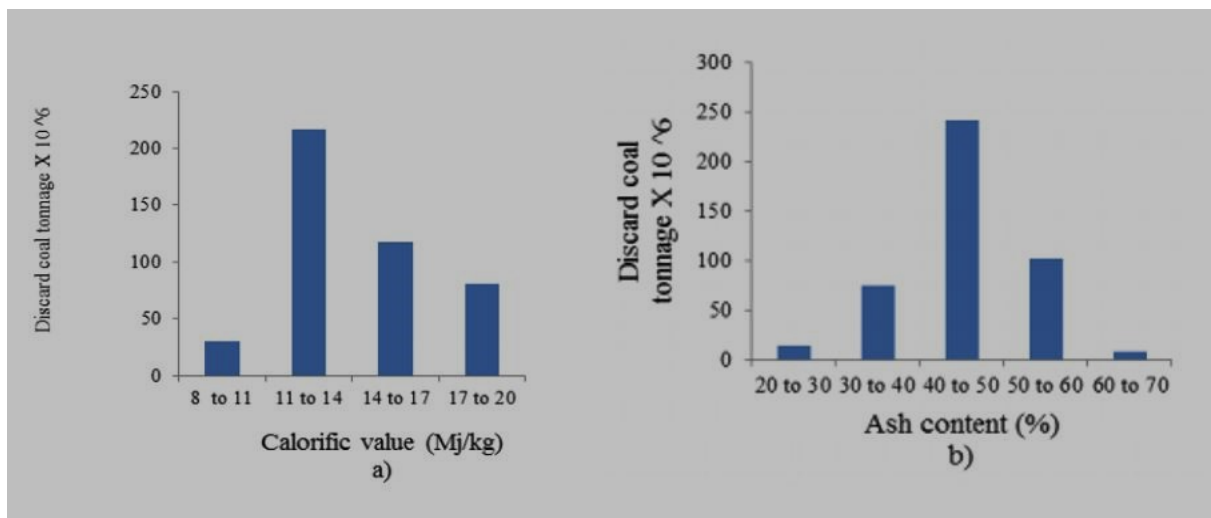


Figure 2-5: Quality properties of coal discard (a) calorific value (b) Ash content (Belaid *et al.*, 2013).

The ultra-fines from slurry ponds or run of mines share similar traits to discard coal, in that, they are considered to be uneconomical, environmentally hazardous and difficult to

process (Gaqa and Watts, 2018). Also, the handling, storage, and disposal operations of coal-fines present significant and unproductive expenses to the mining industry. White and Ariz, (1999) observed that in the USA around 15-25 % of the tonnage mined consisted of coal fines ranging in size from small granules to very fine powder. The authors further reported that in as much as a portion of the fines may be combined with coarser fractions of saleable products, adding these fines would lead to the reduction in the quality of the product to below-market grade. The underutilization of coal fines in their original state is due to their relatively high moisture content, which largely affects its calorific value and the cost of coal per ton. Henceforth, the coal industry usually reduces the moisture in coal before dispatch by drying. However, reducing moisture content in coal leads to more production of coal fines, which are generated by the weakening of the coal structure and the attrition of coal particles (White and Ariz, 1999). Moreover, the coal-drying process added to the operating expenses in the coal processing industry.

The aforementioned problems, along with strict customer demands on coal quality and of rising stringent regulation regarding mine waste disposal practices, have led to coal fines utilization to be re-looked at by the industry. With the proper beneficiation process designed according to the coal mineralogy, the coal product of different grades can be produced to match different combustion technologies and applications (Gaqa and Watts, 2018). This includes the densification of coal fines with biomass as a binder to form durable pellets or briquettes.

2.5. BIOMASS ENERGY

There is a growing interest in the utilization of biomass along with other waste resources for tackling environmental issues, energy security in addition to long-term fuel sustainability (Hamzah *et al.*, 2017). Bio-renewable sources are referred to as all resources of biological origin such as plants and animal organisms along with their derived waste and residues present in an ecological system (Krylova and Zaithenko, 2018). Bio-energy is reportedly the largest contributor to the global renewables as of 2018, similarly providing energy security to billions of people and stimulates rural development (Pradhan *et al.*, 2018). Perlack *et al.* (2011) and Saba *et al.* (2017) reported that biomass is the largest and most abundant source of renewable energy and its greenhouse gas emission status is zero to net negative as plant uptake carbon dioxide during their growth. Safarian *et al.*

(2019) reported that the current contribution of biomass to the world's primary energy requirements is 9.7 %, which is primarily from ethanol, biodiesel, and waste. The use of biomass as an energy source has gained recent popularity in South Africa. The use of biofuels from biomass as an alternative energy source has contributed nearly 13.6 % to South Africa's total energy supply needs (Mosito, 2016). Furthermore, a research conducted by Shuma, (2018) reported that there is a huge opportunity for biomass-based energy due to the established agriculture and forestry industries in South Africa. Nevertheless, the global contribution made by South Africa, as of 2013 in biofuel production was reported to be less than 0.01 % (Mosito, 2016).

Biomass resources are available on a renewable basis, that is, they regenerate at a rate that is accessible for the next generations (Krylova and Zaithenko, 2018). These resources are found to be a potential alternative renewable energy source for power generation due to low emissions, low ash and total sulphur content among other fuel characteristics (Rousset *et al.*, 2011 and Teixeira *et al.*, 2012). The major components in biomass include cellulose, hemicelluloses, lignin, and numerous other compounds characterised as extractives (Tekin *et al.*, 2014). However, the concentrations of each compound differ depending on the biomass species, type of plant tissue, stage of growth, and growing conditions (Tekin *et al.*, 2014).

The chemical properties of plant species depend significantly on certain fundamental processes for growth and reproduction, however, they evolved to accommodate a great variety of ecosystems and environmental conditions (Jenkins *et al.*, 1998). Thus, they show certain gross similarities in properties, but with substantial specific variation (Jenkins *et al.*, 1998). The main differences in chemical groups of the major biomass components, as reported by Zhang and Pang, (2019) is that generally the hemicellulose contains a larger share of C=O composites, cellulose has more OH and C-O chemical groups, whereas lignin is greatly rich in C=C, C-O-C, and methoxyl-O-CH₃ chemical groups. A number of these properties are significant for technically sound design and operation of conversion facilities, though not all properties are equally important for all conversion techniques (Jenkins *et al.*, 1998). The primary element in biomass is carbon with a composition of 30 to 60 %, while on average; oxygen (being second most abundant) makes up about 30 to 40 weight % of the dry matter (Tekin *et al.*, 2014). The third major component is hydrogen, comprising typically of five to six %. Conversely, nitrogen,

sulfur, and chlorine can be found in the biomass, usually, less than 1 % of dry matter, although occasionally the quantity may be more (Jenkins *et al.*, 1998).

The use of raw biomass does pose several obstacles, and these can have a negative effect during its application in its natural state. Properties such as low bulk density, low carbon content, high alkali, and alkaline earth metal composition and low energy density impact on its usage (Kambo and Dutta, 2014). Furthermore, these characteristics, along with its high moisture content create challenges such as high transportation, storage and handling cost, and low conversion ratio of the biomass to higher value-based products for energy and other carbon-based applications (Kambo and Dutta, 2015). The physicochemical properties of biomass are key to its application for gasification, pyrolysis, and combustion (Jenkins *et al.*, (1998).). The presence of alkali and alkaline earth metals, along with other fuel elements such as silica, sulphur and chlorine are responsible for many undesirable reactions occurring in the combustion furnaces and boilers (Jenkins *et al.*, 1998).

Biomass resources are versatile in that they can be converted into gaseous, solid, and liquid products. The conversion of biomass into different states requires conversion technologies such as biochemical, physicochemical and thermochemical treatment. (Wang *et al.*, 2018). A study by Kubacki *et al.* (2012) reported that co-combustion of biomass and coal allowed coal to ignite and burn at a lower temperature region due to the interaction with the early combustion of the biomass volatile matter. The authors concluded that the reduction in the emissions noted is due to the enhanced reaction between coal and biomass volatiles in a hot oxidising atmosphere. Moroń and Rybak, (2015) performed an investigative study on the NO_x and SO₂ emissions from coal/biomass blends in an oxy-fuel environment. In the study, the authors observed that the NO_x and SO₂ emissions reduced significantly with the addition of biomass to the coal, but this also leads to the increase in the NO emissions (Moroń and Rybak, 2015). These studies have proven that the addition of biomass to coal can have a positive influence on the environment, thereby enabling nations with sizeable deposits of coal to adapt their boilers or build new power plants that could support the co-firing of coal with biomass. This transition could lead to a cleaner means of generating power without compromising the energy security of the country and the economy.

2.5.1. Types of Biomasses

All biomass sources contain stored chemical energy which is obtained through photosynthesis (Rycroft, 2016). This energy can be harvested from those plants that possess higher energy yield, which gives the greatest yield in a sustainable and viable way. Sources of biomass are broadly categorised as either woody (lignocellulosic) or non-woody (also named herbaceous). Woody biomass is rich in lignocellulosic material (hemicellulose, cellulose, and lignin), while herbaceous biomass has lower concentrations of these components. As depicted in Figure 2-6, biomass can further be categorised into their natural origin as crops and residues, sewage, municipal solid waste, animal residues, industrial residues, forestry crops, and residues.

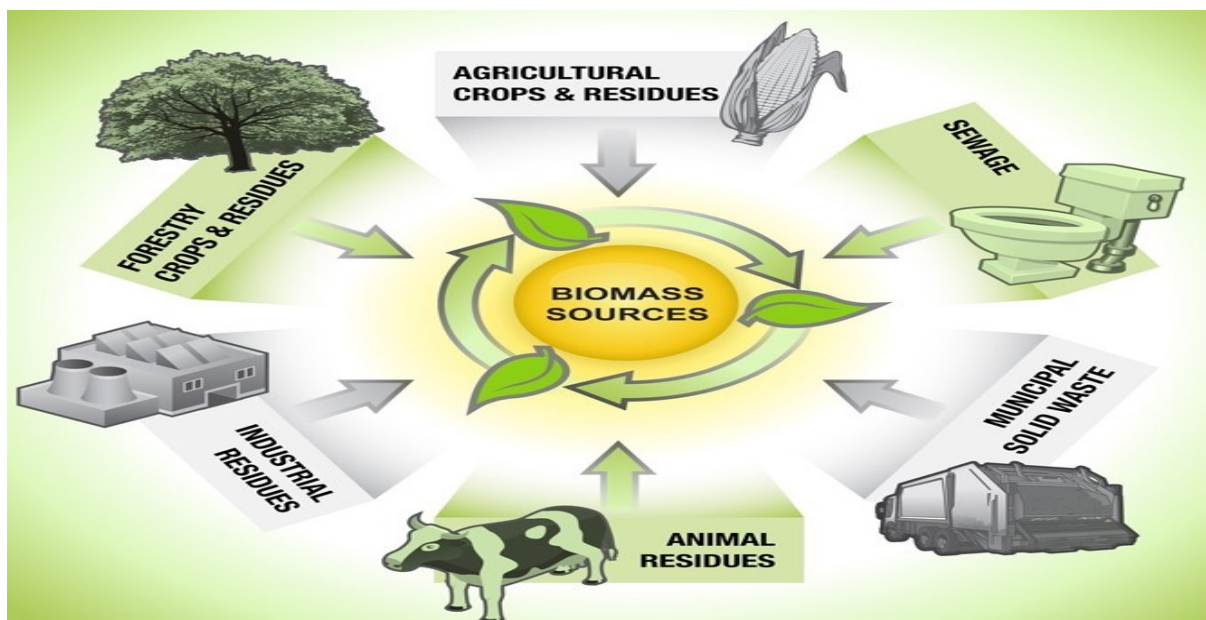


Figure 2-6: Types of biomasses (Zafar, 2019).

2.5.1.1. Agricultural Crops and Residues

Agricultural residues are categorised by seasonal availability and are inclusive of agro-industrial wastes comprising of corn stover/stalk, sugarcane bagasse, sawdust, and rice straw/husk their characteristics; which differ from other solid fuels such as wood, charcoal and char briquettes (Zafar, 2019). Zafar, (2019) reported that on an annual basis, globally, there are significant quantities of biomass that remain in the field after maize crops are harvested such as dried leaves and corn cob which can be used as a source of bioenergy (Zafar, 2019). The shell and fiber residues from the harvesting and processing of coconuts

are available in large quantities and can be utilised in energy production. The current practice for managing these waste materials is to plough them back into the soil as fertilizer, burn them and left to decompose, or grazed by cattle. These residues may be processed into liquid fuels or thermochemically processed to produce electricity and heat (Zafar, 2019). Hrnčič *et al.* (2016) reported that on an annual basis huge amounts of waste are produced by the agricultural sector. It's been reported by Yeoh *et al.* (2018) that in Malaysia alone the residues produced have an estimated energy of 55,000 GWh.

Zhu *et al.* (2018) studied the effect of HTC operating conditions (reaction temperature and residence time) on the pelletisation and combustion properties of cornstalk hydrochar which is a form of agricultural residue. In the study, three reaction temperatures (180, 240, 300 °C) and residence times of (30, 120, 240 minutes) were investigated. The author observed a decreasing effect in mass yield from 70.57 % to 33.40 % for the HTC treatment of cornstalk as the temperature increases. The residence time was found to have less effect on the mass yield when compared to temperature. The energy content went from 16.35 MJ/kg to 26.31 MJ/kg and the study revealed that both time and temperature had a significant contribution to this upgrade. A study on the HTC of whole and blends of farm residues was undertaken by Seyedsadr *et al.* (2018). Three biomass substrates namely biogas sludge (BS), barley (B) and maize silages (MS) were used in producing hydrochar which they termed HTC-biochar at 200 °C and residence time of 6 hours. The results showed that the calorific value was greatly enhanced when all the three feeds underwent HTC. The authors concluded that the hydrochar produced by the co-HTC of different feedstocks proved to possess greater potential in the energy sector than the blend of individual hydrochars from the same feedstocks.

2.5.1.2. Sewage Sludge

Another study was conducted by Ruksathamcharoen *et al.* (2019) on the potential of turning lignocellulosic residue from a fresh palm oil fruit bunch called empty fruit bunch (EFB) into a hydrochar by densification via pelletisation. The raw EFB had a calorific value of 18.00 MJ/kg with an ash content of 4.40 %, while the treated hydrochar had heat content of 23.24 MJ/kg with an ash content of 3.20 %. The results show that HTC had a great impact on lowering the ash whilst simultaneously increasing the calorific value. Moreover, the carbon content also increased from 45.25 to 55.41 % indicating

carbonisation had indeed taken place. The hydrochar pellets were found to have a better durability ranging from 98.7-99.5 %, which met the highest European pellet standard (ENPlus) of (A1 and A2 class), with the raw pellets at (78.1 - 92.8 %).

Sewage sludge (SS) from the wastewater treatment plants is also considered a biomass source, which can be used for power generation through combustion or gasification. It is also considered a renewable source, but with low energy density (high moisture content), a large quantity of salts and heavy metals, and high ash content (Wang *et al.*, 2017), compared to the biomass obtained from the lignocellulosic biomass/plants. This is further corroborated by (Peng *et al.*, 2016) wherein he reported that SS contains high moisture levels leading to poor dewaterability and is frequently found to contain heavy metals. There is a limited report in the literature on the use of HTC process for treating and improving the energy characteristic of a sewage sludge and wastewater solid (Danso-Boateng, 2015).

A research was conducted by Danso-Boateng, (2015) to produce a carbon-rich material through the HTC of the human faecal waste, and to reduce the ash and other mineral matters associated with solid sewage sludge. The study looked at two sources of sewage feedstock: primary sewage sludge (PSS) and synthetic faeces (SF) of varying moisture contents. The decomposition kinetics of both solid materials were investigated after undergoing HTC treatment at temperatures of 140 - 200 °C for 4 hours (Danso-Boateng, 2015). The resultant hydrochar from PSS was found with a higher energy content that ranged from 21.5 to 23.1 MJ/kg from the initial feedstock of 16.33 MJ/kg.

In the co-hydrothermal treatment of primary sludge with microalgae (*Chlorella* sp.), Lee *et al.* (2019) showed improvement in the properties of primary sludge. With an increase in temperature, the primary sludge achieved a calorific value of 18.67 MJ/kg while the mixture gave 21.73 MJ/kg. The study showed that the mixture could make for an attractive solid fuel as a clean energy source. From the investigation conducted by Peng *et al.* (2016) on the HTC of sewage sludge (SS) at varying operating parameters, the calorific values obtained were found to range from 9.8 – 12.06 MJ/kg with the highest energy increase experienced at the 260 °C and 60 minutes residence time. The ash content of the SS produced after the HTC test was found to increase from 49.85 % to 59.53 % at 260 °C.

The authors concluded that the hydrochars of SS found optimum conditions in terms of calorific value, yield and performance at 260 °C and residence time of 60 minutes.

2.5.1.3. Municipal Solid Waste

Every year there are tonnes of household waste being collected with the vast majority disposed of in an open field. Peng *et al.* (2016) reported that annually around 1.7 - 1.9 billion metric tons (MSW) are produced in the world. Municipal solid waste (MSW) biomass resource comprises of putrescible, paper and plastic and their average is about 80 % of the total MSW collected (Zafar, 2019). The composition of the MSW differs from country-to-country due to the laws and regulations that govern the said country (Kim *et al.*, 2015). The organic components of MSW can be converted into energy by either direct combustion, or by natural anaerobic digestion in the engineered landfill (Zafar, 2019). Another technology is using HTC to convert the organic feedstock into hydrochar that can either be co-fired with coal or fired solely.

Ismail *et al.* (2019) reported that there have been few studies undertaken on the HTC of MSW as compared to lignocellulosic biomass. Some of the MSW created is recycled; however, most of it is taken to landfill sites, and used in producing gas, known as landfill gas (LFG). This is produced through the natural decomposition of MSW (approximately 50 % methane and 50 % carbon dioxide) cleaned and fed into internal combustion engines or gas turbines to generate heat and power (Zafar, 2019). The author suggested that the organic part of the MSW can be stabilized in an anaerobic digester for the production of biogas to be used in power generation (Zafar, 2019).

A study conducted by Prawisudha *et al.* (2012) looked into the production of biocoal using MSW as a feedstock via hydrothermal processing. The result obtained by the author showed an improved hydrochar with an energy content higher than that of the raw MSW ranging from 16.1 – 27.2 MJ/kg. Kim *et al.* (2015) treated two types of MSW's consisting mainly of food, paper, plastic, and fibers. The raw MSW 1 and MSW 2 used had fixed carbon of 6.0 % and 8.3 % before being subjected to hydrothermal treatment (HT), and after the test, reported fixed carbon of 15.1 % and 14.5 %, respectively. The calorific values of 17.1 MJ/kg for MSW 1 and 16.3 MJ/kg for MSW 2 hydrochars shows improvement over the original heat contents of 15.1 MJ/kg and 14.4 MJ/kg respectively.

In addition, the nitrogen concentrations for MSW 1 decreases from 1.8 % to 1.1 %, while MSW 2 decreases from 2.3 % to 1.4 % indicating that HT aids in lowering the nitrogen content. The utilization of this fuel in a power plant could lead to a reduction in NO_x emissions.

Three types of MSW feedstocks obtained from China, India and Japan were hydrothermally treated to be used for co-firing with coal by Lu *et al.* (2011). The samples underwent hydrothermal treatment at 200 °C for 30 minutes at a pressure of 2.4 MPa. The MSW had varied composition, in that the Chinese MSW comprised mainly of food at 58.8 % with the ash of 11.6 %, while the Indian MSW consist of wood 40.8 % and ash content of 14.6 %. The third sample from Japan was composed of 42.9 % paper, with an ash content of 10.2 %. The heating values for the samples increased from 17.6 to 24.9 MJ/kg, 15.7 to 17.9 MJ/kg and 16.1 to 16.4 MJ/kg for the Chinese, Indian and Japanese, respectively. The HT was found to be suitable in converting differently composed MSW feedstocks into high energy solid fuel similar to coal, which can be used for co-combustion.

2.5.1.4. Animal Residues

Animal residues include substances such as cow manure and poultry litter. There exists a wide range of animal wastes that are produced in large amounts on an annual basis that can be used as an energy source (Zafar, 2019). In the past, this waste is recovered and sold as a fertilizer or simply spread onto agricultural land, however, the introduction of tighter environmental controls on odour and water pollution means that some form of waste management is now required, which provides further incentives for waste-to-energy conversion (Zafar, 2019). Zhang *et al.* (2014) reported that in 2009, there were approximately 209.3 million tons of pig manure produced in China alone. The authors further reported that the huge amounts of animal manure caused inhabitable environmental issues when left out in the fields or close to production factories. Obidike, (2016) reported that in South Africa around 400 billion tons of solid waste is produced annually since 2013.

One of the most attractive conversions technologies of these organic waste materials is anaerobic digestion which produces biogas that can be employed as fuel for internal

combustion engines, electricity generation from small gas turbines, burnt directly for cooking, or for space and water heating (Zafar, 2019). However, anaerobic digestion comes secondary to hydrothermal conversion as it is more efficient, the feed can be processed within minutes to hours and the reaction vessel can take feedstock with a wide variety of moisture contents (Danso-Boateng, 2015). Cao *et al.* (2011) looked at producing char from swine manure for use as soil improvement to enhance soil fertility. The authors investigated the changes to the chemical composition of swine manure under different carbonisation conditions and found the hydrochars produced to have increased content of aromatic carbons; however, they reported little information on the processed wastewater characteristics and energetic aspects of the hydrochar.

2.5.1.5. Industrial Residues

This category of waste is generated by all sectors within the food industry from animal remains in meat production, establishments such as abattoirs and slaughterhouses. Peels, scraps, and pulps from food processing also constitute to this category of biomass sources (Zafar, 2019). Moreover, pulp and papermaking, winemaking, poultry and fish, fruit and vegetables blanching form part of this category of biomass sources.

The waste materials are produced from all segments of the food industry and can be utilised as energy sources. Solid wastes, which include peelings and scraps from fruit and vegetables, food that does not meet quality control standards, pulp and fibre from sugar and starch extraction, filter sludges and coffee grounds can also be used for the same purpose (Zafar, 2019). These wastes are usually disposed of in landfills which make them readily and cheaply available feedstocks for thermochemical conversion into hydrochar. On the other hand, liquid wastes are also created from this industry when washing meat, fruit, and vegetables, blanching fruit and vegetables, pre-cooking meats, and poultry and fish processing, as well as winemaking (Zafar, 2019). These wastewaters contain sugars, starches, and other dissolved and solid organic matter, which can be anaerobically digested to produce biogas, or fermented to produce ethanol and energy.

The pulp and paper industry is thought-out to be one of extremely polluting industries and consumes a large amount of energy and water in various unit operations (Zafar, 2019). The wastewater discharged by this industry contains compounds from wood or other

processed chemicals from different raw materials (Zafar, 2019). Grape marc, a residue from the winery processing industry was studied for its application as a solid fuel. It underwent hydrothermal processing at 3 different processing temperatures (180, 220, 250 °C) and 3 residence times (1, 3, 8 hours) (Basso *et al.*, 2016). The results showed great improvements in physicochemical properties wherein the higher heating value increased by 54 % (at high temperature and long residence time). Another study by Sabio *et al.* (2016) examined the influence of reaction temperature (T), residence time (t) and the biomass/water ratio (R) of tomato peel waste through HTC. Furthermore, the study used the Design of Experiments (DOE) method approach to study the influence of the variables on the solid yield and energy densification of the hydrochar. The study concluded that the solid yields ranged from 87.7 % - 27.6 % while the heating values went from 23.6 – 34.6 MJ/kg. The research concluded that temperature had a greater impact while the biomass/water ratio had the very least effect although there were interactions among the variables T, t, and R.

In their study, Oyelaran *et al.* (2018) investigated the use of tannery waste for producing solid fuels i.e. briquettes. The authors reported that the leather industry is amongst the highly polluting industries and generates around 0.8 million tons of tannery waste on an annual basis globally. The study looked at four different tannery wastes namely: BD- buffing dust, CS- chrome shavings, FS- fleshing, and HR- hair. The waste was then calcinated and subsequently mixed with starch to facilitate the binding. FS had the highest calorific value at 21.86 MJ/kg followed by BD at 20.18 MJ/kg and CS and lastly HR at 19.82 and 18.03 MJ/kg, respectively. The samples had durability that ranged from 92.12 – 95.04 % suggesting good durability as they will not disintegrate. The authors concluded that the briquettes met the requirements for domestic use in heating and cooking along with home industries.

2.5.1.6. Forestry Crops and Residues

The forestry crops and residues are produced when processes such as thinning of plantations, clearing for logging roads, extracting stem-wood for pulp and timber, and natural attrition take place (Zafar, 2019). However, harvesting operations on average remove only 25 to 50 % of the total volume, leaving the remains available as biomass for energy (Zafar, 2019). Gosens, (2015) reported that in China the power produced from

forestry crops and residues accounted for the biggest share when looking at current installations, as well as future policy targets.

Bach *et al.* (2016) in their work used freshly cut and dried forest residues to investigate what effects, pre-drying of the raw material has on the HTC product quality of the hydrochar. The results showed that pre-drying of feedstock affects its structure, thus should be avoided. High moisture content feed gave superior results as well as better mass and energy yield up to 9.7 % and 11.4 %, respectively. The HTC of forest residue was undertaken by Liu *et al.* (2017) at heating temperature of 200 to 240 °C. The authors reported an increased stability in the chemical composition of the hydrochars as the process temperature increases, furthermore energy content increased from 14.06 MJ/kg for the raw sample to 27.17 MJ/kg for hydrochar at 240 °C. The O/C and H/C ratios decreased with increasing temperature, which indicated a chemical transformation of the structure. On the thermal properties, the hydrochar's thermostability showed improved characteristics with increasing temperature. The study demonstrated that the increase in temperature greatly influences the hemicellulose' properties.

2.5.2. Biomass Utilised

The two tree species utilised in this study, *Searsia lancea* and *Tamarix usneoides* were harvested from the West Wits mining operations (Madala and Redsoils), and the Vaal River mining operations (West Complex and Mispah). The *Searsia lancea* is known as *Rhus lancea* and *Tamarix usneoides* also called the *Salt Cedar*, both trees are part of the Mine Woodlands Research Project, initiated by AngloGold Ashanti Limited, in 2002. The trees were planted for phytoremediation of AMD in treating platinum and gold tailings storage facility (TSFs), as well as rehabilitating polluted soils (Dye *et al.*, 2008). The two trees are amongst the suitable species allowed by the South African legislation to be planted for reforestation and rehabilitation purposes; as these species are indigenous to the immediate area surrounding the rehabilitation site (Lange *et al.*, 2012). These species have proven to be of high tolerance to high concentrations of potentially toxic elements (PTE) without having any sign of growth distortion.

Figure 2-7 shows a typical *Searsia lancea* tree species. This species is widely distributed across the entire Southern African landscape. It is reported to be extremely drought

resistant and very hardy (Lange *et al.*, 2012). The species is also known to have a dense root mat for microbial activity, which is also used in binding, uptake of metals as well as binding loose soils for erosion control and soil stabilization. It is highly tolerant of competition from adjacent trees and is highly tolerant of AMD and salinity (Arendze, 2015).



Figure 2-7: *Searsia lancea* tree species (Stern, 2008).

Figure 2-8 depicts a picture of a 4-year old *Tamarix usneoides* tree species planted at the Vaal River Mispah tailings facility. Arendze, (2015) reported that *Tamarix usneoides* is a halophyte and a salt hyper-accumulator. It has been found that this species hyper-accumulates sodium chloride (NaCl) in its leave. The leaves are known to contain salts ranging from 2 -10%, and excrete these salts via foliar glands, mainly in the form of gypsum (calcium sulphate) and halite (sodium chloride), with lesser amounts of other metal sulphates and chlorides depending on the quality of the AMD water (Arendze, 2015). The CaSO_4 formed is chemically non-toxic and of low solubility (Arendze, 2015).

Most of these trees were planted between 2003 and 2008 on an estimated 320 hectares of land, now all matured they may be cut and utilised as firewood by the community (Dye *et al.*, 2008 and Mosito, 2016). The use of these trees as firewood would only contribute to GHG emissions, poor air quality and undermining the potential of these trees as an

alternative energy source. Therefore, based on the above-mentioned drawback, this study seeks to use these species under HTC to produce quality fuel that may be blended with coal to produce a densified domestic and reliable cleaner solid fuel. The co-firing of the tree's leaves with coal is another study undertaken in the Clean Coal Technology group for the reduction of SO₂ and SO_x emissions in the coal and enhance the coal desulfurization in power plants.



Figure 2-8: *Tamarix Usneoides* (Phephu, 2012).

2.6. BIOMASS PRE-TREATMENT METHODS

Many investigations have been conducted on the pre-treatment of biomass by different researchers including Zhang and Pang, (2019); Safarian *et al.* (2019); Kambo and Dutta, (2015) and so forth. The type of feedstock and desired end properties of biochar (which ultimately determine the end-use) dictate the type of pre-treatment method to be utilised (Kambo and Dutta, 2015). Harnessing energy from biomass or any other organic solid waste necessitates using chemical, biochemical and/or thermochemical processes. The most commonly applied thermochemical pre-treatment methods include; pyrolysis, gasification, torrefaction and HTC (also commonly referred to as wet torrefaction) (Kambo and Dutta, 2015). All these methods produce three product phases, namely;

solids, liquids, and gases, although in varying proportions depending on the severity of the processing conditions.

2.6.1. Gasification

Vidya, (2017) explained that gasification is the conversion achieved through partial combustion of any carbonaceous material such as coal or biomass to form synthetic gases. Kambo and Dutta, (2015) reported that the combustion of biomass takes place over high temperatures (600-900 °C) and short residence times (10-20 sec), and its main primary product is a synthetic gas that comprises largely of CO, CO₂, and H₂. Kambo and Dutta, (2015) also described that the product distribution of gasification is such that, solids are (5-10 %), liquid (< 5 %) and gases (> 85 %). Zhang and Pang, (2019) found that gasification technology has high conversion efficiency (70–80 %) of solid fuels into a gas which renders great flexibility for its use in numerous products. Safarian *et al.* (2019) stated that the recovery rate of electricity production from gasification was more per kilogram of biomass/municipal waste when compared to technologies such as incineration or digester biogas.

Biomass gasification has been reported to be a two-stage process. The first stage, which essentially is the initial devolatilization, where the carbonaceous feedstock is partially converted into producer gas, char, and tar (Zhang and Pang, 2019). The composition of the producer gas is CO, N₂, H₂, CH₄, CO₂, NH₃, H₂O and other hydrocarbons (Sethuraman *et al.*, 2011). Whilst in the secondary phase, gases produced under stage one (CO and H₂O) are chemically reduced by the charcoal or char to produce more CO and H₂. In biomass gasification, two of the most problematic by-products are the biochar (char) and tar formations. The biochar produced from the process has a high concentration of alkali and alkaline earth metals and polycyclic aromatic hydrocarbons (PAHs) that are highly toxic and its use is potentially problematic (Ippolito *et al.*, 2012). Furthermore, tar compounds, which are formed during the first stage, have proven to be one of the key issues hindering the commercialisation of biomass gasification. Tar compounds are initially formed in the vapour phase, however, during the downstream processing, they are condensed into a viscous liquid leading to contamination and blockage in equipment including valves and pipes (Zhang and Pang, 2019).

2.6.2. Pyrolysis

Pyrolysis is the thermochemical decomposition of any carbonaceous material taking place in the absence of oxygen thus inhibiting complete combustion (Vidya, 2017). The main products of pyrolysis are biochar and volatile matter which can be turned into bio-oil and non-condensable gases such as CO, CO₂, CH₄ and H₂ (Mohan *et al.*, 2006; Brownsort, 2009 and Kambo and Dutta, 2015). The pyrolysis process consists of four sub-divisions namely: flash, fast, slow and intermediate pyrolysis that is greatly dependent upon the reaction time, temperature, and heating rate (Kambo and Dutta, 2015). Slow pyrolysis is considered the most productive out of all the other pyrolysis processes due to its higher solid product yield to produce biochar.

Slow pyrolysis decomposes biomass at a temperature between 300-600 °C in the absence of air at residence time ranging from 5 minutes to 12 hours, and its product fractions are roughly distributed in the same ratio (Mohan *et al.*, 2006; Brownsort, 2009 and Kambo and Dutta, 2015). Slow pyrolysis produces products with approximately equal proportions in all the phases, and thus the phase composition consists of solid (25–35 %), liquid (20–30 %) and, producer gas (25–35 %) (Kambo and Dutta, 2015). The higher solid yield of biochar (25-35 %) obtained from slow pyrolysis makes it the favourite choice when compared to other forms of pyrolysis.

The application of pyrolysis has taken place successfully for the conversion of different kinds of biomass including waste. The biochar from pyrolysis has been studied towards application in the soil amendment (Oram *et al.*, 2014), wastewater treatment (removal of heavy metals) (Inyang *et al.*, 2016) and rarely has it been applied in the energy generation sector. The primary reason for the frequent use of pyrolysis as reported by Krylova and Zaitchenko, (2018) is for liquid products. Moreover, the solid yield although higher than that from gasification, but very low compared to processing technologies such as torrefaction and HTC (Kambo and Dutta, 2015). Biochar is the main target product in HTC, although producer gas and liquid are also produced (Krylova and Zaitchenko, 2018). Many terms, including biochar (Reza *et al.* 2014), biocoal (Danso-Boateng, 2015), HTC chars (Kambo and Dutta, 2015) have been used to describe products of HTC process. Nevertheless, as suggested by Libra *et al.* (2011), the word hydrochar/hydrochars is used in this study to describe the HTC products.

2.6.3. Torrefaction

Torrefaction produces the highest yield range of all thermal pre-treatment processes and only produces two products, solid and gases. As a mild pyrolysis treatment method, it uses an inert atmosphere at a temperature range of 200-300 °C and periods of 30 minutes to 4 hours (Bergman *et al.*, 2005; Pimchuai *et al.*, 2010; Rousset *et al.*, 2012 and Kambo and Dutta, 2015). The treatment method results in approximately 30 % mass loss, while 10 % of the energy confined within the biomass feedstock is transformed into gases (Kambo and Dutta, 2014). The product obtained from torrefaction is of higher physicochemical characteristics compared to the raw feedstock such as high energy density, improved resistance to water and reduced moisture content amongst others (Bergman *et al.*, 2005; Kambo and Dutta, 2014, 2015).

Kludze *et al.* (2013) and Kambo and Dutta, (2015) stated that the disadvantages of torrefaction are the drying pre-requisite for the feedstock and its failure in the removal of alkali and alkali earth metals from the torrefied product. Furthermore, Kambo and Dutta, (2015) argued that the solid product from gasification is not regarded as biochar due to its very low solid yield, as it does not contain the same properties as those of biochar. Furthermore, the failure to remove alkali group metals as well as heavy metals from the biochar of the above-mentioned thermochemical pre-treatments renders the biochar ash a hazard (Kambo and Dutta, 2014). Even though pellets from torrefied materials characterize a significant improvement over the raw biomass pellets, handling them becomes an issue, as they possess weak strength and low durability (Kambo and Dutta, 2014).

Given the above challenges associated with the aforementioned methods, i.e. pyrolysis, gasification and torrefaction, this research seeks to utilize the (HTC) process for upgrading the biomass from the *Searsia lancea* and *Tamarix usneoides* trees in producing new energy products.

2.6.4. Hydrothermal Carbonisation

This research goal is to utilise HTC to produce new energy product fuels or alternative solid fuels, known as biocoal pellets. HTC is characterised as a thermochemical conversion technique used to transform wet biomass into a product mainly consisting of a carbonaceous solid hydrochar with improved physical and chemical properties when

compared to raw biomass (Hoekman *et al.*, 2017 and Wang *et al.*, 2018). HTC is reported to have been first carried out in 1913. Its development first took place in the early decades of the twentieth century by Friedrich Bergius (Danso-Boateng, 2015). Park *et al.* (2018) along with Yeoh *et al.* (2018) reported that HTC has the advantage of directly hydro-treating wet or green biomass material without a need to undergo pre-drying. In addition, the technique had also been used for producing biofuel and upgrading solid fuels (Saba *et al.*, 2017). Hydrochar, which is the end product from HTC has received great attention due to its ability as a precursor for soil remediation, activated carbon in wastewater pollution remediation, catalysts, solid fuels, and many other carbonaceous materials for a wide range of applications (Wang *et al.*, 2018).

Above and beyond lignocellulose biomass used as sustainable feedstock, HTC has seen applications in upgrading municipal solid waste, algae, sewage sludge, agricultural waste, and bio-refinery waste, as well as to solve real-world problems and create desirable carbonaceous products (Wang *et al.*, 2018). The natural coalification of cellulose occurs during this process leading to the carbonisation of biomass sources in the presence of water at temperatures ranging between 150–350 °C for the production of biocoal (Danso-Boateng, 2015). Kambo and Dutta, (2015) reported that the process takes place at a temperature between 180-260 °C and residence times of 5 minutes to 12 hours. Kruse and Dinjus, (2007) and Saba *et al.* (2017) also indicated that the process wastewater could further be utilised due to its solvent properties at high temperatures and pressures for hydrochar production. Heidari *et al.* (2018), similarly reported that the temperature range for the HTC process ranges between 180-350 °C with the biomass immersed in water while heated under pressure (2-6 MPa) for 5-240 minutes. The latter report can be said to be more accurate in terms of temperature range since different feedstock requires diverse processing conditions. Thus, the issue of temperature should always be balanced with product quality, cost of production as well as profitability.

As a rule of thumb, Silakova, (2018) thus stated that the lowest temperature limit for hydrolysis takes place around 180 °C. Furthermore, Silakova, (2018) also reported that the main influencing factor in HTC processing is the reaction temperature. The higher the reaction temperature, the higher the decomposition rate and the extent of biomass degradation. The subcritical nature of the water utilised during the HTC process at temperatures from 200-260 °C, also influenced the degradation of the biomass. From these

temperatures, the water is noted to be of high ionic and low dielectric constant, i.e. the water becomes less or non-polar similar to organic solvents (Bandura and Lvov, 2005 and Saba *et al.*, 2017).

Figure 2-9 shows an illustration of the plot of temperature, dielectric constant and water pressure. At standard conditions (25 °C and 0.1 bar), water has a dielectric constant of 78 which renders it a polar solvent not suitable for organic compounds (Tran, 2016). However, at the critical point (374 °C and 221 bar) water seems to act as a non-polar solvent, i.e. an effective reaction medium for organics (Tran, 2016). This attribute is due to the reduction in the order of hydrogen bonds per molecule of water (Kumar *et al.*, 2018); hence, with an increase in temperature, the affinity of water towards hydrophilic molecules increases (Weingärtner and Franck, 2005). Thus, making water a suitable medium for solvating organic molecules and leading to a single-phase reaction. More so, a higher reaction rate owing to improved nucleophilic substitutions and eliminations is seen to occur (Xu *et al.*, 1990) as well as succeeding hydrolysis reactions (Sasaki *et al.*, 2002).

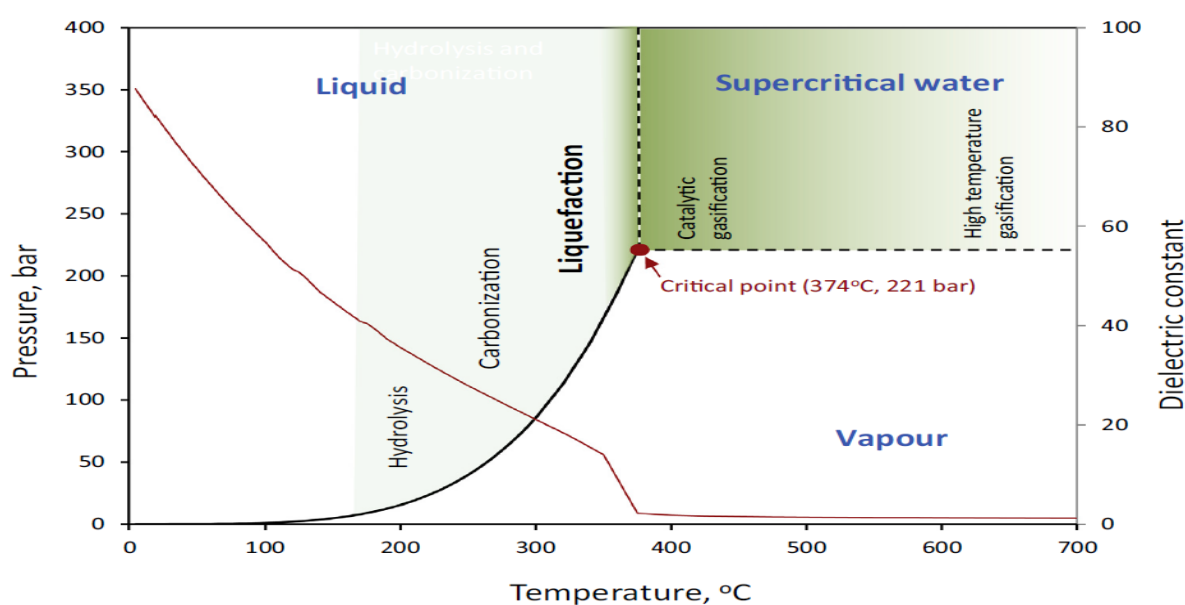


Figure 2-9: Phase diagram of water (pressure-temperature) and static dielectric constant at 200 bar (Kumar *et al.*, 2018).

2.6.4.1. Hydrothermal Carbonisation of Lignocellulosic Biomass

There exists an extensive literature on the hydrothermal treatment of lignocellulosic biomass, compared to sewage sludge and wastewater solids (Danso-Boateng, 2015). The hydrothermal process has been used for the modification of raw bamboo as a metallurgical reductant. The investigation was conducted by Kudo *et al.* (2014) to enhance the plasticizability of bamboo and promote its particle coalescence/fusion during briquetting to a reasonable extent. This technique had also been found to remove highly volatile cellulosic material, i.e., cellulose and hemicellulose, thereby converting the biomass into a solid that is mainly composed of lignin (Kudo *et al.*, 2014). With the application of this technique, modification is made to the structure of biomass leading to the production of solid fuel (hydrochar) with similar properties to coal. Figure 2-10 illustrates the van Krevelen diagram, which is a plot of the ratio of O/C and H/C diagram. This diagram provides the basic information needed to compare the physicochemical properties of raw biomass, hydrochar, and coal of different ranks. From this figure, it can be observed that the hydrothermally carbonised hydrochar are of similar characteristics to lignite coal (Hoekman *et al.*, 2017).

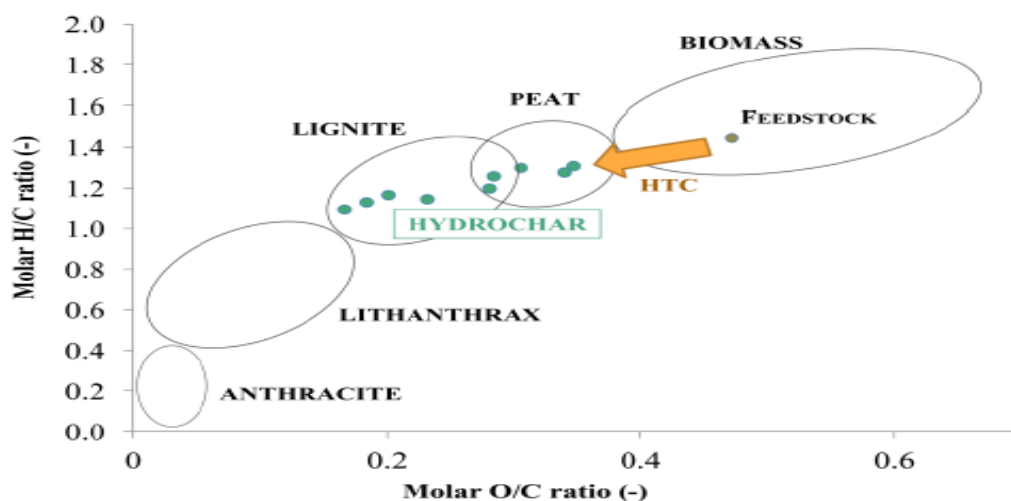


Figure 2-10: Van Krevelen diagram (Hoekman *et al.*, 2017).

Figure 2-11 depicts the correlation between the hydrothermal process severity and energy content of hydrochar. Another key factor in HTC is the severity of the process and this depends on the extent to which the process parameters and conditions (temperature, residence time or reaction time) are being utilised. Hoekman *et al.* (2017) conducted a

study where a comparison was made between the hydrochar produced from the batch and continuous systems. They found a strong correlation between severity, energy content and O/C ratio and also observed that severity may be a worthwhile predictor of the hydrochar energy content (Hoekman *et al.*, 2017). An investigation conducted by Silakova, (2018) also shows that the severity does influence the carbon content in hydrochar. Whilst the study by Reza *et al.* (2013) indicates that the degree of ash yield from the biomass leaching increases as the severity in the hydrothermal reaction condition changes.

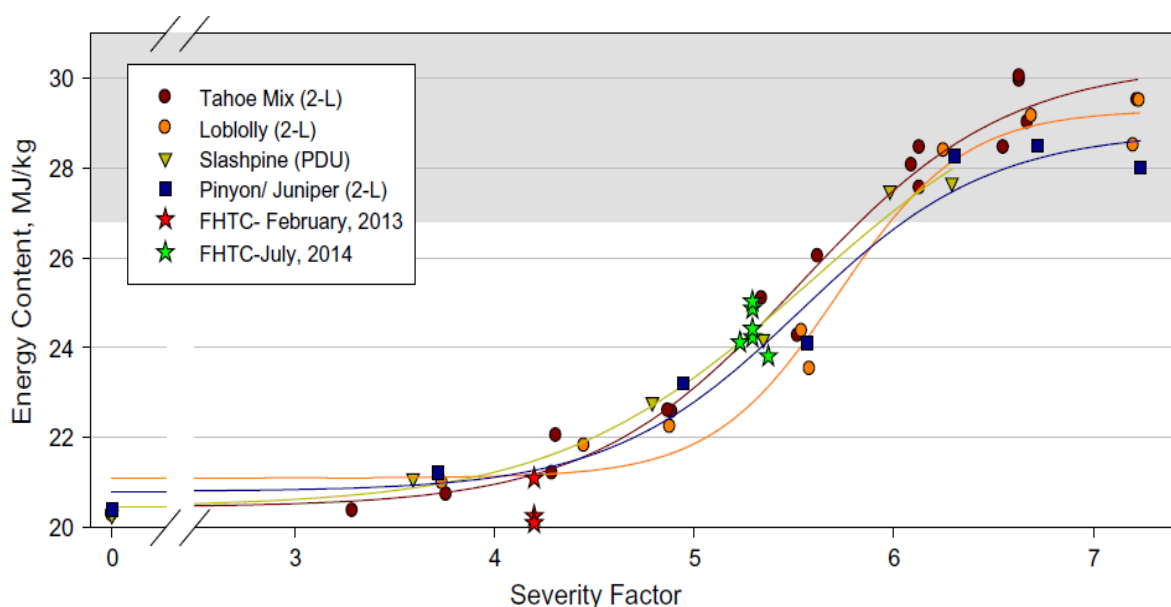


Figure 2-11: Relationship between HTC process severity and energy content of hydrochar (Hoekman *et al.*, 2017).

2.6.4.2. Influence of Hydrothermal Carbonisation on Organic Composition

Table 2-1 shows a summary of some recent studies in the field of HTC. The table presented results from a different range of feedstock that has been used in the production of hydrochar under various conditions. It can be noted from this table that the temperatures in which all the investigations are conducted fall within the range of 200-260 °C. The calorific values for the samples were seen to increase as the hydrothermal temperature increases across all the different feedstock.

The investigation conducted by Reza *et al.* (2013) on the production of hydrochar from four different agricultural residues (corn stover, miscanthus, rice hull, and switchgrass)

using HTC indicates an upgrade in the feed materials. The biomass feeds were hydrothermally carbonised at 200, 230 and 260 °C and held for five minutes. The ash composition for the three samples excluding rice hulls, i.e., the raw samples and the biochar seems to be relatively low ranging from 4.1 to 9.9 %. The rice hulls contain the highest amount of ash with the raw sample at 21.1 % and this increases successively with increasing hydrothermal processing temperature to 25.0 % (200 °C), 26.0 % (230 °C) and 29.8 % (260 °C) %. The calorific values for corn stover and switch grass were found to increase with increasing hydrothermal temperature from 15.6 to 24.1 MJ/kg for corn stover and 15.3 to 21.0 MJ/Kg for switch grass (Reza *et al.*, 2013). The same trend was also achieved with the Miscanthus sample. A study was also undertaken by Saba *et al.* (2017b) on the co-HTC of two different feeds (biomass and coal). The effect of HTC on the individual coal and miscanthus, and their co-blended slurries at a temperature of 200 °C, 230 °C and 260 °C were determined. For all the experiments, the reactor was subjected to different set temperatures and was held for 30 minutes. The energy content of the coal ranged from 27.4 to 30 MJ/kg, while the miscanthus with a calorific value of 19.5 MJ/Kg was increased to 28.7 MJ/kg for HTC treated at 260 °C. On the co-HTC blends, the author achieved an energy content of 24.6 to 27.9 MJ/kg.

In addition, the mass yield obtained from the HTC processed miscanthus displayed a notable decrease with yield as low as 46.2 % at a temperature of 260 °C. This decrease is attributed to the decomposition of miscanthus chemical structures i.e. cellulose, hemicellulose and lignin, and subsequently dissolving and forming of gaseous and liquid products (Saba *et al.*, 2017b).

Table 2-1: Summary of some studies done on hydrothermal carbonisation.

Feedstock	CV ^a (MJ/Kg)	Ash (%)	VM ^b (%)	FC ^c (%)	S ^d (%)	Reference
Raw corn stover	15.6	8.2				Reza <i>et al.</i> (2013)
HTC 200 °C	19.1	8.3				
HTC 230 °C	20.0	8.9	—	—	—	
HTC 260 °C	24.1	8.1				
Raw miscanthus	17.4	4.4				Reza <i>et al.</i> (2013)
HTC 200 °C	20.6	4.1				
HTC 230 °C	19.8	4.1	—	—	—	
HTC 260 °C	22.0	4.1				
Raw rice hull						Reza <i>et al.</i> (2013)
HTC 200 °C	20.3	21.1				
HTC 230 °C	20.3	25.0	—	—	—	
HTC 260 °C	20.9	26.0				
	24.6	29.8				
Raw switch grass	15.3	9.1				Reza <i>et al.</i> (2013)
HTC 200 °C	19.0	9.9				
HTC 230 °C	19.7	9.4	—	—	—	
HTC 260 °C	21.0	9.5				
Raw Coal*	27.4 ± 0.0	11.1 ± 0.6	34.3 ± 0.0	63.8 ± 1.2	4.6 ± 0.8	Saba <i>et al.</i> (2017b)
HTC 200 °C	29.8 ± 0.2	6.6 ± 0.4	38.2 ± 2.8	71.4 ± 1.2	3.0 ± 0.2	
HTC 230 °C	29 ± 1.0	9.5 ± 1.1	36.4 ± 2.2	69.2 ± 1.6	3.8 ± 0.1	
HTC 260 °C	28.1 ± 0.5	6.6 ± 0.6	35.4 ± 2.0	69.1 ± 2.4	3.5 ± 0.1	
Raw Miscanthus	19.7 ± 0.2	1.3 ± 0.1	84.5 ± 0.4	48.7 ± 0.1	0.0 ± 0.0	Saba <i>et al.</i> (2017b)
HTC 200 °C	20.4 ± 0.4	0.1 ± 0.0	84.4 ± 0.4	52.4 ± 0.2	0.0 ± 0.0	
HTC 230 °C	24.6 ± 0.4	0.0 ± 0.0	77.6 ± 0.7	59.3 ± 1.5	0.0 ± 0.0	
HTC 260 °C	28.6 ± 0.1	0.2 ± 0.2	51.5 ± 0.5	69.6 ± 1.8	0.0 ± 0.0	
Blend**						Saba <i>et al.</i> (2017b)
HTC 200 °C	24.8 ± 0.2	3.7 ± 0.1	62.7 ± 3.8	58.2 ± 3.5	1.2 ± 0.4	
HTC 230 °C	26.1 ± 0.6	5.3 ± 2.3	41.3 ± 3.8	67.2 ± 2.0	2.0 ± 0.3	
HTC 260 °C	27.3 ± 0.6	3.0 ± 0.9	43.1 ± 1.6	68.7 ± 1.0	1.6 ± 0.1	

*= Clarion type #4A coal: bituminous coal with a moisture content of 10 %. **=Blend: represents the Co-Hydrothermal Carbonisation (Co-HTC), where coal and biomass blends were treated. CV^a= Calorific Value; VM^b=Volatile Matter; FC^c=Fixed Carbon; and S^d=Total Sulphur.

2.6.4.3. Influence of Hydrothermal Carbonisation on Inorganic Composition

Heavy elements also known as major elements are considered of great importance in the ecosystem, however their presence at an elevated concentration can prove fatal for humans and animal (Demirbaş, 2005). Table 2-2 provides a summary of the concentrations of heavy metals obtained from some of the biomasses commonly used in energy applications. The investigation by Demirbaş, (2005) shows the influence of gas and toxic metal emissions on the environment as a result of the firing and co-firing of wheat straw and beech wood. The study showed that beech wood contained a higher concentration of As (3.5 mg/kg), Cd (1.0 mg/kg) and Cu (43 mg/kg), more than the wheat straw which had the lowest concentrations overall of As (0.18 mg/kg), Cd (0.2 mg/kg) and Cu (0.06 mg/kg). In the table, of all the reported biomasses, Demol timber displayed the highest concentrations in the order Pb (6300 mg/kg) > Mn (2500 mg/kg) > Cu (1080 mg/kg) > Cr (1060 mg/kg) > As (584 mg/kg) > Hg (10 mg/kg).

The sewage sludge was found to contain most of the reported heavy metals and has the highest concentration of Zn (1318 mg/kg) followed by Mn (950 mg/kg) and Cu (330

mg/kg), while the lowest metal concentration was Hg at 2.7 (mg/kg). The study by Mellem *et al.* (2009) on *Amaranthus dubius* planted on a landfill site showed a high concentrations of Cu (69.7 mg/kg), Pb (54.9 mg/kg) and Cr (34.9 mg/kg) with the lowest concentration of Hg (8.2 mg/kg). Between the *P.nigra* branches and *P. nigra* leaves, only three elements were analysed. The *P. nigra* leaves had more concentrations of Pb (423 mg/kg), Zn (118 mg/kg) and Cd (10 mg/kg), than the branches: Pb (60 mg/kg), Zn (50 mg/kg) and Cd (2 mg/kg). This is expected, as the leaves are the excretion points for the trees.

With an increase in the co-firing of biomass with coal in traditional coal-fired boilers, it is paramount that the emitted gases and ash composition for these new fuels be studied, especially for an existing fossil-fuel-based power boiler. The sole purpose of cofiring in the existing plant is to take advantage of the large investment and infrastructure already available and to reduce the traditional pollutants (SO_x, NO_x, etc.) and net greenhouse gas (CO₂, CH₄, etc.) emissions.

Table 2-2: Concentration of some heavy elements in biomass.

	[mg/kg]									
Biomass	As	Cd	Cu	Hg	Mn	Ni	Pb	Zn	Cr	References
Wheat straw	0.18	0.20	25.1	0.062	-	-	5.68	-	3.08	Demirbaş, (2005)
Beech wood	4.12	0.84	29.3	0.126	-	-	35.0	-	4.38	Demirbaş, (2005)
Demol timber	550	8	1080	10	2500	-	6300	-	1060	Nzihou and Stanmore, (2013)
<i>Amaranthus dubius</i>	21.6	-	69.7	8.2	-	24.8	54.9	-	34.9	Mellem <i>et al.</i> (2009)
Sewage sludge	10	38	330	2.7	950	39	159	1318	91	Werther and Ogada, (1999)
<i>P. nigra</i> branches	-	2	-	-	-	-	60	50	-	(Giudicianni et al., 2017)
<i>P. nigra</i> leaves	-	10	-	-	-	-	423	118	-	

Table 2-3: Ash results for heavy element limits results for different applications (Fuller *et al.*, 2015).

Country	Finland	Finland	Germany
Use	Forestry	Agriculture	Fertilizer
Maximum metal content [mg/kg]			
As	30	25	40
Cd	17.5	1.5	1.5
Cu	700	600	-
Hg	1.0	1.0	1.0
Mn	-	-	-
Ni	150	100	80
Pb	150	100	150
Zn	4500	1500	-
Co	-	-	-
Cr	300	300	-

Table 2-3 presented the standard concentration limits for heavy metals in ash. With this information, the required concentration for disposal could be established in order not to harm the environment. The table displays the ash concentration limits for three application areas, i.e., forestry, agriculture, and fertilizers from Finland and Germany. The ashes of wheat straw and beech wood contain heavy elements at maximum metal content, thus can be used in any of the applications without requiring further processing. Demol timber, on the other hand, is out of specification for As, Cd (for agriculture and fertiliser use), Hg, Pb, and Cr while Cd concentration at 8 mg/kg is suitable for forestry use only. Moreover, the concentrations for Ni and Zn are not reported and Mn has not been specified for end-use application. *Amaranthus dubius* concentrations for As, Cu, Ni, Pb, and Cr fall within maximum allowable limits for all applications however, only Hg concentration of 10 mg/kg is above the maximum metal content of 1.0 mg/kg. Sewage sludge complies in all-metal concentration except for Cd of 38 mg/kg while the maximum limit is 17.5 g/kg and Pb of 159 mg/kg is only suitable for agricultural use.

The Cd concentration in *P. nigra* branches and *P. nigra* leaves can be used in the forestry industry however, not for agriculture and fertiliser purposes. Zn concentration is within specification for both tree components however, the Pb content for leaves is outside the allowable metal contents for all the three uses. Employing a metal recovery process to the

ashes such as the demol timber (having significant metal concentrations) before other utilizations will lead to a higher value residual ash for the market, and the cost of recovery may be paid by selling of the metals (Fuller *et al.*, 2015).

2.6.4.4. Influence of HTC on Combustion Characteristics

Smith *et al.* (2018) reported that using biomass in pulverized coal-fired power plants have proven advantageous as they employ current infrastructure with little to no moderation required. The authors further reported that the fuel combustion behaviour is one of the parameters used by power plant designers as a measure to assess boiler performance. Combustion behaviour tracks the changes in a weight loss of the sample while undergoing heating from room temperature to 850 °C, 900 °C and even as high as 1000 °C, depending on the technology applied (Zhu *et al.*, 2018 and Smith *et al.*, (2018).

Thermogravimetric analysis is a technique employed in characterising materials by tracking their change in mass as a function of temperature (Lu *et al.*, 2011). Equipment such as thermogravimetric analyzer (TGA) is used in the study of combustion characteristics. Thermogravimetric (TG) and first derivative thermogravimetric (DTG) profiles are used in analysing and interpreting key combustion parameters. These are given as the initiation temperature often indicative of initiation of volatile matter, maximum or peak temperature where the weight loss is at its maximum (T_{max}), burnout temperature wherein the weight has reached constancy (T_b) and (R_{max}) is the maximum weight loss experienced by the sample (Smith *et al.*, 2018 and Yeoh *et al.*, 2018).

The combustion behaviour of raw biomass is different from that of coal, however, HTC treated biomass tends to behave similarly to coal in combustion behaviour. Co-combustion of raw biomass with coal offers both advantages and disadvantages. Liu *et al.* (2016) reported that the combustion behaviour of raw biomass feedstocks displays a disconnected devolatilization (evident by the presence of multiple peaks during combustion) and partial combustion processes due to high volatile matter content inherent in the material. The high volatile matter allows the raw biomass to ignite at low temperatures, however this characteristic along with disconnected devolatilisation subjects the raw biomass to increased pollutant emissions (Liu *et al.*, 2016). (Makwarela, 2016) reported that biomass co-combustion with coal would result in reductions of both fossil fuel usage and

greenhouse gas emissions, it may also lead to a higher propensity for slagging and fouling due to its high inorganic matter if combusted alone. Thus, a treatment method that will be able to overcome these challenges in biomass will help in solidifying its case as an abundant renewable source of energy amongst other uses.

Research in combustion and co-combustion of treated biomass with coal is seasoned and continues. Hydrothermally carbonised biomass sources such as municipal waste, sewage, agricultural waste, industrial waste, forestry crops, and animal residues have been extensively studied as reported in this literature review in earlier sections. The studies have proven that a wide range of biomass sources can be accommodated with the use of the HTC treatment process. Smith *et al.* (2018) investigated the use of early harvested *miscanthus* in producing biocoal via the HTC process. The author looked at the feasibility of using HTC to overcome combustion limitations experienced as a result of the inorganic elements present in early harvested *miscanthus*. Liu *et al.* (2016) reported that the burning profile of pellets containing hydrochar displays a heightened thermal conversion efficiency thus leading to a reduction in emissions. Moreover, due to their higher energy density, the pellets display a more continuous burning profile leading to flame stability necessary in boiler efficiency (Smith *et al.*, 2018).

2.6.5. Current State of Hydrothermal Carbonisation Technology

Hydrothermal technology does have several challenges in producing targeted fuels for the transportation sector and as raw materials for the chemical industry (Kumar *et al.*, 2018). Considering these challenges, this technology holds an integral promise for the production of new fuel for these industries. As research and development continues concerning this technology, some of the obstacles associated with the technology for plausible market integration into the future have been overcome (Kumar *et al.*, 2018). The current numbers of companies involved in the manufacturing of industrial-scale hydrothermal reactors have increased, as seen in Table 2-4. Each of the manufacturers offers a slightly different service and some do provide support to the industry across the entire value chain from the production up to commissioning at the customer's premises (Silakova, 2018).

Table 2-4: Industrial Manufacturers of HTC Reactors.

Manufacturer	Equipment	Capacity (per year)
AVA-CO ₂	Batch reactors	9000 tons of hydrochar
SunCoal Industries	Continuous type reactors	5000 tons of Feedstock
TerraNova Energy	Continuous type reactors	single unit capacity allows conversion of 1500 tons
Ingelia	Continuous type reactors	6000 tons of the wet raw material

AVA-CO₂ industrial plant converts residues in a profitable and technologically efficient manner into high-grade biochar or biocoal and operates the HTC plants on behalf of its customers (Kläusli, 2010). AVA-CO₂ pioneered the world's largest HTC plant in 2010 making them as the first company to industrialise the HTC technology (Kläusli, 2010). At its inception, the processing plant had an overall volume of 14400 litres with a capacity to process 8,400 tonnes of biomass annually (Kläusli, 2010). The process developed by AVA-CO₂ comprises of three major components: Biomass mixing station, actual reactor and, the storage tank. In the first compartment, the biomass is mixed with water, and then heated up to 150 °C; the reactor is then set to 220 °C and at a pressure of 22 bar wherein the actual reaction takes place, and; lastly the outlet buffer tank serves as an intermediate storage for the end product (Kläusli, 2010).

SunCoal industries develops and commercializes innovative hydrothermal processing technology using biomass to produce carbon-based products like chemicals or biofuels (SunCoal Industry, 2019). The company reports to carry out the whole R&D (research and development) during the development of the process, and this consists of the following:

- Screening experiments in the laboratory.
- Sample production in the laboratory.
- PQM (product quality management) and application tests.
- Pilot plant sample production.
- PQM and application engineering.
- Results for engineering and plant design (SunCoal Industry, 2019).

TerraNova Energy uses the TerraNova® Ultra HTC process to employ a technology that simulates the natural coalification of carbonaceous material by creating and fast-tracking the processing. It utilizes a sewage sludge by processing it for two hours at a temperature of around 200 °C and a pressure ranging between 20 to 35 bar and hence transforms it into a product fuel much like lignite coal (TerraNova Energy, 2019). The TerraNova® Ultra process allows for energy-efficient sludge drying to a small amount of solid fuel and integrated Phosphorous recovery – thus treatment and disposal costs are reduced (TerraNova Energy, 2019). Using a TerraNova Energy system at a sewage treatment plant for 100,000 inhabitants can, therefore, generate approximately 3400 MWh of environmentally friendly energy per year.

Ingelia also regards itself as the first company in the world to offer continuous HTC processing on an industrial scale. As of 20th of September 2019, Ingelia is reported to have built two plants operating in Spain and the other in the United Kingdom (European CEO, 2019). The company was established in 2005 and processes around 6000 tonnes of bio-waste annually with 98 % recovery (European CEO, 2019). The company has two more plants planned under construction in Italy and Belgium; moreover, both projects are to begin operations in the first semester of 2020 (European CEO, 2019). Ingelia designs modularised biomass HTC plants such that the processing capacity can be adapted to that of the Customer's needs (Ingelia, 2019). (Ingelia, 2019). The Ingelia HTC plant produces a product with LHV of around 24 MJ/kg, similar to brown coal (i.e. lignite) and a carbon content ranging between 54 and 62 % (Ingelia, 2019). Moreover, elements such as K, Cl, etc. dissolve in the liquid phase hence resulting in a hydrochar with low salinity and ash melting points of above 1250 °C (Ingelia, 2019). Ingelia uses reverse osmosis that concentrates the hydrochar and extracts the organics from the liquid fraction thus producing 80 to 200 kg of clean water per ton of bio-waste processed (Ingelia, 2019).

According to Silakova, (2018), some of the major reasons why there are only a few service providers in the manufacturing of industrial-scale and support to the industry are outlined below:

- The cost of raw biomass material as well as the feeding process and type;
- The type and the capacity of the equipment are defined by the size of the particles.
- The large amounts of water required for feedstock processing; as well as

- The heating of the feedstock, drying of the produced hydrochar needs effective design.
- The high temperature and pressure requirements, which increase costs (*Kumar et al.*, 2018).

2.7. PELLETISATION PROCESS

Coal fines agglomeration also known as densification is not a new concept; it has been around for at least a century as reported by (Gaqa and Watts, 2018). Densification methods commonly used are pelleting (also known as pelletisation), briquetting, and extrusion processing (Tumuluru *et al.*, 2010). The technique is one of the promising options for overcoming low energy and low densities biomass and coal products. The process can be carried out with or without the addition of a binding agent (binder) (Tumuluru *et al.*, 2010). On a commercial basis, densification is mostly applied to biomass and it's performed using equipment's such as pellet mills, briquetting presses, or roller presses as a mechanism to help overcome storing, handling, and transportation problems (Tumuluru *et al.*, 2010). According to Bajwa *et al.* (2018), pelletizing is a process where the solid particles are consolidated through either compression or extrusion, to form a product with much higher quality and characteristic.

Furthermore, Gaqa and Watts, (2018) described that the pelleting of coal fines consist of applying pressure onto small coal particles, with or without the addition of a binder to form a densified product for applications in the domestic or industrial markets. Pelletisation is generally applied to low bulk density feedstock, for instance, biomass, to improve its energy density and energy efficiency when used in systems such as fluidized-bed (Bajwa *et al.*, 2018). Pelletisation is regarded as an important method for increasing the mass and energy density of raw woody biomass materials along with improving their handling, transport, and storage (Hoekman *et al.*, 2014). Further increases in mass and energy density are possible by thermal pre-treatment of raw biomass before pelletisation, via thermal pre-treatment like torrefaction or HTC (Hoekman *et al.*, 2014).

Tumuluru *et al.* (2010) reported that the quality of a densified biomass depends on several process variables, such as die diameter, die temperature, pressure, usage of binders, and preheating of the biomass. Pelletizing is a complex process that requires incorporating

different types of fine-grained material and taking into consideration the importance of binding agents to hold coal fines together (Gaqa and Watts, 2018). The cost of adding these expensive binders to the coal fines leads to an expensive product difficult to market to the end-users (Mangena and du Cann, 2007).

2.7.1. Binderless Agglomeration

This is an agglomeration method performed without the addition of a binding agent in making a pellet or briquette. Mangena and du Cann, (2007) did a study on the binderless briquetting of selected South African coals, i.e. prime coking coal, blend coking coal and weathered bituminous coals and how the coal properties influenced the quality of the briquettes produced. The authors reported that the coals were made into briquettes under different moisture contents and pressures, with the fresh vitrinite-rich coking and blend coking coals forming a better binderless briquette, compared to the fresh inertinite-rich Witbank coals (Mangena and du Cann, 2007). The high bonded briquettes produced from both the coking coals were found to be strongly correlated with the high proportion of fresh vitrinite macerals in the two coals leading to a significant deformation and subsequent consolidation (Mangena and du Cann, 2007). On the other hand, in the same study, weathering was found to have an adverse effect on the coal's amenability during the binderless briquetting process, thus, in this case, the addition of binders was recommended.

2.7.2. Binder Agglomeration

The addition of binders is often necessary when the raw materials (ores, minerals, biomass, etc.) required in producing the pellet or briquette do not have the characteristic of a binder (Bajwa *et al.*, 2018). Bajwa *et al.* (2018) found that the addition of binder aid in lowering the pressure required for satisfactory compaction. More so, the percentage proportion of binder was also found to be detrimental to the tensile strength or durability of the products (Bajwa *et al.*, 2018). Gil *et al.* (2010) and Kumar *et al.* (2018) reported that the quality of a pellet is measured in terms of its mechanical durability, i.e. its ability to remain intact during storage and/or handling. The application of the hydrothermal process as a pre-treatment method for carbonisation and co-carbonisation of coal/biomass has been found to have a tremendous influence on the durability of pellets (Saba *et al.*, 2017b). The

hydrochar produced by Hoekman *et al.* (2017) at a temperature of 200 °C, exhibited good durability, with increase in HTC temperature while, Kumar *et al.* (2018) observed that the pellet durability can be further enhanced, but with an increase in the product's brittleness.

A pilot test investigation was conducted by Borowski and Hycnar, (2013) on the production of briquettes from three types of coal, with the addition of binder components such as potato starch, molasses, and wood biomass. In this study, the materials were well homogenized before being pressed roll, and the products obtained were subjected to strength and waterproof testing, combustion, ash, and dust emissions to determine their quality and suitability for power generation. The authors reported that the briquettes prepared from the potato starch met the minimum required quality or standard, whereas, molasses with coal did not provide good quality briquettes. Also, the authors stated that a good quality briquette was produced with approximately 20 % biomass, but at this ratio in the coal/biomass blend, there was no significant reduction in emissions during the combustion tests. However, as the proportion of the biomass increases above 20 %, a reduction in gas emissions (NO_x, SO₂, CO₂, etc.) was noted, as well as ash reduction. In summary, the fuel produced by the authors with heating values ranging between 22–24 MJ/kg was found to be suitable as an alternative fuel for combustion in an industrial and domestic boiler.

The influence of a binder in producing durable pellets with an improved fuel characteristic was reported by Gaqa and Watts, (2018). The investigation of fine coal of -150 µm with microalgae biomass as the sole binding agent was observed. The blends comprised of two mixing ratios i.e. 90 wt. % coal + 10 wt. % algae and 80 wt. % coal + 20 wt. % algae. From the compression resistance test (crushing resistance) conducted on these samples, the results obtained indicated that pellets made of 80 wt. % coal + 20 wt. % algae mixture were stronger than those made from the 90 wt. % coal + 10 wt. % algae mixture (Gaqa and Watts, 2018). Concerning the impact of moisture, pellets produced from the sample with ±17 wt. % moisture content were found to exhibit the strongest resistance of 1.8 kg/mm² for the 80 wt. % coal + 20 wt. % algae mixture centrifuged for 24 hours. The criteria for the transportation of pellet and briquette are based on the fuel's physical properties namely; abrasion, moisture uptake resistance, impact and crushing resistance (Shuma, 2018). These properties make certain that the pellets do not undergo premature

crushing and disintegration when transported and under storage conditions. In this study, only the latter three will be investigated.

2.7.3. Water Resistance Index

The water resistance index (WRI) of a pellet or briquette is determined by completely submerging the product in water for a fixed period. A WRI greater than 95 % should be obtained after 30 minutes according to Richards (1990), as this is used as a comparative standard. Hoekman *et al.*, (2014) methodically investigated the pelletisation properties of hydrochar produced from woody biomass and compared the product (hydrochar) with pellets made from raw and torrefied woods. The authors found that at a temperature below 200 °C, a less durable pellet that swelled when immersed in water was produced, while hydrochar from HTC produces highly stable, water-resistant pellets (Hoekman *et al.*, 2014). For acceptable minimum requirements for transport and storage, the densified biomass should be robust and water-resistant (Hoekman *et al.*, 2014). The results from this investigation showed that torrefied biomass pellets do not satisfy the WRI requirements without incorporating an additional binder material. Furthermore, the authors showed that hydrochar from HTC yields pellets that are extremely stable and water resistant, however, considering the high costs of a commercial HTC process, the most effective use of hydrochar may be as a low-concentration binder blended with raw or torrefied biomass (Hoekman *et al.*, 2014).

According to Gaqa and Watts, (2018), the equation seen below is used in determining the WRI of pellets after being immersed in tap water for 30 minutes, by subtracting the weight % of water absorbed by the densified product or pellet.

$$WRI = 100 - \text{Mass \% of water after 30 minutes} \quad (2-1)$$

The authors reported in their findings that pure coal pellets failed the water-resistance test. They completely disintegrated within five minutes, having started to disintegrate within a few seconds of being submerged. The pellets (mixed and centrifuged at 17 % moisture) made from the 90 wt. % coal + 10 wt. % algae mixture completely disintegrated in water, while those made from the 80 wt. % coal + 20 wt. % algae mixture had a WRI of 88.9 (Gaqa and Watts, 2018). For samples centrifuged after 24 hours, nevertheless, the pellets made from the 90 wt. % coal + 10 wt. % algae mixture had a higher WRI of 75.5, compared

to those of the pellets made from the 80 wt. % coal + 20 wt. % algae mixture at 65.5 (Gaqa and Watts, 2018). At a moisture content of ± 22 % (mixed and centrifuged) the pellets showed that those made from the 80 wt. % coal + 20 wt. % algae were more water-resistant, at WRI of 81.3 than pellets made from 90 wt. % coal + 10 wt. % algae (mixed and centrifuged) which had a WRI of 75.6 (Gaqa and Watts, 2018). In conclusion, these pellets showed a WRI of less than 95 % after 30 minutes in water, and thus would not be able to handle higher humidity conditions (Gaqa and Watts, 2018). This implies that care would need to be taken during the packaging, transportation, and storage to avoid exposure to humidity as much as possible (Gaqa and Watts, 2018).

Shuma (2018) performed a water penetration test by immersing a single pellet in water for 10 minutes while applying finger pressure to check disintegration with a maximum test cycle of 30 minutes. The results showed that most of the briquettes herein studied failed within seven of the 10 minutes.

Figure 2-12 depicts a test carried out by Fosnacht *et al.* (2018) on determining the level of disintegration over 24 hours for two briquettes. The briquettes are comprised of a mixture of birch bark waste that was processed using {HTC (PF T1)} and commercially torrefied wood, while the second mixture comprised of {HTC (HTC-Com T2)} and commercially torrefied wood (T2). With an increase in the percentage proportion of hydrochar in the briquettes, starting from zero % (no inclusion) – 100 % inclusion level, the more moisture resistance product was produced. The {HTC (HTC-Com T2)} was hydrothermally treated at 220 °C for 180 minutes, while the birch bark waste {HTC (PF T1)} was prepared at 235 °C for 20 minutes. The birch bark waste HTC briquettes {HTC (PF T1)} were seen to be more resistant to moisture at lower levels of hydrochar inclusion than the HTC briquettes with {(HTC-Com T2)} (Fosnacht *et al.*, 2018). The results indicate that higher percentage inclusions of hydrochar led to briquettes becoming more moisture resistant (Fosnacht *et al.*, 2018). In addition, the authors also observed that higher HTC temperatures are crucial to the hydrophobicity of HTC products, as with the HTC (PF T1) prepared at 235 °C for 20 minutes.

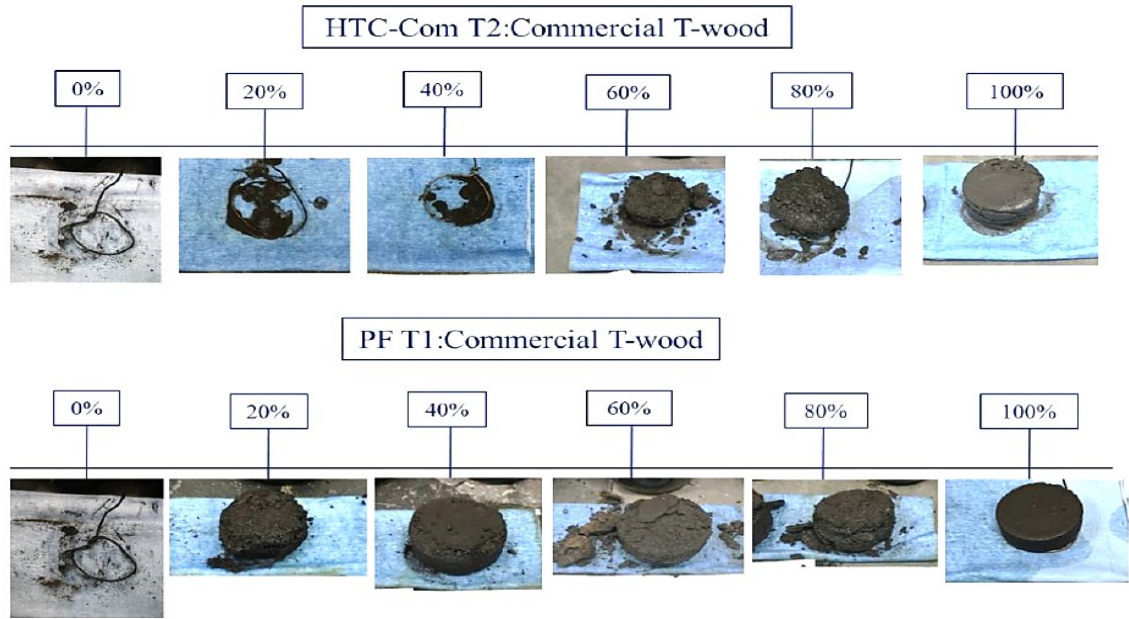


Figure 2-12: Comparison of moisture resistance of briquettes with increasing HTC levels (Fosnacht *et al.*, 2018).

2.7.4. Impact Resistance Index

The impact resistance (or drop resistance/shattering resistance) test may well simulate the forces encountered during the process of offloading densified products from trucks onto the ground, or from chutes into bins (Kaliyan and Vance Morey, 2009). The index measures whether the pellet can withstand impact when in contact with equipment or other pellets. Gaqa and Watts, (2018) conducted the downfall durability by dropping the pellets on a concrete floor from a height of 1.85m and the impact resistance index (IRI) was calculated using Equation 2-2.

$$IRI = \frac{100 \times N}{n} \quad (2-2)$$

N Represents the number of drops and n , the total number of pieces from the dropped pellet.

Table 2-5: Impact resistance index of the pellets (Gaqa and Watts, 2018).

<i>Sample ID</i>	<i>IR at 3 500 psi, sample moisture = $\pm 17\%$</i>	<i>IR at 3 500 psi, sample moisture = $\pm 22\%$</i>
Pure coal	50.0	68.9
Coal _{90%} -algae _{10%} mix (mixed & centrifuged)	125.0	133.3
Coal _{80%} -algae _{20%} mix (mixed & centrifuged)	88.9	81.3
Coal _{90%} -algae _{10%} mix (centrifuged after 24 hours)	153.8	105.3
Coal _{80%} -algae _{20%} mix (centrifuged after 24 hours)	105.3	133.3
IR = impact resistance		

Table 2-5 provides a summary of the impact resistance (IR) testing of the pellets produced by Gaqa and Watts, (2018) on the blend of different coal/algae. This test shows the difference in the impact resistance of four coal/algae blends, in comparison with 100 wt. % coal. The pellets made from the 90 wt. % coal + 10 wt. % algae mixture appeared to have more substantial impact resistance than those produced from the 80 wt. % coal + 20 wt. % algae mixture. From this same Table (2-5), it is observed that the sample with the lower moisture content does have a better impact resistance than that with higher moisture content. All the blends were seen with a much higher impact resistance than coal, with a minimum threshold above 50, which is the acceptable level for a good pellet (Richards, 1990; Kaliyan and Vance Morey, 2009 and Gaqa and Watts, 2018). A similar investigation was carried out by Kambo and Dutta, (2014) to determine the impact resistance of a densified and pre-treated samples obtained from miscanthus feedstock. Each pellet sample was dropped from a height of 1.85 m onto a metal plate four times and the change in the weight percentage after the drop test was expressed as the pellet durability (Kambo and Dutta, 2014). The IR index for the raw miscanthus pellets was found to be 92.2 %, and the value increases as the HTC reaction temperature increases from 190 to 225 °C.

2.7.5. Compressive Resistance

Kaliyan and Vance Morey (2009) defined compressive resistance (crushing resistance or compression strength) as the maximum crushing load a pellet/briquette can endure before cracking or breaking and this can be determined through a diametrical compression. The standard coal compressive strength acceptable to the industry is reported as 0.38 MPa or 380 KPa, which is the value adopted for the benchmark laboratory-scale work reported by Gaqa and Watts (2018) on their coal/algae products. In addition, the compression strength

is calculated by dividing the maximum force (at the point of breakage) by the surface area exposed to the force. This value provides a measure of the quality of the densified product and should be greater than 100 Kg/cm². The compressive strength is calculated using the following equation:

$$\sigma = \frac{2F}{\pi dl} \quad (2-3)$$

Where F represents the maximum compressive force, and d and l represent the diameter and length of the pellet, and σ is the compressive strength respectively. Compressive strength durability is defined as the ability of pellets to remain intact during impact.

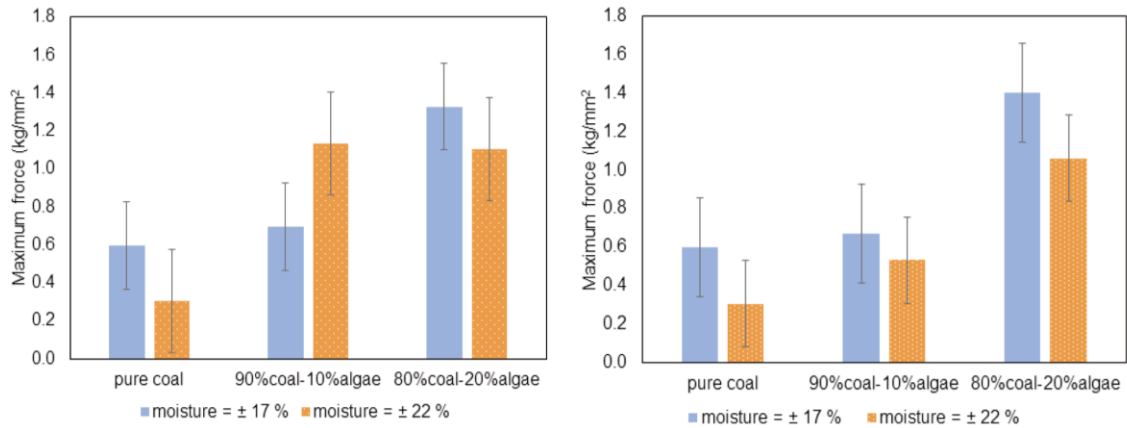


Figure 2-13: Compression strength of the pellets (Gaqa and Watts, 2018).

Figure 2-13 depicted the compression strength results from the pellets made from two different blend ratios of coal and microalgae (Gaqa and Watts, 2018). The pellets were made from the samples with moisture contents of 17 % and 22 %, respectively, and subjected to a pressure of 3500 psi (24.13 MPa) while held under the same pressure for one minute. The pellet samples with 17 % moisture content had more compression resistance than those made from samples with a moisture content of 22 % (Gaqa and Watts, 2018). The 90 wt. % coal + 10 wt. % algae pellets with a moisture content of 17 %, had a maximum crushing force of 0.7 kg/mm² (6.86 MPa) while those with a moisture content of 22 % had a maximum crushing force of only 0.5 kg/mm² (4.90 MPa) (Gaqa and Watts, 2018). The 80 wt. % coal + 20 wt. % algae pellets with a moisture content of 17 % had a crushing load of 1.4 kg/mm², while those of 22 % had a crushing load of 1.0 kg/mm² (Gaqa

and Watts, 2018). This test showed that the pelletisation of Coalgae® (a mixture of coal and microalgae) using microalgae as a binder is a promising technology in the recovery of coal fines (Gaqa and Watts, 2018).

An investigation by Richards, (1990) on briquettes made with a mixture of sub-bituminous coal and starch-based binder showed a result with compressive strength of less than 375 KPa (0.038 kg/mm²). The author concluded that the briquettes failed to meet the minimum compression strength of 375 KPa, which is the value adopted as the benchmark for laboratory-scale work. The pellets made from Coalgae by Gaqa and Watts, (2018) was found to have a better compression resistance of more than 0.038 MPa as stipulated by Richards, (1990).

Another study undertaken by Reza *et al.* (2014) tested the durability of engineered pellets (a mixture of torrefied biochar and HTC hydrochar) of loblolly pine produced under different torrefaction temperatures (250, 275, 300, or 300 °C) and a hydrothermal temperature of 260 °C. In the study, the authors observed that with an inclusion amount of just 10 wt. % of hydrothermally produced (HTC 260) biochar, a significant improvement was achieved for the engineered pellets such that, the durability went from 77 % to 95 % for the dry 250 biochar, 78 % to 92 % for the dry 275 biochar, and 56 % to 83 % for the dry 300 biochar (Reza *et al.*, 2014). On the other hand, the addition of 25 wt. % HTC 260 biochar further improved the durability of the dry torrefied 275 and dry torrefied 300 pellets (Reza *et al.*, 2014). When the HTC 260 biochar was added at 25 to 50 wt. %, the durability increased only slightly for the dry torrefied 250 and dry torrefied 275 biochar pellets.

2.8. CONCLUSION

The current global energy landscape including that of South Africa is still largely dependent on fossil fuels, reported at 78.4 % making them the most widely, used resources for energy production. The overwhelming dominance of coal might seem impossible to break because coal is not only a relatively cheap source for energy production but also a key economic driver. However, its mining, production, and subsequent use as a fuel in power plants has had and continues to have significant environmental and health effects. Two of the by-products formed in the coal processing industry is the discard generated in

the country from the washing plants, and from the fines generated during mining or screening, which are disposed of as the ultra-fines in the slurry ponds. These resources are considered uneconomical, environmentally hazardous, and difficult to process. In addition, the handling, storage, and disposal operations of these coal-fines present significant and unproductive expenses to the mining industry.

The chapter provides information on different sources and use of biomass resources such as those from agriculture, forestry, industrial and municipal solid waste with the aid of reducing environmental pollution. In addition, an extensive literature of the two indigenous trees species utilised as biomass in the study was provided. The application of the hydrothermal process among other coal beneficiation processes is outlined in this chapter. A detailed review of pelletisation of coal fines with biomass to form durable pellets and subsequent areas of utilization was outlined.

CHAPTER 3: MATERIALS AND METHODS

3.1. INTRODUCTION

This chapter presents the materials, methods, and equipment used in this research. *Searsia lancea* and *Tamarix usneoides* tree species along with discard coal were used as feedstock for this study. All the samples were subjected to different physicochemical analyses to determine their suitability as solid fuel. Based on the results obtained from these analyses, samples were chosen for (HTC). The hydrochars produced were sub-divided, blended with discard coal at different weight percentages, and further underwent mechanical tests to ascertain their suitability and durability as solid pellet fuels. The experimental steps undertaken in the production of hydrochars and pellets are illustrated in Figure 3-1.

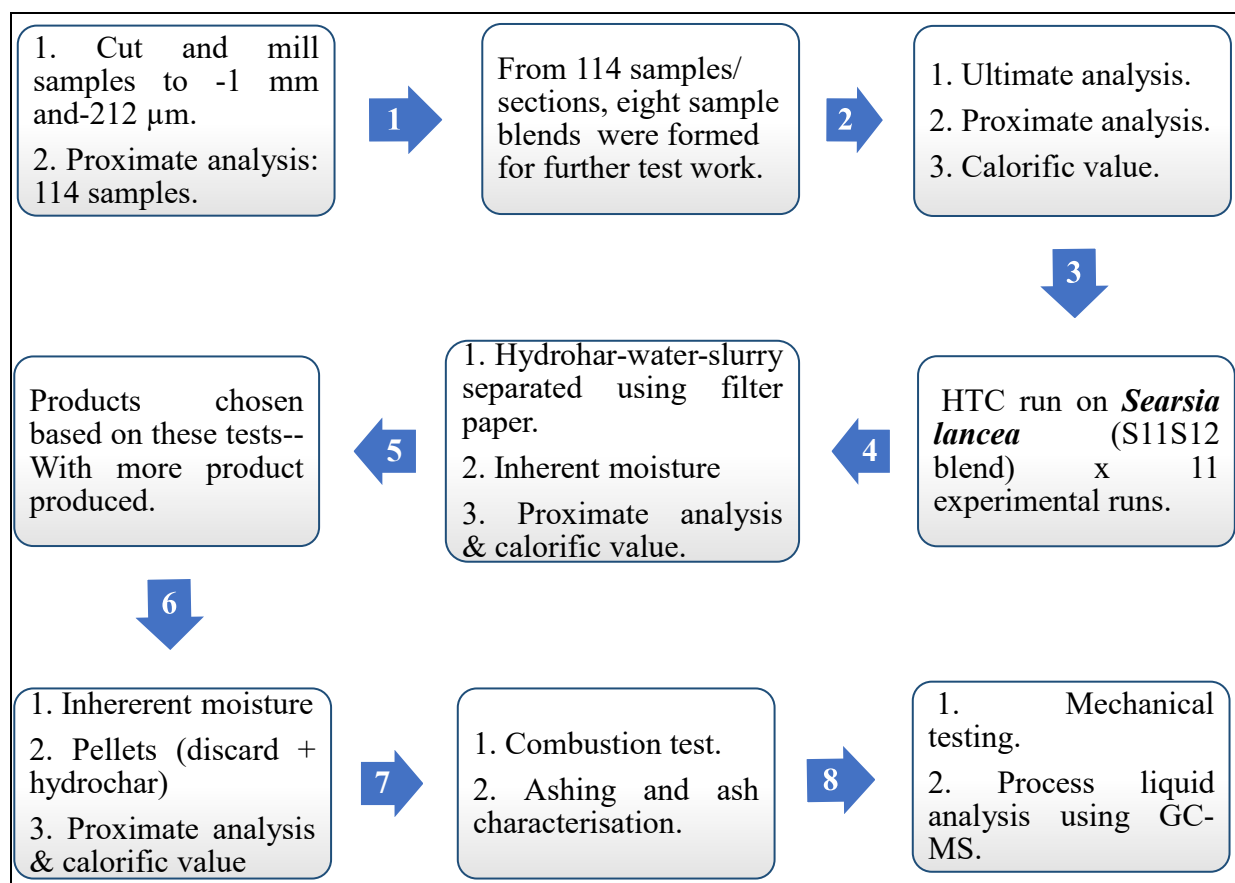


Figure 3-1: Process flow diagram.

The trees were harvested from four tailings facilities (Madala, Redsoils, West Complex and Mispah), with each species comprising of four trees per site (two *Searsia lancea* and

two *Tamarix usneoides*) thus totalling 16 trees as illustrated in Figure 3-2. The different tailings sites are distinctive in terms of their environmental conditions. The sites are first classified by their actual soil forms such as Mispah, Hutton, etc., followed by the sub-classification, and then the AMD concentration from the site. Joubert, (2017) reported that each mining operation had a nutrient-rich soil (Redsoils and Mispah) and a nutrient-poor soil (West Complex and Madala). Additionally, Buckham, (2012) reported that the main source of AMD is pyrite (FeS_2) undergoing rapid oxidation when exposed to oxygen and water along with other sulphidic minerals. Furthermore, the author stated that the tailings storage facilities contain as much as between 0.2-3 % concentration of pyrite.

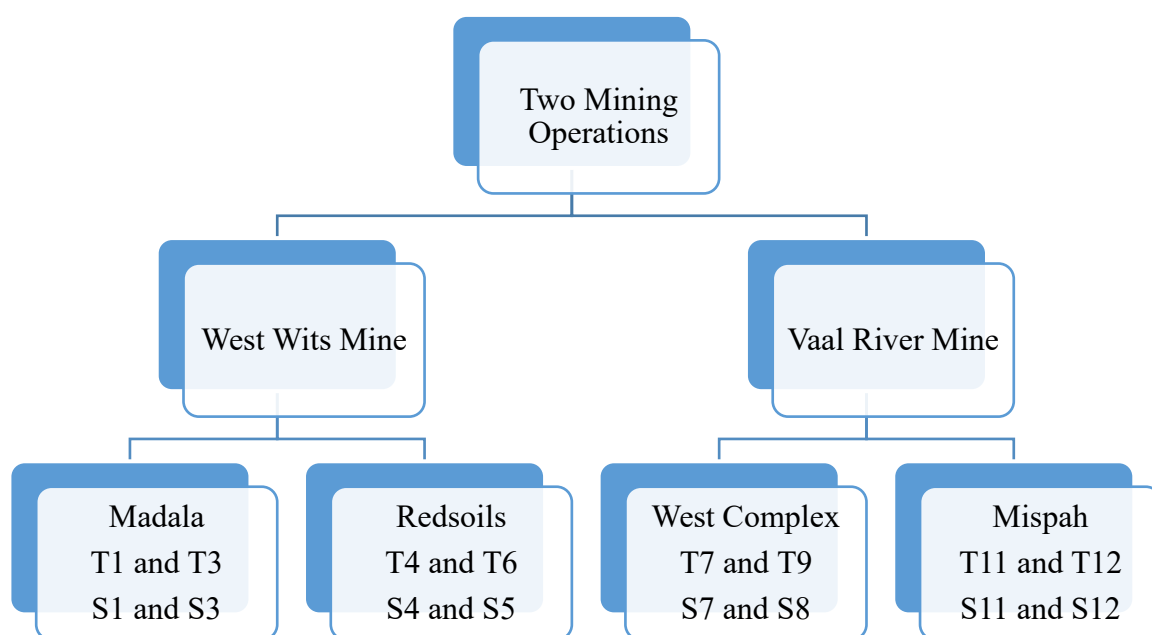


Figure 3-2: Mining Operations and their tailings facilities.

In total, 114 samples of both *Searsia lancea* and *Tamarix usneoides* tree sections comprising of different compartments such as leaves, twigs, wood, root (fine-medium root), root ball (coarse root), stump and dry biomass (deadwood) were collected and cut to small sizes using Band Saw Machines. The sizes were small enough to go through the Retsch SM 200 cutting mill and then subsequently milled to two sizes, -1 mm and -212 μm size fractions. After milling, the samples were verified for the targeted size fractions by performing a sieve analysis test and then stored in plastic bags. The -1 mm fraction was used for the HTC, while the -212 μm size fraction was used for the physicochemical analyses. For the characterisation test, 114 tree compartments were subjected to proximate

analysis while 28 samples were analysed for their calorific values. The results from the proximate and calorific value analyses informed the decision to have the samples blended, and which section of the tree to be excluded from carrying out the next batch of tests. The results from these analyses indicated that the species planted and harvested from the same site, have similar properties, therefore different sections of *Tamarix usneoides* and *Searsia lancea* trees were blended to make a whole tree. That is, *Searsia lancea* trees (S1 and S3) from the Madala tailing site were blended and the sample is denoted as an S1S3 blend. Eight different samples were then obtained after the blending, and all the samples were further characterized for their suitability, with the S11S12 blend chosen to produce hydrochar and the subsequent pellets produced in this study.

To make a further comparison of the quality of the solid fuels produced from the HTC test, the design of experiment software was used to manage, compare and understand the results of the combinations of the two process parameters (temperature and residence time) for the experimental cycles performed.

3.2. MATERIALS AND EQUIPMENT

3.2.1. Gases

Air, nitrogen, oxygen, and argon gases were used in carrying out the physicochemical characterisation and HTC of the biomass.

3.2.2. Raw Fuels

The bulk samples of the *Searsia lancea* and *Tamarix usneoides* tree species along with discard coal from a coalfield in Mpumalanga Highveld were used as feedstock for this study.

3.2.3. Equipment Utilised

This list comprises equipment used in conducting all the experimental tests, including the physicochemical characterisation, mechanical property testing for the pellets and the HTC test.

- Band Saw Machines.
- Retsch SM 200.
- Drying oven.

- TGA Instrument (Leco TGA 701).
- Leco AC500 Bomb Calorimeter.
- Berghoff BR-1500 High-Pressure Laboratory Reactor with Accessories.
- Manual Hydraulic Laboratory Pellet Press.
- Balances.
- Kenwood Type KVL40 (Chef XL) Mixer.
- Compressive resistance machine.
- 4 x 200 ml containers.
- 4 x small hand-made strainers.
- Metal wire.
- Metal plate.

3.3. FUEL CHARACTERISATION

3.3.1. Proximate Analysis

The proximate analysis determines the sample's inherent moisture, ash content and volatile matter present in the sample, with fixed carbon calculated by difference and are all expressed in percentage. The analysis was conducted following the ASTM D-5142 standard. 1g of the sample was placed in each crucible in the TGA 701 Leco instrument for the analysis. ASTM D-5142 method involves using N₂ atmosphere for drying and devolatilisation and subsequently, combustion in O₂ atmosphere. The drying step measures the moisture content by mass loss starting from room temperature to 107 °C at a heating rate of 6 °C /min points in time. The devolatilisation is measured as the mass loss within a temperature range between 107 °C to 950 °C, whereas the combustion step evaluates the mass loss under oxygen between the temperature range of 650 °C and 750 °C. The residual mass left after the analysis is then taken as the total ash in the sample. Each experiment was done twice for better precision.

3.3.2. Calorific Value Determination

The calorific value is a measure of the heat energy content and was determined for all the samples using a Leco AC500 bomb calorimeter following the ASTM D5865-04 standard. The bomb calorimeter calculates the total amount of heat released from the complete combustion of one-unit mass (1 g) of fuel under the oxygen atmosphere at high pressure. The system makes use of an electronic thermometer with a measuring accuracy of 0.0001

°C to measure the temperature every 6 seconds, with the results acquired within 4.5 to 7.5 minutes. The sample is loaded into a crucible and placed on a sample holder inside the bomb. The top lid is screwed in place onto the bomb calorimeter and oxygen gas is charged up to a pressure of 3000 KPa using a valve pin into the bomb. The bomb, known as the combustion vessel, is then placed inside a bucket of water, with the electrodes connected to the loading mechanism for the analysis to commence. The results were repeated twice, and the average was taken for better precision.

3.3.3. Ultimate Analysis

The ultimate analysis was conducted according to the ASTM D3176-89, standard test method for coal and coke. The equipment used was an Elemental Analyzer Vario EL Cube. Samples (of between 5-10 mg) were weighed into a tin foil capsule and loaded into the instrument combustion vessel automatically where the samples were first flushed with helium (He), which acts as a carrier gas to remove atmospheric nitrogen. Thereafter, the combustion of the samples was then carried out at 1150 °C, under an oxygen atmosphere. The percentage composition of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) were determined analytically, while that of oxygen (O) was estimated by difference.

3.3.4. Ashing and Ash Characterisation

Five different samples were ashed and characterised for their elemental composition. Two of the samples were a blend of 25 and 50 wt. % hydrochar and the balance supplemented by discard coal. The remaining three samples consisted of the untreated raw sample, 100 wt. % hydrochar, and 100 wt. % coal samples. Ashing of the samples was done in two folds. The untreated raw sample and 100 wt. % hydrochar were ashed using the Biomass Ashing CEN/TS 14588 standard method while the 100 wt. % discard, 50 wt. % hydrochar/50 wt. % coal, and 25 wt. % hydrochar/75 wt. % coal was ashed in an atmosphere of air according to the standard ISO 1171:2010 for Coal Ashing. The blended samples with the coal ratio above 50 wt. % were ashed using the coal standard due to the high coal composition in the blend.

The ash characterisation was performed for the major and trace elements depicted in Table 3-1. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used for

detecting the major elements while inductively coupled plasma mass spectrometry (ICP-MS) was used to detect trace elements. Both methods are known as destructive analysis methods. The difference between the two techniques is that ICP-OES measures the excited atoms and ions at the wavelength characteristics that match the elements being measured, while, the ICP-MS uses an atom's mass by mass spectrometry (MS) to conduct the measurement (ThermoFisher, 2019).

Table 3-1: Major and trace elements tested in the ash and process liquid samples.

Major Elements	Trace Elements
Calcium (Ca)	Arsenic (As)
Sodium (Na)	Chromium (Cr)
Magnesium (Mg)	Copper (Cu)
Manganese (Mn)	Lead (Pb)
Phosphorus (P)	Manganese (Mn)
Potassium (K)	Mercury (Hg)
Sulfur (S)	Nickel (Ni)
Chlorine (Cl)	Titanium (Ti)
Aluminium (Al)	Uranium (U)
Iron (Fe)	Vanadium (V)
Silicone (Si)	Cobalt (Co)
	Cadmium (Cd)
	Gold (Au)
	Zinc (Zn)

The instrument used is the PerkinElmer NexION 300X ICP-MS (KED mode). Approximately 0.5 g of sample underwent microwave-assisted digestion in 9 ml nitric acid (HNO₃) and 3 ml hydrochloric acid (HCl). Calibration standards ranged from 0.1-10 µg/l and included a calibration blank. Scandium (Sc) and Iridium (Ir) were added to all samples and standards as internal standards. NIST 1640 was used to verify the calibration curves. The calibration standards produced a linear response, against which the samples were measured. By using the straight-line equation, the concentration of the unknown can be determined. The results were blank corrected.

3.3.5. Process Liquid Analysis

The process liquid from the hydrochar production process was taken in for analysis of dissolved organic matter using gas chromatography-mass spectrograph Shimadzu GCMS-2010. The oven temperature was initially set for 140 °C for four minutes then increased to

250 °C at a heating rate of 4 °C/min with a holding time of 12.5 minutes, but the injection temperature was set at 220 °C using the splitless mode. The instrument was set according to the following parameters;

Sampling time	: 1.00 minute
Flow Control Mode	: Pressure
Pressure	: 100.00 kPa
Total Flow	: 50.00 ml/min
Column Flow	: 1.13 ml/min
Linear Velocity	: 40.1 cm/s
Purge Flow	: 3.00 ml/min
Split Ratio	: -1.00 ml/min

The identification of the compounds was done by using the NIST database and comparing with published mass spectra.

3.3.6. Differential Thermogravimetric (DTG) Analysis

The reactivity test for all the samples was conducted in a TGA 701 Leco instrument. The test took place under air at a volume flow of 3.5 l/min with approximately 150 mg of fuel used for each experiment. The operating procedure involved heating all samples at a constant heating rate of 10 °C/min, under a non-isothermal temperature range of 25-850 °C and held until there was a constancy in weight loss. The combustion characteristics of the fuels tested are determined from the DTG curves or thermographs generated for individual fuel or blend.

3.4. HYDROTHERMAL CARBONISATION TEST

3.4.1. Hydrothermal Carbonisation Reactor

The HTC of the tree species used in this study was conducted in a high-pressure Berghof BR-1500 (Figure 3-3 A). The Berghof BR-1500 comes with an internal volume of 1.75 L; however, the samples were kept such that no more than 80 percent of this volume was filled as recommended by the manufacturer. The Berghof Stirring Systems BRM consists of a stirrer drive, magnetic clutch, speed controllers, stirrer with a detachable bottom axis and PTFE components, along with other accessories. The reactor also has a temperature and data logger available to regulate the heating systems and thus the temperature of the

laboratory reactor. The vessel heater has a heating power (up to a maximum of 3000 Watts), which automatically switches off in case of sensor breakage or an interruption in the compensation line. The BTC-3000 temperature and data logger unite all control and regulate parameters in a single, compact unit and the built-in data logger allows the parameters to be documented on a computer.

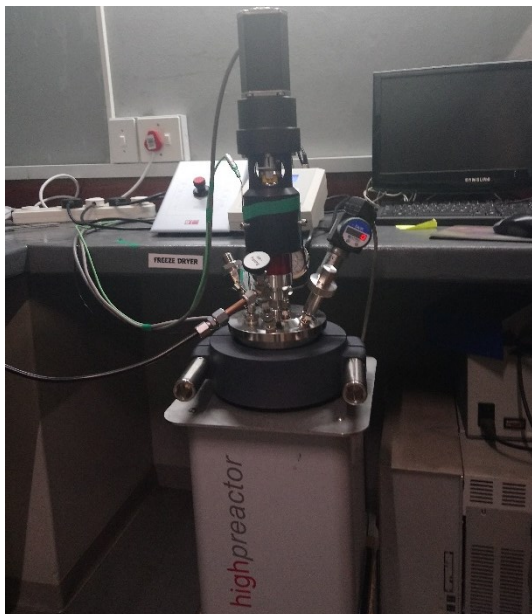


Figure 3-3A: Berghof Stirring Systems BRM. Axis.



Figure 3-3B: Stirrer with Bottom



Figure 3-3C: Stainless steel reactor vessel. Key.

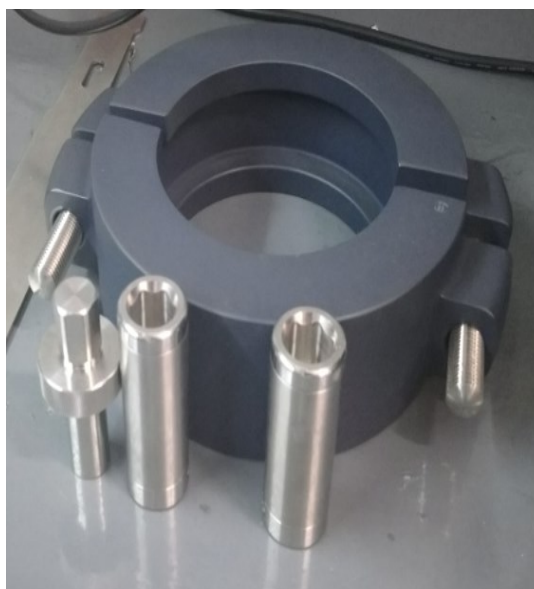


Figure 3-3D: Clamps, screws and LC-

3.4.2. Hydrochar Production

The samples (tree species) utilized for the HTC test had a top particle size of - 1 mm, and the test was conducted under different process conditions, at the temperature range of 200-280 °C and residence time of 30-90 minutes. For each test, the reactor was pressurized under argon at 20 bar for all the tests (Table 3-2), while the temperature and the reaction residence time was varied. The reactor was opened only after a safe temperature (less than 100 °C) was reached and gases produced were released to the atmosphere before the hydrochar slurry was separated using filter paper 609WS 240 mm discs into the wet solids and the process liquid.

The wet HTC hydrochars or solids were tested for moisture and then subsequently oven-dried at 105 °C for 24 hours, then stored in an airtight plastic container. The liquids were poured into bottles and stored in a -4 °C refrigerator. Initially, five parameters were proposed for consideration as stated in the proposal, but only two parameters were eventually investigated. This was due to the limited quantity of samples available for the research, and the fact that studies have shown that temperature is the most important factor responsible for changes in the physicochemical properties of hydrochar (Zhu *et al.*, 2018 and Heidari *et al.*, 2018). Therefore, after the physiochemical analyses were conducted according to the setup in Table 3-2, the hydrochar produced at 280 °C and residence time of 90 minutes was chosen as a superior product for hydrochar production and a blend for coal/hydrochar pellets.

The influence of reaction temperature and residence time on the hydrochar characteristics were studied by the application of a design of experiment method using Design-Expert software version 7.0 (STAT-EASE Inc., Minneapolis, USA). The HTC experiment was designed using Design-Expert software (version 7.0.0) from Stat-Ease, Inc. The software was used to analyse the regression of experimental data, and to determine their statistical significance. Central composite design (CCD) was used in this study to assess the impact of reaction temperature and residence time on the fuel characteristics of the hydrochars produced. The central composite model is commonly used to implement the response surface methodology (RSM) (Zhao *et al.*, 2011; Xin-hui *et al.*, 2014, and Sureshkumar and Susmita, 2018). There were two different factors in this study: reaction temperature (T) and residence time (t). The structure and design matrix of the HTC experiments are shown in Table 3-2 with a complete design matrix of 13 runs. There are four factorial

points, four axial points, and five central points, which have been repeated five times to obtain an accurate estimate of the experimental error.

Table 3-2: Experimental Design Matrix for the HTC test.

Run Order	Factors Coded		Factors Actual	
	T	t	T	t
1	0	0	250	60
2	1	-1	280	30
3	0	1	250	90
4	1	1	280	90
5	0	-1	250	30
6	0	0	250	60
7	0	0	250	60
8	-1	0	200	60
9	0	0	250	60
10	-1	-1	200	30
11	0	0	250	60
12	1	0	280	60
13	-1	1	200	90

T – Temperature; t – Residence time

Table 3-3: Experimental process parameters for each test run.

Run	Temperature (°C)	Time (min)	Pressure (bar)	Initial mass (g)	Biomass-to-Water Ratio
1	200	30	20	100	1:8
2	280	30	20	100	1:8
3	200	90	20	100	1:8
4	280	90	20	100	1:8
5	200	60	20	100	1:8
6	280	60	20	100	1:8
7	250	30	20	100	1:8
8	250	90	20	100	1:8
9	250	60	20	100	1:8
10	250	60	20	100	1:8
11	250	60	20	100	1:8
12	250	60	20	100	1:8
13	250	60	20	100	1:8

3.5 MIXING AND PELLETISATION

The hydrochar and discard coal were mixed at two different ratios: 25 wt.%/75 wt.%/ and 50 wt.%/50 wt.%/ with the first number denoting the hydrochar percentage and the second one discard coal percentage in the biocoal blend. The samples were mixed using the Kenwood Type KVL40 (Chef XL) mixer. The mixing procedure started with running the mixer empty then slowly adding the hydrochar. This was done to break out lumps that formed during the drying stages of the hydrochar. After the lumps were disintegrated, the required discard coal fines percentage of particle size <1 mm were added into the mixer and ran for five minutes.

Subsequently, the blended samples were formed into pellets using Manual Hydraulic Laboratory Pellet Press (Figure 3-4). The pellets were subjected to different mechanical testing and the process liquid was tested using Shimadzu GC-MS 2010 for dissolved organic matter. All the pellets produced at these different blending ratios were tested for proximate, calorific value, combustion, and elemental composition.



Figure 3-4: Manual Hydraulic Laboratory Pellet Press (Specac, 2018).

The hydraulic press is amongst the applications of Pascal's law wherein a small force applied on a column of liquid is converted to a much greater force on another column of

liquid connected to the first. The manual hydraulic press was designed for a wide variety of applications, but specifically to press pellets. The hydraulic press consists of:

- A 40-ton pressure gauge.
- Lid screw attached to a top bolt.
- Press handle grip.
- Pressure release handle.
- Pressing station.

Along with a hydraulic press, a 20 mm die set was used to form and press the pellets. In this study, samples are weighed and then loaded into the die. The samples are placed in the centre of the hydraulic press station and then the pressure release handle rotated until it became firmly tightened. The press handle grip was used to pump up the die thereby building up enough pressure of the hydraulic liquid thus also making sure the parts to be pressed have come into contact. The press handle grip was pumped back and forth until the required tonnage (pressure) was reached and subsequently densifying the powder inside the die. The applied pressure was 159.9 MPa with a holding time of one minute. After pressing the sample, the pressure release handle was used to hold the pressed sample for one minute and afterward employed in lowering the die from the raised pressing station.

This process was repeated for all the pellets produced from the four batches of samples (hydrochar/coal) blends, at different masses. Pellets were produced from 100 wt. % hydrochar of 2 g, 25 wt. % hydrochar + 75 wt. % discard coal (5 g), 50 wt. % hydrochar + 50 wt. % discard coal (5 g) and 100 wt. % discard coal (5 g). Another batch of pellets was also produced wherein 2 g of each sample was used to compare the results/products produced on a mass basis. The final densified products were subjected to different mechanical tests listed herein.

3.6. MECHANICAL TESTS

The mechanical tests listed below are used to assess the suitability of the hydrochar/coal blend for transport and storage purposes. The densification of biomass into a specific shape, like pellets or briquettes, increases its bulk density and overcomes handling difficulties. This can also lead to the reduction in transportation and handling costs

associated with biomass processing and coal fines significantly, especially with biomass acting as a binder.

3.6.1. Compressive Resistance

Kaliyan and Vance Morey (2009) defined compressive resistance (crushing resistance or compression strength) as the maximum crushing load a pellet/briquette can endure before cracking or breaking and this can be determined through a diametrical compression. The standard coal compressive strength acceptable to the industry is reported as 0.38 MPa or 380 kPa, which is the value adopted from the work of Richards (1990) for the benchmark laboratory-scale work reported by Gaqa and Watts (2018). The compressive strength is calculated using equation 3-1:

$$\sigma = \frac{2F}{\pi dl} \quad (3-1)$$

Where F represents the maximum compressive force, d and l represent the diameter and length of the pellet, respectively and σ is the compressive strength. It was noted that the length of each pellet differed from each batch, however for those samples in the same sample batch, the length remained fairly the same. Two representative pellets from each batch were used to measure length and diameter. The compressive resistance was determined following ISO 4700:2007(E) which stipulates a method that measures the compressive load attained to cause breakage of pellets. A load cell of 1000 N was used as the maximum load for the crushing of the pellets. Initially, the pellets were placed flat onto the crushing surface of the compression machine. However, this method only led to the pellets being further densified as opposed to being crushed. Thus, the pellets were then turned on their sides to subject them to the crushing strength and this was carried out for all the samples. Five pellets per sample batch were crushed and the average taken and reported for better accuracy.

3.6.2. Impact Resistance Index

The acceptable level for a good pellet is a minimum impact resistance index (IRI) of 50 %, as stipulated by Richards, (1990); Kaliyan and Morey, (2009) and Gaqa and Watts, (2018). The impact/drop resistance assessment mimics the forces encountered by the

pellets during the process of offloading densified products from trucks onto the ground, or from chutes into bins (Kaliyan and Morey, 2009). The impact durability is defined as the ability of pellets to remain intact after impact. This index measures whether the pellet can withstand impact when in contact with equipment or other pellets.

The drop durability method employed in this study is a slight variation of the one used by Kambo and Dutta, (2014) in their investigations of the impact resistance of densified and pre-treated samples obtained from miscanthus feedstock. The downfall durability was conducted firstly by taking the mass of each pellet before the drop test and after the drop test. Five pellets per sample were dropped and the average calculated and reported for better accuracy. The pellets were dropped from a height of 1.0 m onto a steel plate and the impact resistance index (IRI) was calculated using Equation 3-2:

$$\% \text{ weight loss} = \left(\frac{\text{Initial mass} - \text{Final mass after 10 drops}}{\text{Initial mass}} \right) \times 100 \quad (3-2)$$

3.6.3. Water Resistance Index

The moisture uptake was determined by submerging individual pellets in a 200 ml container filled with tap water. The pellet's mass was weighed, and this was recorded as the initial mass. After taking the weight, the pellet was placed inside a metal basket and then underwent immersion in tap water for 30 minutes. Therefore, the moisture uptake was determined by:

$$\% \text{ Moisture Uptake} = \left(\frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \right) \times 100 \quad (3-3)$$

At the end of the submersion period, the pellet was removed and placed on a paper towel to air out the surface moisture for 2 minutes, after which the final mass determined. After the moisture uptake test is completed, a water resistance index (WRI) was determined using results from equation 3-3 into equation 3-4 as follows:

$$WRI = 100 - \text{Mass \% of water after 30 minutes} \quad (3-4)$$

A WRI greater than 95 % should be obtained after 30 minutes according to Richards (1990), as this is used as a comparative standard. Five pellets per sample were immersed and then dried and the average was taken and reported for better accuracy.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1. INTRODUCTION

The results obtained from the physicochemical characterisation of the raw *Searsia lancea*, *Tamarix usneoides* and the discard coal used in this study are presented and discussed in this chapter. The hydrochars produced at different carbonisation temperatures of 200 °C, 250 °C and 280 °C and residence times of 30, 60 and 90 minutes were also characterised, and their properties discussed. The mass yield of the hydrochars produced was also presented, and the effect of two key process parameters: the reaction temperature and residence time were evaluated and optimized using RSM. The reactivity of the discard coal/hydrochars pellets produced, along with their mechanical properties was presented. In addition, the organic and inorganic composition of the process water was determined, while the elemental composition of the ash derived from the combustion of the pellets produced was also established.

4.2. PHYSICO-CHEMICAL PROPERTIES OF THE BIOMASS SAMPLES

The proximate analysis results presented in Table 4-1 to Table 4-4 are from trees harvested from four different sites in which AMD rehabilitation trial test was conducted. The tests are conducted on each section of the trees to determine their individual properties and suitability as a potential raw sample for hydrochar production. All the Tables show that the bottom compartment of the trees tested (roots, rootball, and stump) contains high moisture content. The ash content of the leaves of *Tamarix usneoides* harvested from the Madala and Mispah sites are within the range of 14.84 % - 15.64 %, while the *Searsia lancea* leaves planted on the same sites are within the range of 4.46 % to 5.87 %.

According to the investigation conducted by Weiersbye and Witkowski, (2007), *Tamarix usneoides* leaves were found to contain a high level of salt (NaCl) ranging from 2 % to 10 %, therefore, the percentage ash content observed in *Tamarix usneoides* leaves utilized in this study is expected. The section with the highest ash content was the Mispah's root, with an ash content of 26.87 %. The *Searsia lancea* leaves were found to possess the highest total carbon and calorific values among all the biomass compartments and much lower ash content compared to the discard coal utilized in this study, as seen in Table 4-5. The blend of all *Searsia lancea* part shows a total sulphur content lower than the *Tamarix*

usneoides. From the proximate analysis conducted on the two tree species (Table 1-4), it is evident that both trees do have different qualities.

Table 4-1: Physicochemical properties of *Searsia lancea* and *Tamarix usneoides* from the Madala Site.

SITE ID	SAMPLE ID	COMPONENTS	TM (%)	VM (%)	ASH (%)	FC (%)
MADALA	T1	LEAVES	8.73	66.99	14.84	9.46
		TWIGS	6.97	69.61	6.63	16.81
		WOOD	7.44	70.29	6.32	15.97
		DB ^A	7.86	69.44	7.38	15.32
		ROOTS	7.53	69.80	7.80	14.89
	T3	LEAVES	7.61	69.75	15.21	7.45
		TWIGS	5.14	72.56	5.22	17.09
		DB ^a	7.00	71.89	6.71	14.41
		STUMP	8.28	67.44	10.06	14.23
	S1	LEAVES	7.58	64.66	4.46	23.31
		TWIGS	8.25	68.72	3.69	19.34
		WOOD	8.02	67.85	3.60	20.54
		DB ^A	7.24	71.55	3.23	18.01
		STUMP	9.06	59.73	8.01	23.21
	S3	LEAVES	7.35	65.57	5.68	21.41
		TWIGS	7.91	65.36	3.93	22.81
		WOOD	8.04	64.67	6.03	21.28
		DB ^A	7.57	71.83	2.82	17.78
		ROOTS	7.34	55.12	19.57	17.99

a: Dry Biomass; TM: Total Moisture; VM: Volatile Matter; FC: Fixed Carbon.

Table 4-2: Physicochemical properties of *Searsia lancea* and *Tamarix usneoides* from Redsoils site.

SITE ID	SAMPLE ID	COMPONENTS	TM (%)	VM (%)	ASH (%)	FC (%)
REDSOILS	T4	TWIGS	6.94	70.90	8.43	13.75
		WOOD	6.92	70.13	2.49	20.47
		ROOTS	8.95	59.85	11.54	19.68
	T6	WOOD	6.92	70.16	2.52	20.41
		DB ^a	8.02	60.18	15.78	16.01
		ROOTS	8.05	60.43	16.05	15.49
	S4	LEAVES	4.18	68.65	4.41	22.77
		TWIGS	7.18	70.50	2.03	20.31
		DB ^a	7.25	71.03	2.35	19.38
		ROOTS	7.15	69.54	2.78	20.54
	S5	LEAVES	4.98	69.01	3.96	22.05
		TWIGS	6.84	69.16	3.29	20.72
		WOOD	8.01	67.98	3.49	20.54
		DB ^a	6.06	77.32	1.19	15.45
		STUMP	9.09	61.59	6.52	22.81
		ROOTS	6.97	67.34	4.55	21.16

a: Dry Biomass; TM: Total Moisture; VM: Volatile Matter; FC: Fixed Carbon.

Table 4-3: Physicochemical properties of *Searsia lancea* and *Tamarix usneoides* from West Complex site.

SITE ID	SAMPLE ID	COMPONENTS	TM (%)	VM (%)	ASH (%)	FC (%)
WEST COMPLEX	T7	LEAVES	7.51	69.39	13.35	9.76
		TWIGS	6.59	71.49	6.20	15.72
		WOOD	5.88	72.40	6.71	15.02
		ROOTS	8.57	67.41	9.88	14.14
		ROOTBALL	8.39	64.70	11.40	15.53
	T9	LEAVES	8.51	67.56	15.59	8.35
		TWIGS	5.07	71.98	5.16	17.80
		WOOD	7.28	68.51	8.36	15.86
	S7	LEAVES	6.87	66.43	4.57	22.14
		TWIGS	5.85	68.12	3.93	22.09
		WOOD	7.35	69.16	2.16	21.34
		DB ^a	7.47	69.28	3.07	20.19
		ROOTS	8.06	62.86	7.06	22.03
		ROOTBALL	7.48	59.72	8.63	24.18
	S8	LEAVES	5.86	67.18	4.31	22.65
		TWIGS	7.17	70.34	1.94	20.56
		WOOD	6.65	72.17	1.33	19.87
		DB ^a	8.07	67.94	2.57	21.44
		ROOTS	7.87	66.20	3.98	21.95

a: Dry Biomass; TM: Total Moisture; VM: Volatile Matter; FC: Fixed Carbon.

Table 4-4: Physicochemical properties of *Searsia lancea* and *Tamarix usneoides* from Mispah site.

SITE ID	SAMPLE ID	COMPONENTS	TM (%)	VM (%)	ASH (%)	FC (%)
MISPAH	T11	LEAVES	8.87	67.01	15.64	8.48
		TWIGS	7.06	69.94	7.96	15.05
		WOOD	8.95	68.66	6.96	15.44
		ROOTS	7.52	59.15	21.47	11.86
		ROOT BALL	7.83	57.06	23.26	11.85
	T12	LEAVES	8.96	66.75	14.24	10.08
		TWIGS	8.05	70.88	7.67	13.42
		WOOD	8.20	66.79	8.61	16.42
		ROOTS	6.49	55.65	26.87	11.00
		ROOT BALL	8.38	61.50	16.62	13.52
	S11	LEAVES	8.00	65.72	5.68	20.61
		TWIGS	7.44	68.11	3.93	20.54
		WOOD	7.72	70.02	2.50	19.77
		DB ^a	7.35	70.76	3.91	18.00
		ROOTS	8.17	67.75	2.67	21.44
	S12	LEAVES	8.49	65.02	5.87	20.62
		TWIGS	7.79	70.28	3.58	18.37
		WOOD	8.00	69.81	3.01	19.20
		DB ^a	8.66	68.36	5.21	17.78
		STUMP	7.49	71.37	2.02	19.13
		ROOTS	8.32	61.52	10.70	19.47
		ROOTBALL	7.55	62.63	10.22	19.62

a: Dry Biomass; TM: Total Moisture; VM: Volatile Matter; FC: Fixed Carbon.

Table 4-5: Physicochemical characteristics of selected blends and coal sample.

Sample ID (Ar)	CV (MJ/kg)	TM (%)	VM (%)	ASH (%)	FC (%)	C (%)	H (%)	N (%)	S (%)	O (%)
T1T3	16.09	8.26	68.96	8.18	14.61	40.92	5.91	0.43	0.96	35.36
S1S3	17.07	8.37	64.7	6.60	20.34	45.35	6.18	0.40	0.14	32.96
T4T6	16.64	8.45	63.90	8.98	18.69	42.39	5.8	0.99	0.81	32.58
S4S5	17.31	8.41	66.77	3.77	21.05	45.16	6.08	0.44	<0.1	36.04
T7T9	16.53	8.18	68.53	8.35	14.95	43.55	6.17	1.05	1.16	31.54
S7S8	17.27	8.35	66.45	3.94	21.28	45.73	6.2	0.46	<0.1	35.22
T11T12	16.26	8.37	68.52	7.48	15.64	43.16	6.38	0.99	1.31	32.31
S11S12	17.23	8.30	69.40	3.91	18.41	45.12	6.35	0.44	<0.1	35.78
Discard coal	16.73	2.06	20.17	41.95	35.83	48.90	2.67	1.15	1.34	1.93

Ar: As received; C: Total carbon; H: Hydrogen; N: Nitrogen; S: Total Sulfur and CV: Calorific value (MJ/kg); O: Oxygen by difference [100 - (M+Ash+S+H+C+N)]; Blend comprises of the tree compartments from both trees. E.g. S4S5 blend is made up of S4 (Twigs, DB and roots) and S5 (Twigs, wood, DB, stump and roots).

4.3. HYDROTHERMAL CARBONISATION

4.3.1. Influence of Temperature and Residence Time on Characteristics of Hydrochars

The HTC test was carried out on the blend of *Searsia lancea* S11 and S12, as this was the only blend with the quantity sufficient to produce hydrochars and pellets. Figure 4-1 depicts the results from the *Searsia lancea* thermally treated in a Berghof reactor at a temperature of 200 °C, 250 °C and 280 °C, pressurized with argon at 20 bar, and under residence time of 30, 60 and 90 minutes, respectively. The fixed carbon content of the raw biomass (18.41 %) increased to 25.51 % at 200 °C and 30 minutes and 50.33 % at 280 °C and same residence time. The increase in temperature was seen to correlate with an increase in fixed carbon and the biomass calorific value from 17.23 MJ/kg to 29.71 MJ/kg. For a 30-minute interval, the calorific value had a range of (17.23 – 20.27 MJ/kg) for 200 °C, (17.23 – 27.55 MJ/kg) for 250 °C and (17.23 – 28.97 MJ/kg) for 280 °C.

The fixed carbon content and calorific values were more pronounced with the increase in the residence time, also known as the degree of severity, of hydrothermally treated *Searsia lancea* at 200 °C and 250 °C. The changes in the energy characteristic and quality of the biomass is as result of the modification to the structure of the biomass utilized at high temperatures and pressure. The decomposition of the hydroxyl group along with the hemicellulose of the *Searsia lancea* is responsible for the increase observed in Figure 4-1, with the majority of the lignin remaining in the solid hydrochar. This result is in agreement with those reported by (Fakkaew *et al.*, 2015; Kambo and Dutta 2015 and Hoekman *et al.*, 2017).

A decrease was also noted in the moisture content of the hydrochars, as well as in the ash content of the products. The decrease noted in the ash content of the hydrochars could be as a result of the decomposition of the inorganic carbonates and oxides of minerals within the biomass into the liquid phase. Kambo and Dutta, (2015) reported that the formation of acetic acid in the liquid by-product stream of an HTC process, resulted in an acid solvation mechanism. This lead to the solubilization and leaching out of inorganic elemental compositions in the biomass, thereby reducing the overall ash content of the solid product, which is not possible in case of dry thermal pre-treatment processes (Kambo and Dutta, 2015). An investigation conducted by Saba *et al.* (2017) also reported a decrease in ash content by up to 71.87 % at 200 °C and 60 minutes. All of these results suggest that the

reaction time and temperature do have a positive effect on the quality of hydrochars with increased concentrated carbon materials at high heating values, and reduced ash content as seen in Figure 4-1.

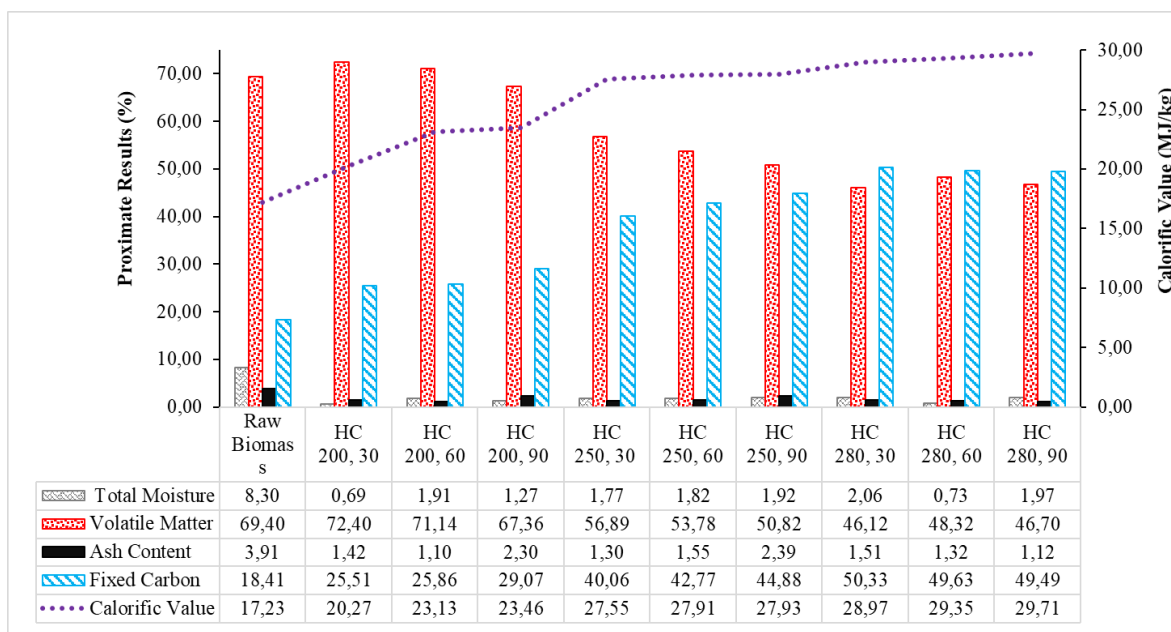


Figure 4-1: Physiochemical properties of hydrothermal hydrochars.

4.3.2. Influence of Temperature and Residence Time on Mass Yield of Hydrochars

The effect of temperature and residence time on the mass yield of hydrochars produced from raw *Searsia lancea* is depicted in Figure 4-2. The loss in sample weight is seen as the temperature increases, which was observed to be relatively fast within the first 30 minutes for all temperatures. At 200 °C, the lowest degradation and depolymerization of the hemicellulose content of the sample was observed, with a mass yield of 67.25 %. Increasing the temperature to 280 °C, lead to a further decrease in the mass yield to 35.61 %, with more hemicellulose being converted into chemical energy in the form of gases and high carbon solid residue. As observed in this study, there is a strong correlation between the weight loss and temperature. It decreases significantly with increase in temperature at each time interval. These results follow a similar pattern to study on thermal treatment of biomass as reported by (Hoekman *et al.*, 2013; Makwarela 2016 and Saba *et al.*, 2017). The decrease noted in the mass yield as observed in this study can be attributed to the decarboxylation and dehydration reactions, which resulted in the degradation of the

biomass functional groups (Reza *et al.*, 2014 and Saba *et al.*, 2017). As reported by Reza *et al.* (2014), the biomass functional groups are converted to an organic acid, thereby, lowering the pH of the reaction substrates and further breaking down of these structures to form a carbon and energy-dense material.

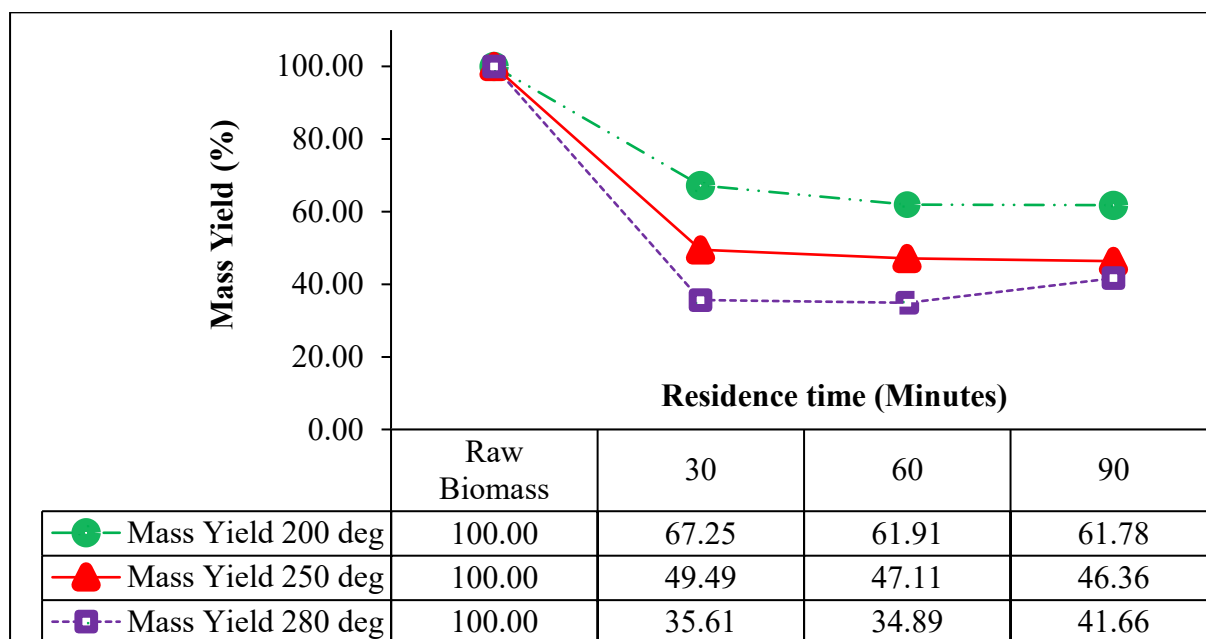


Figure 4-2: Mass yield profile of hydrothermal hydrochars at different temperatures and residence time.

4.4. REGRESSION AND STATISTICAL ANALYSIS

4.4.1. Regression Model Development

The CCD was used to develop polynomial regression equations, which measure the interactions between the process variables (temperature and residence time) and the identification of significant factors that contribute to the regression model. The experimental design, along with the experiment response values, is expressed in Table 4-6. The regression analysis was performed to fit the response functions of mass yield (%), ash content (%) and calorific value (MJ/kg). In addition, the regression models provide a mathematical framework for future analysis of the three responses. The empirical models in terms of the process variables for the hydrochar characteristics, mass yield, calorific value, and ash content are as follows:

$$\text{Mass yield (\%)} = 204.75 - 0.72T - 1.04t + 2.24 \times 10^{-3}Tt + 5.35 \times 10^{-4}T^2 + 4.01 \times 10^{-3}t^2 \quad (4-1)$$

$$\text{Calorific Value } \left(\frac{\text{MJ}}{\text{kg}}\right) = (-)36.05 + 0.38T + 0.19t - 5.54 \times 10^{-4}Tt - 5.45 \times 10^{-4}T^2 - 2.21 \times 10^{-4}t^2 \quad (4-2)$$

$$\text{Ash (\%)} = 32.96 - 0.24T - 0.91t + 6.35 \times 10^{-3}Tt + 4.61 \times 10^{-4}T^2 + 2.96 \times 10^{-3}t^2 - 1.12 \times 10^{-5}T^2t - 1.05 \times 10^{-5}Tt^2 \quad (4-3)$$

A positive symbol in front of the constant and/or the process factors indicates synergistic effect with the responses, whereas negative sign shows an opposing influence on the responses (Sahu *et al.*, 2010).

Table 4-6 shows the predicted values compared to the experimental values, which are the actual measured responses. There is a good correlation between the model predictions and the actual values as confirmed by the R^2 values of 0.9537, 0.9525 and 0.9789 for mass yield, CV and ash content respectively, indicating that the regression models provide a good fit.

Table 4-6: Experimental values vs Predicted values of the Experimental design responses.

Sample ID	EV	PV	EV	PV	EV	PV
	Mass Yield (%)		CV (MJ/kg)		Ash (%)	
HC _{200, 30}	67.25	68.18	20.27	20.78	1.42	1.42
HC _{200, 60}	61.91	61.24	23.13	22.42	1.10	1.09
HC _{200, 90}	61.78	61.52	23.46	23.66	2.30	2.30
HC _{250, 30}	49.49	47.61	25.55	26.84	1.30	1.29
HC _{250, 60}	47.11	44.03	27.91	27.65	1.55	1.54
HC _{250, 90}	46.36	47.66	27.93	28.06	2.39	2.38
HC _{280, 30}	35.61	36.56	28.97	29.17	1.51	1.52
HC _{280, 60}	34.89	34.98	29.35	29.48	1.32	1.31
HC _{280, 90}	41.66	40.62	29.71	29.39	1.12	1.13

HC: Hydrothermal carbonization; EV: Experimental value; PV: Predicted value; CV: Calorific value.

Figure 4-3 is a visual representation of Equations 4-1 to 4-3. Figure 4-3(a), (b) and (c), which shows the 3D surface response plots of the combined effect of temperature and residence time on the mass yield, calorific value, and ash content of the hydrochars produced, respectively. The response surface plots were used to illustrate the effect of changing reaction temperature and residence time on the responses. 3D plot is also used to check model accuracy (Bezener, 2015). As Fig. 4-3 reveals, the curve tends to fit well with the design points which are the actual observed points. None of the design points are seen to be far above or below the surface curve, showing the model's accuracy. The singular model term (T) had the greatest effect on mass yield while calorific value was influenced by both (T) and (t). The interaction model term (Tt) and time (t) had an influence on the ash content.

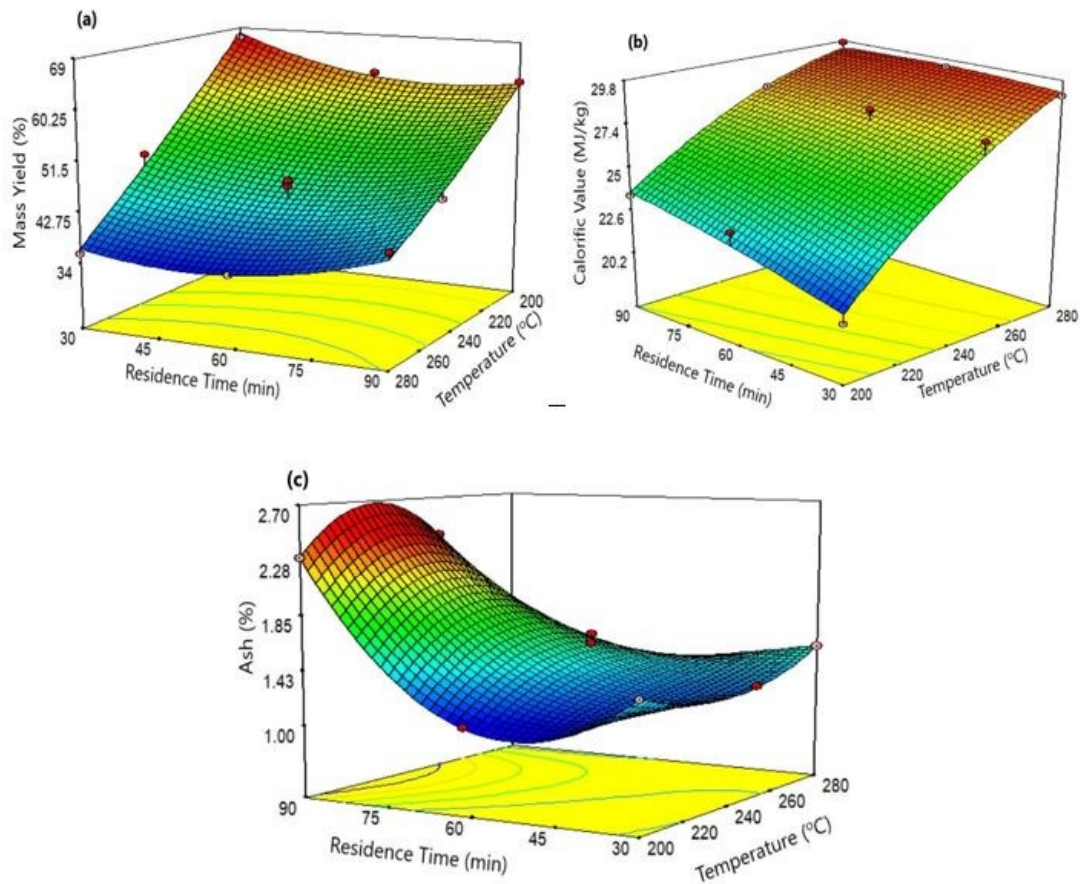


Figure 4-3: Combined effect of temperature and residence time on fuel characteristics of the produced hydrochars (a) Mass yield (b) Calorific value (c) Ash content.

4.4.2. Statistical Analysis

The analysis of variance (ANOVA) is performed to demonstrate the suitability of the model developed for each response. The ANOVA for the quadratic models of mass yield, calorific value and ash content are shown in Tables 4-7, 4-8 and 4-9. The values of "Prob > F" below 0.05 indicate that the model terms are significant (Zhao *et al.*, 2011). In the case of mass yields as can be seen in Table 4-7, T is the only significant model term. For the calorific value (Table 4-8), T, and t, are the significant model terms, while the t, Tt, T², t², T²t, and Tt² are all significant model terms for the ash content as seen in Table 4-9. Also assessed is the suitability of the model equations with correlation coefficients (R²), which are 0.9537 for the mass yield model equation, 0.9525 for calorific value and 0.9789 for the ash content model equation. The closer the R² value is to 1, the more fitting is the model equation. The R² values for mass yield, calorific values, and ash content are relatively high, which suggests good agreement between experimental data and the model prediction. The R² value obtained from the calorific value in this study was found to be higher than the 0.50 and 0.8197 reported by Danso-Boateng, (2015) and Sabio *et al.* (2016), respectively for the same property. Checking the model's suitability is a key aspect of the data analysis process because if the fit is unsatisfactory, it could lead to poor or misleading results (Körbahti and Rauf, 2009).

Table 4-7: ANOVA for response surface quadratic model of mass yield.

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	R ²
Model	1197.11	5	239.42	28.82	0.0002	0.9537
T	1034.38	1	1034.38	124.50	< 0.0001	
t	2.50	1	2.50	0.30	0.6005	
Tt	29.36	1	29.36	3.53	0.1022	
T ²	1.73	1	1.73	0.21	0.6623	
t ²	35.98	1	35.98	4.33	0.0760	
Residual	58.16	7	8.31			
Lack of Fit	8.63	3	2.88	0.23	0.8698	
Pure Error	49.52	4	12.38			
Cor, Total	1255.27	12				

Df - degree of freedom; Prob. – Probability; T: Temperature; t: time

Table 4-8: ANOVA for response surface quadratic model of calorific value.

Source	Sum of Squares	df	Mean Square	F Value	Prob. > F	R ²
Model	89.88	5	17.98	28.08	0.0002	0.9525
T	74.69	1	74.69	116.69	< 0.0001	
t	3.56	1	3.56	5.55	0.0506	
Tt	1.80	1	1.80	2.82	0.1371	
T ²	1.79	1	1.79	2.80	0.1382	
t ²	0.11	1	0.11	0.17	0.6915	
Residual	4.48	7	0.64			
Lack of Fit	1.55	3	0.52	0.71	0.5955	
Pure Error	2.93	4	0.73			
Cor. Total	94.36	12				

Df - degree of freedom; Prob. – Probability; T: Temperature; t: time.

Table 4-9: ANOVA for response surface reduced quadratic model for ash content.

Source	Sum of Squares	df	Mean Square	F-Value	Prob. > F	R ²
Model	1.79	7	0.26	33.20	0.0007	0.9789
T	0.02	1	0.02	3.09	0.1392	
t	0.74	1	0.74	95.61	0.0002	
Tt	0.40	1	0.40	52.36	0.0008	
T ²	0.26	1	0.26	33.97	0.0021	
t ²	0.41	1	0.41	52.81	0.0008	
T ² t	0.33	1	0.33	42.72	0.0013	
Tt ²	0.20	1	0.20	25.72	0.0039	
Residual	0.04	5	0.01			
Lack of Fit	0.00	1	0.00	0.04	0.8436	
Pure Error	0.04	4	0.01			
Cor. Total	1.83	12				

Df - degree of freedom; Prob. – Probability; T: Temperature; t: time.

4.4. COMBUSTION CHARACTERISTICS

4.5.1. Combustion Profiles of Coal, Raw *Searsia lancea* and Hydrochars

The thermographs presented in Figure 4-4, show the profiles for the raw *Searsia lancea*, discard coal and hydrochars produced at 200 °C, 250 °C, and 280 °C and residence time of 90 minutes. The DTG and TG plots show that the raw *Searsia lancea* has the lowest ignition temperature compared to other fuels. The same sample also reaches its peak temperature at 308.11 °C compared to hydrochar produced at 200 °C with a peak temperature of 310.50 °C, but higher reactivity. Liu *et al.* (2016) noticed a similar trend in their study and wrote that the combustion behaviour of raw biomass feedstocks displayed multiple peaks during combustion which is evidence of disconnected devolatilisation. The

authors further noted that this was due to presence of high volatile matter thus subjecting the raw biomass to increased pollutant emissions.

The higher reactivity noted for the hydrochar produced at 200 °C after the initiation of the fixed carbon (IT_{FC}) might be as a result of the increase in its fixed carbon from 18.41 % to 29.07 %. Both samples were seen with two distinguishable peaks, showing the hemicellulose and lignin functional groups within the biomass. The hydrochar produced at a temperature of 250 °C was also seen with two peaks, but much lower hemicellulose, while the one produced at 280 °C, was seen with a single peak, which indicates a complete degradation in its hemicellulose content and increases lignin content. The hydrochar produced at 280 °C was seen with the highest burnout temperature of all the biomass samples and possesses the largest area covered under the peak, as a result of its increase in carbon content. The area covered under the peak can be denoted to be proportional to the total heat released by the fuel, which could be related to the heat content or calorific value of the fuel. The discard coal was found with the highest burnout temperature of 825 °C, and about 41.95 % ash residue, followed by the raw *Searsia lancea* with about 3.91 % ash residue. The decrease in the percentage ash content or non-combustibles in the hydrochar produced is because of the inorganic minerals in the biomass reporting to the water phase, rather than the solid. Moreover, the high ash content in the raw biomass denotes a large presence of alkali and alkali earth metals presence indicating that a likelihood for slagging and fouling does exist.

Another phenomenon that was noticed was an increase in the burnout temperatures of the products (HC_{200} , HC_{250} and HC_{280}) significantly compared to the raw biomass which would make the products more suitable as fuel in boilers than their raw counterparts when compared to the discard coal. The same outcome was discovered by (Smith *et al.*, 2018; Yeoh *et al.*, 2018).

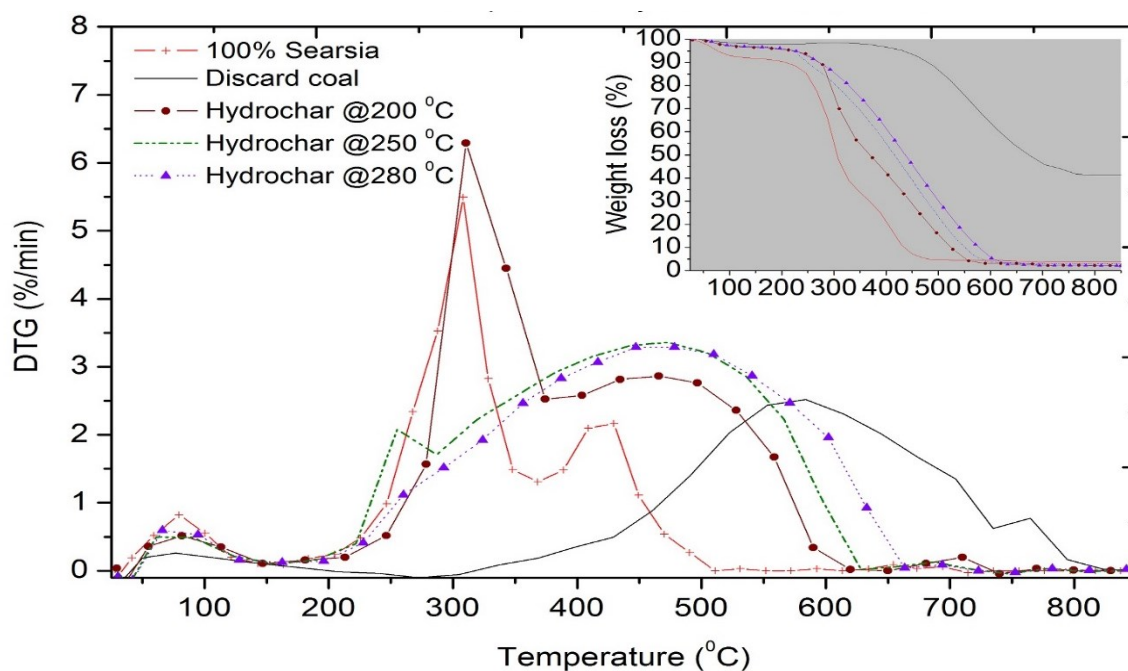


Figure 4-4. DTG curves for the combustion of raw *Searsia lancea*, coal and hydrochars.

4.5.2. Combustion Profiles of Coal, Raw *Searsia lancea* and Hydrochars

The DTG curves obtained from the reactivity test conducted on the raw *Searsia lancea*, discard coal and hydrochars produced at 280 °C and at different residence times are depicted in Figure 4-5. The DTG shows the different decomposition stages and a breakdown in the sample's functional groups (hemicellulose, cellulose, and lignin) as the hydrothermal temperature increases. The raw *Searsia lancea* was found with the highest peak, i.e., highest reactivity, and two pronounced shoulders denoting its hemicellulose and lignin content. The derivative curves for the hydrochars produced at 280 °C and the residence time of 30 and 60 minutes were seen with smaller peaks compared to that of the raw *Searsia lancea*. This shows a reduction and degradation in the hemicellulose and cellulose content of the hydrochars produced at a holding time of 30 and 60 minutes. With the increase in the holding time to 90 minutes, the hydrochar produced was seen with a single peak, predominantly lignin, with a similar profile to that of coal, but with lower burnout temperature. From the TG curve in the same figure, the raw *Searsia lancea* was seen with the highest composition of non-combustible matters compared to the other biomass fuels.

Here it can be noted that when temperature is held constant increasing residence time affects the number and height of peaks as well as burnout temperature in the combustion

profiles but not to the extent as when temperature is varied. This shows that temperature has more effect on combustion properties than residence time.

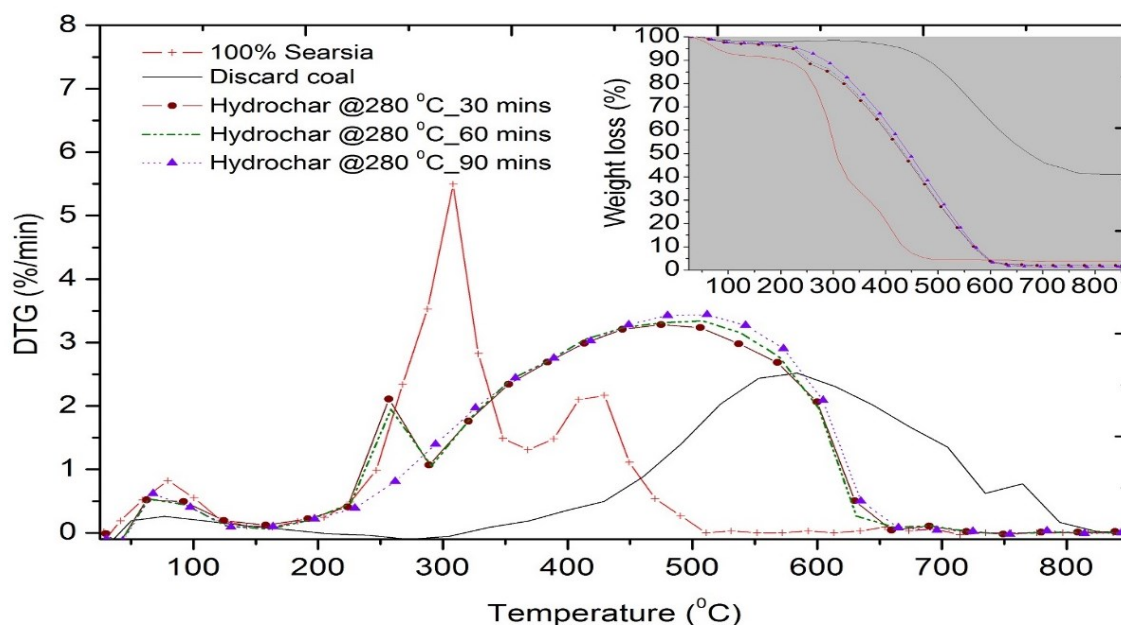


Figure 4-5. DTG curves for the combustion of raw *Searsia lancea*, coal and hydrochars produced at 280 °C.

4.5.3. Combustion Profiles of Pellets

The combustion profiles of the hydrochar pellet produced at 280 °C and residence time of 90 minutes, along with pellets produced from the blend of coal and hydrochar at different weight percentage ratios are presented in figure 4-6. The raw *Searsia lancea* pellet has the lowest ignition temperature, followed by the hydrochar pellet produced at 280 °C and holding time of 90 minutes. It was observed from the DTG profile as the percentage coal in the blend increases, the ignition temperature of the samples moves to a higher temperature region. The BC₂₅ HC/75 C (25 wt. % hydrochar + 75 wt. %) discard coal pellet was seen to be more compatible to the discard coal pellet, in terms of combustion reactivity and similar burnout temperature. The burnout temperature of the discard coal used was reduced with the addition of hydrochar. The weight loss curve (TG) shows an increase in the sample's weight loss as the percentage ratio of coal in the blend decreases for all samples, and the hydrochar pellet has the lowest non-combustible residue. In summary, it will be noted that the combustion efficiency of a high ash discard coal can be improved

by pelletizing it with biomass, and the blend or pellet with the higher coal indicates close compatibility.

Liu *et al.* (2016) reported that the burning profile of pellets containing hydrochar displays a heightened thermal conversion efficiency thus leading to a reduction in emissions. Moreover, due to their higher energy density, the pellets display a more continuous burning profile leading to flame stability necessary in boiler efficiency (Smith *et al.*, 2018). This proves that a mixture of hydrochar and discard coal would work well if not more as a fuel source in boilers as coal.

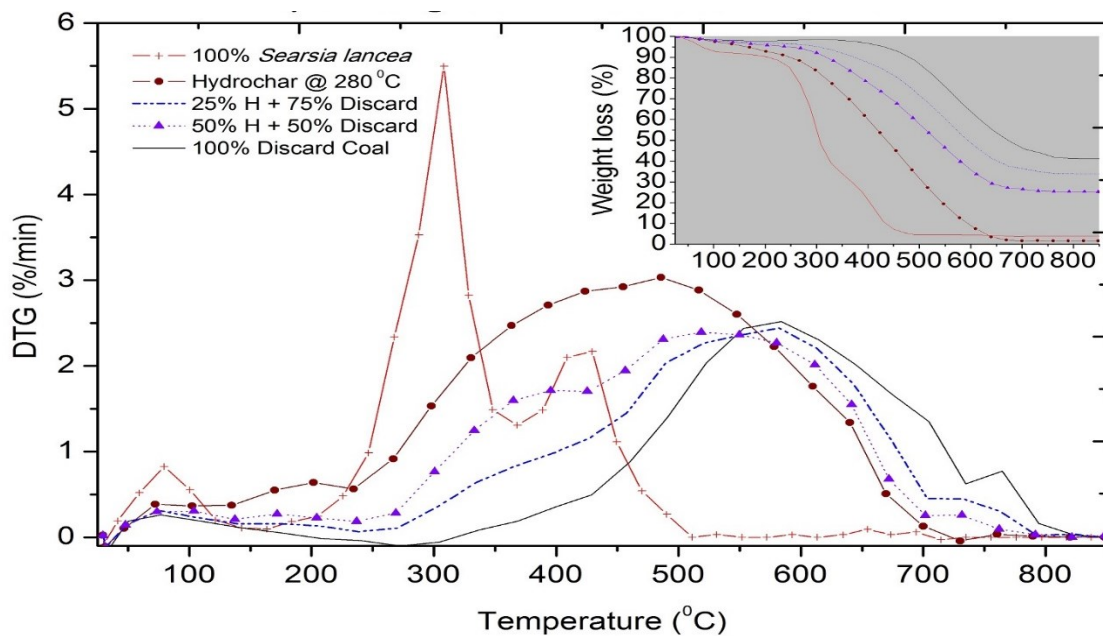


Figure 4-6. DTG curves for the combustion of raw *Searsia lancea*, hydrochars and hydrochar coal pellets.

4.6. ASH CHARACTERISATION

Phytoremediation biomass from acid mine drainage and polluted land can be expected to contain elevated concentrations of contaminants. In this case, the raw *S. lancea* biomass utilised for the hydrochar products was known to contain higher than average levels of sulphur and metals in tree biomass (Joubert, 2018). The concentrations of major and trace elements in the raw biomass, hydrochar, discard coal and biocoal pellets at different weight percentages are depicted in Figure 4-7 and 4-8, respectively. The biocoal (BC) is a blend of hydrochar and discard coal (C). Calcium is the most abundant element in all the

samples analysed in the raw biomass and hydrochar. The high concentration of Al obtained from the coal is expected, along with the increase as seen in the biocoal pellets made from the blends of discard coal and hydrochar. The concentration of Ca and P are higher in the ash content of the hydrochar, and this trend is similar to the result obtained by (Poerschmann *et al.*, 2014). The concentrations of the plant macronutrients P, S, Ca, K and Mg in the hydrochar are within the range for blending into fertiliser compounds. The concentrations of the plant micronutrients Fe, Cu, Co, Ni, Mn and Zn are elevated, but well within physiological norms for soil and blending in fertilisers. Mercury (Hg) was below detection limits and the contaminants of concern As, Cd, Cr, Pb and U were within regulatory guidelines and below plant toxicity levels, although V was in excess. Repeated application on land of such ash could lead to elevated concentrations of potentially toxic elements in produce. Similar results were conducted by Poerschmann *et al.* (2014) for the dissolved organic matter phases from hydrothermal carbonisation products.

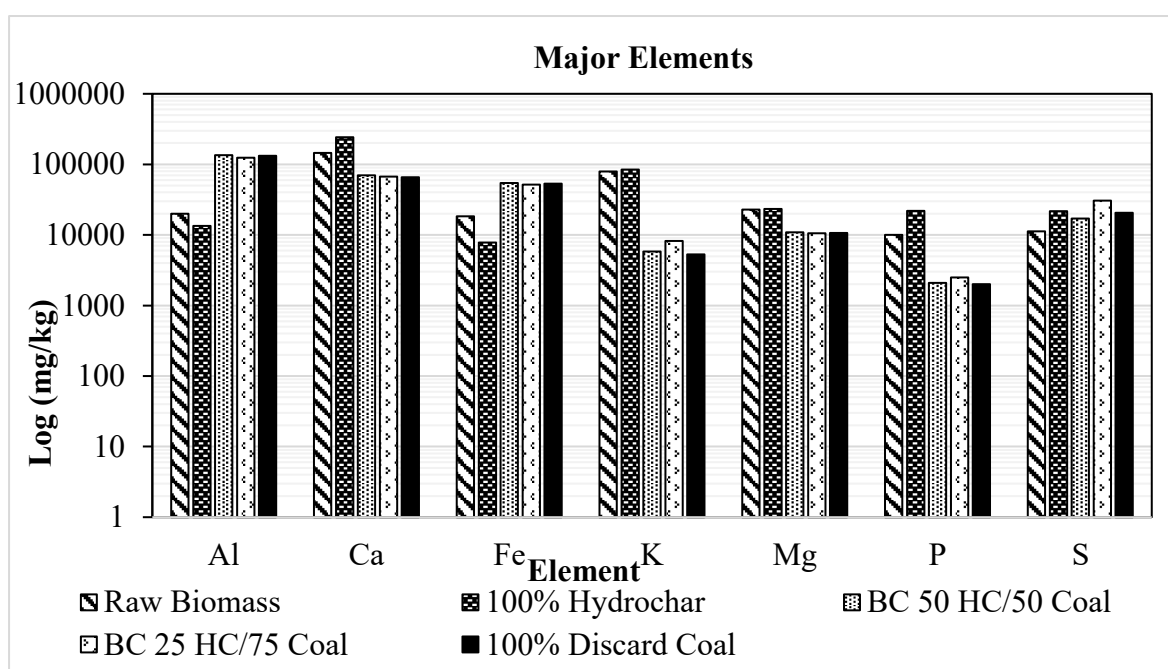


Figure 4-7. Concentrations of major elements in the ash of raw biomass, hydrochar, coal and HTC biocoals.

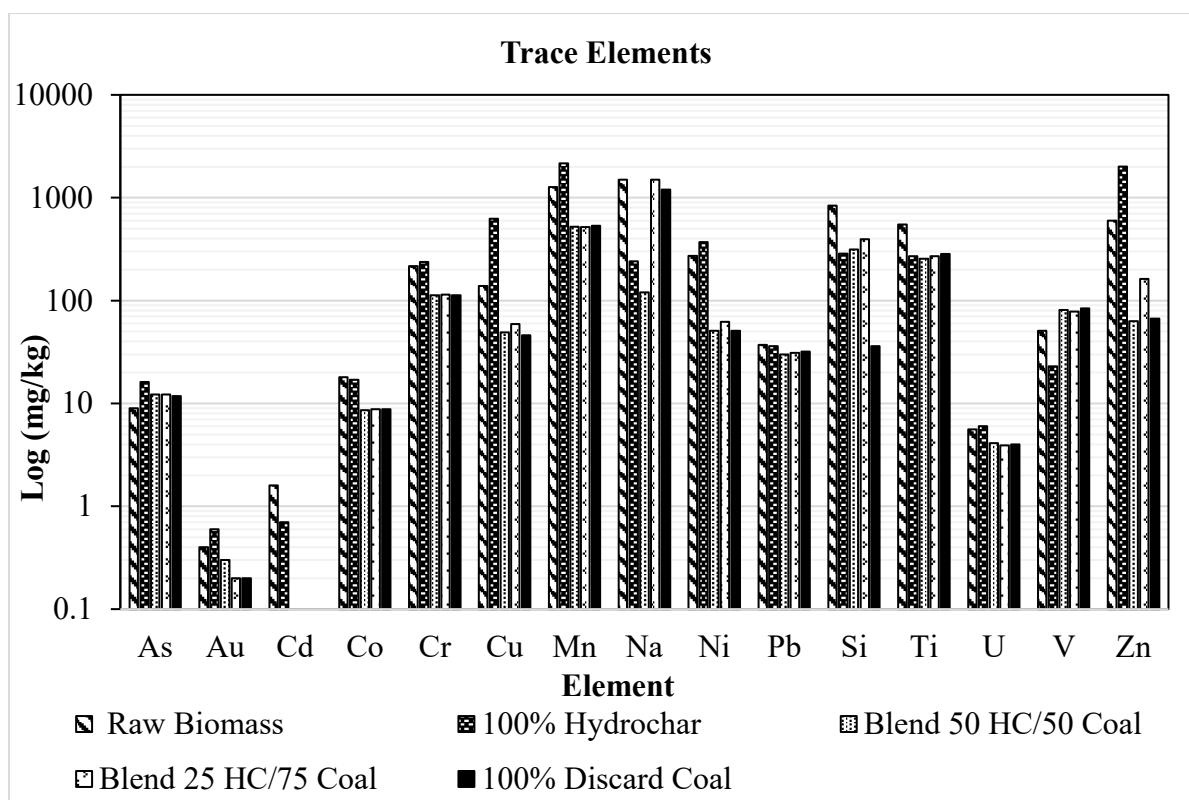


Figure 4-8. Concentrations of trace elements in the raw biomass, hydrochar, coal and HTC biocoals.

Table 4-10: Ash results for heavy element limits results for different applications (Fuller *et al.*, 2015).

Country	Finland	Finland	Germany
Use	Forestry	Agriculture	Fertiliser
Maximum metal content (mg/kg)			
As	30	25	40
Cd	17.5	1.5	1.5
Cu	700	600	-
Hg	1.0	1.0	1.0
Mn	-	-	-
Ni	150	100	80
Pb	150	100	150
Zn	4500	1500	-
Co	-	-	-
Cr	300	300	-

The increase noted in some elements within the ash obtained from the hydrochar might be as result of the decomposition of minerals at high temperature during ashing. The blending of coal with this biomass has led to the reduction in most of the trace elements in the species and thereby provide an opportunity for its potential applications in other sectors. As a general guide to the suitability of the ash for different agronomic applications, the elemental concentrations of these ashes were compared to those of biomass fly ash as summarised by Fuller *et al.* (2015) in a survey of the compliance limits for plant macro and micronutrients and non-nutrients in ash. Most of the elements within the ash produced from the *S. lancea* biomass and coal utilized are within the European compliance maximum metal concentrations for fertiliser and application to agricultural or forestry land. However different limits may be relevant to the southern African soils, climate and social setting when using ash from biomass produced on acid mine drainage.

Table 4-10 presents the acceptable levels of heavy metal compositions in ash for different applications. As can be seen in (Figure 4-8), most of the samples depicted in this table have trace elements that are below the reported disposal concentration from this study, and thus will be safe for disposal or to be used in the three above-mentioned applications. Cr, Pb, Hg, Zn, and Cd (except in raw biomass for the agriculture and fertiliser industries) all have element compositions that are below the maximum metal content across the three sectors. For Cu, all the reported results are below the maximum allowable metal content except 100 wt. % hydrochar (Figure 4.8), which meets the forestry limits but exceeds those of agriculture by 25 mg/kg. Ash content obtained from the 100 wt. % discard coal, BC₅₀ HC/50 C and BC₂₅ HC/75 C samples have Ni content that is below maximum metal contents for all the applications on this Table, while raw biomass and the 100 wt. % hydrochar concentrations exceed all and thus will require prior treatment to apply. Overall, the biocoals formed meet the disposal standards herein discussed.

4.7. HTC PROCESS WATER

4.7.1. Dissolved Organic Matter in the HTC Process Water

Water plays a significant role in the acceleration of hydrothermal processes in producing a carbonized biomass product (Danso-Boateng, 2015). Hot compressed water is known to act as a reaction medium with some polar solvent organic properties, and as a catalyst for creating organic compounds with a higher degree of ionization at higher temperatures

(Akiya and Savage, 2002; Kritzer, 2004). This leads to the hydrolysis, cleavage and ionic condensation of the biomass functional groups (Danso-Boateng, 2015). The amount of water contained in the biomass feedstock influences the product characteristics and distribution (Behar *et al.*, 2003).

In this study, the dissolved organic matter in the process water was determined using Shimadzu GCMS-2010. The different analytes present in the liquid residue from this test are presented in Figure 4-9, with hexadecenoic acid – 2,3 bis having the highest concentration followed by Tetradecane. These are aliphatic hydrocarbons which can only be extracted with super-heated water steam. It was reported in a study conducted by Köchermann *et al.* (2018) that the process water of HTC does contains large quantities of dissolved organic matter that mainly consists of organic acids (formic, acetic, lactic, and propionic acid), sugars (glucose, fructose, and xylose), furans (furfural and 5- HMF) and phenols (phenol, guaiacol, cresol, and catechol). Therefore, analysis of the process water confirms the study done by (Köchermann *et al.*, 2018). It is paramount that this water residue should be analysed before being discharged. The full list of all the compounds analysed for in the process water can be found in Appendix B (Table B2).

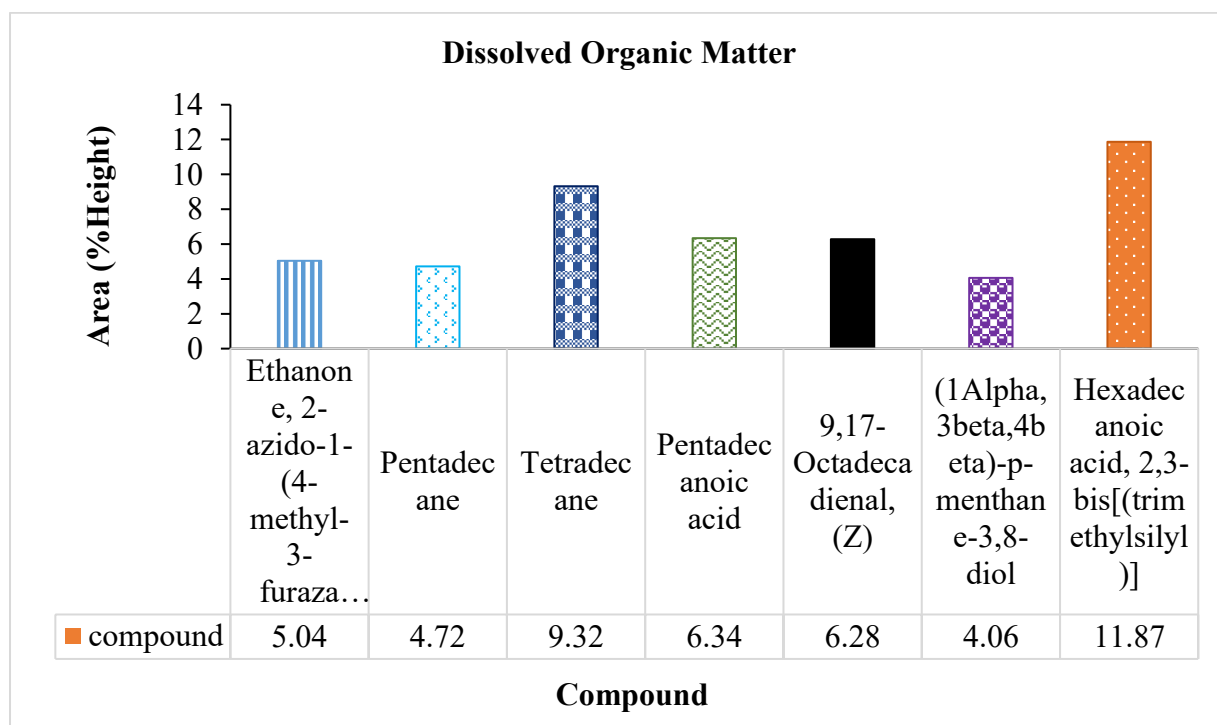


Figure 4-9: Dissolved organic matter in process water.

4.7.2. Dissolved Inorganic Matter in the HTC Process Water

The inorganic elements in biomass or any solid fuel can be classified as, major or trace elements. The analysis of these constituents, in terms of the percentage composition of the elements in the wastewater provides an insight into the treatment method and the method of disposing the water. The results of the major elements are presented in Figure 4-10. Calcium is noted as the most abundant element at 671.60 mg/l followed by potassium at 416.06 mg/l and magnesium at 104.00 mg/l. Sulphur is present at only 43.00 mg/l, with no Fe and Na detected, this indicates that all the Fe and Na might have been retained in the hydrochar.

The most abundant inorganic elements in the process water were calcium (Ca) > potassium (K) > magnesium (Mg) > sulphur (S). Sodium (Na), Iron (Fe), titanium (Ti) and mercury (Hg) were not detectable. Mercury levels were negligible to non-detectable in the raw tree biomass whereas Na and Fe were present at trace levels (Joubert, 2018; Dye and Weiersbye, 2020). This indicates that all the Fe and Na might have been retained in the hydrochar. Contaminants of concern in the process water are copper (Cu), chromium (Cr), cobalt (Co), cadmium (Cd), arsenic (As), vanadium (V), nickel (Ni), zinc (Zn), lead (Pb) and uranium (U), all present at concentrations which approach or exceed the legal limits for discharge to fresh waterbodies. The gold (Au) concentration of 1.89 ug/l is slightly below the level considered economically viable for recovery from wastes (>2 g/ton).

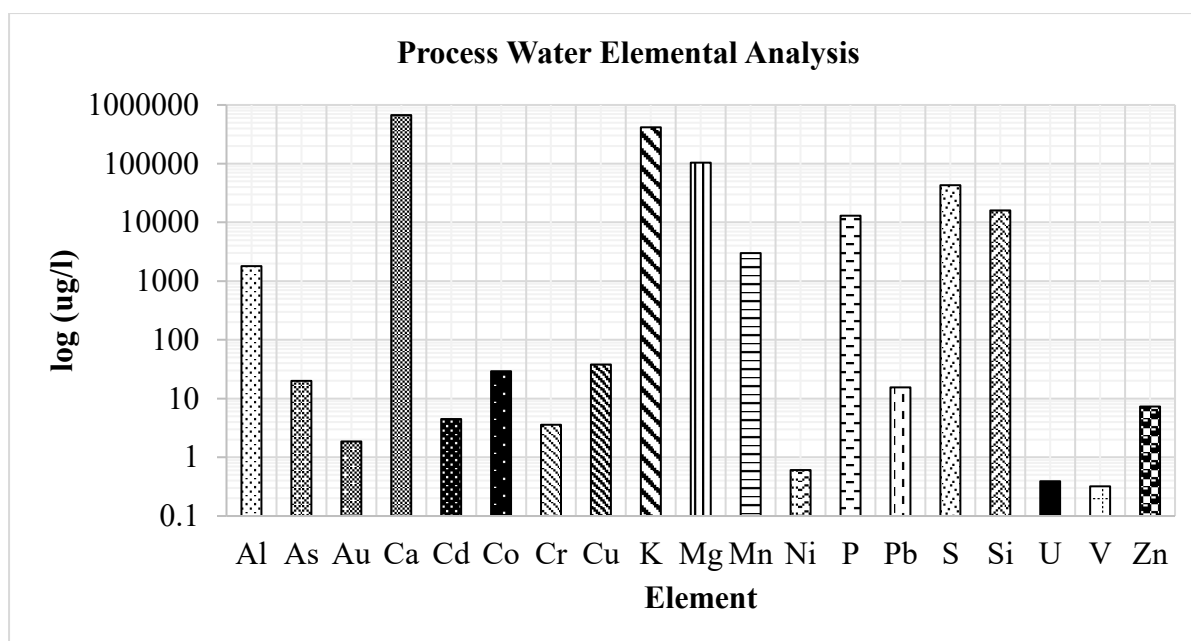


Figure 4-10: Process Water Elemental Analysis.

4.8. MECHANICAL PROPERTIES

4.8.1. Effect of Hydrochar Inclusion on Compression Strength of Pellets

Figure 4-11 shows the results obtained from the compression strength test carried out on the pellets made from the 100 wt. % discard coal, biocoal and 100 wt. % hydrochar. The compression strength denotes the measure of the maximum strength a pellet can withstand before shattering or disintegrating, as well as provide an insight to the degree of internal bonding strength created between the hydrochar and the coal. The hydrochar produced at 280 °C, residence time of 90 minutes and biomass-to-water ratio of 1:8 was utilized. Pellets of 2 g were produced from each sample using a 20 mm die, with more (volume) required in producing a 2 g 100 wt. % hydrochar, compared to other samples. From all the 2 g weighted samples, the BC₂₅HC/75 C was seen with the highest compressive strength of 3.06 MPa and the BC₅₀HC/50 C followed with the strength of 2.67 MPa. The 100 wt. % hydrochar was found with the lowest compressive strength, this shows that the high composition of lignin, noted as a natural binder during pelletization and its interaction with coal particles resulted in the strength noted in BC₂₅HC/75 C sample. From this result, it could be seen that all the samples tested do meet the compressive strength standard required for pellet storage and handling.

In terms of the compressive strength obtained from pellets produced using the same sample volume (measured), the BC₂₅HC/75 C sample still possesses the highest strength.

The 100 wt. % hydrochar was seen with a higher compressive strength than both the 100 wt. % discard coal and BC₅₀ HC/50 C, the variation in the trend noted might be as a result of the increase in the mass and thickness of the 100 wt. % hydrochar to withstand more crushing load. On a pellet-to-pellet basis, however, the 2 g pellets outperformed the volume “measured” pellets. All the pellets exceeded the standard industry coal compressive strength of 0.38 MPa as reported by (Kaliyan and Vance Morey, 2009). The findings in this work however were much lower than those reported by Gaqa and Watts (2018) ranging from (4.90 MPa – 24.13 MPa). These variations maybe due to a variety of factures such as the method used in testing the compressive strength, crushing load, material used, material composition, moisture content of the starting materials amongst other variables.

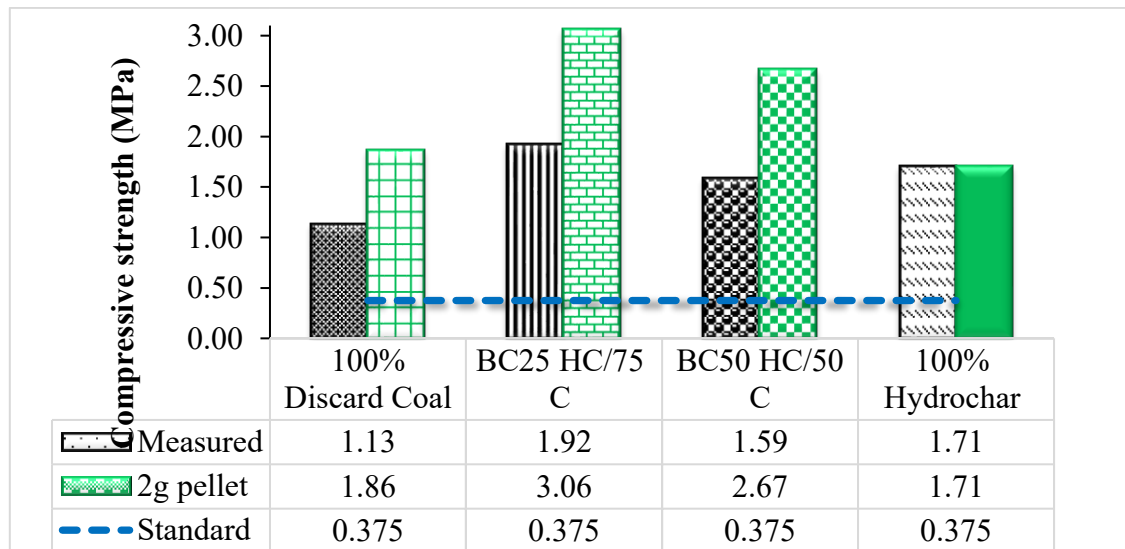


Figure 4-11: Effect of hydrochar inclusion on the compression strength of pellets.

4.8.2. Effect of Hydrochar Inclusion on Impact Resistance of Pellets

The drop durability test conducted in this study utilizes a similar method to that used by (Kambo and Dutta, 2014). The samples were all dropped at a height of 1.0 m onto a steel plate and the impact resistance index (IRI) determined using equation 3-2, outlined in chapter 3. The impact resistance durability (IRD) of the 100 wt. % hydrochar pellet was 98.03 % and increased relatively by 0.32 for the BC₂₅ HC/75 C pellet. This shows that the impact resistance for the BC₂₅ HC/75 C pellet still has a slight durability over all the samples tested. Despite the similarity in the durability of the samples, all the samples meet the acceptable standard for pellet storage and handling.

Kambo and Dutta, (2014) investigated the effect of temperature on durability and stated that raw miscanthus pellets had an IR index of 92.2 %, and the value increased as the HTC reaction temperature increased from 190 to 225 °C. Gaqa and Watts, (2018) on the other hand, investigated how moisture content affected the impact resistance of pellets. The authors observed that pellets with the lower moisture content had a better impact resistance than those with higher moisture content. This research however investigated how hydrochar inclusion affects impact resistance and further research into the outcome will be necessary.

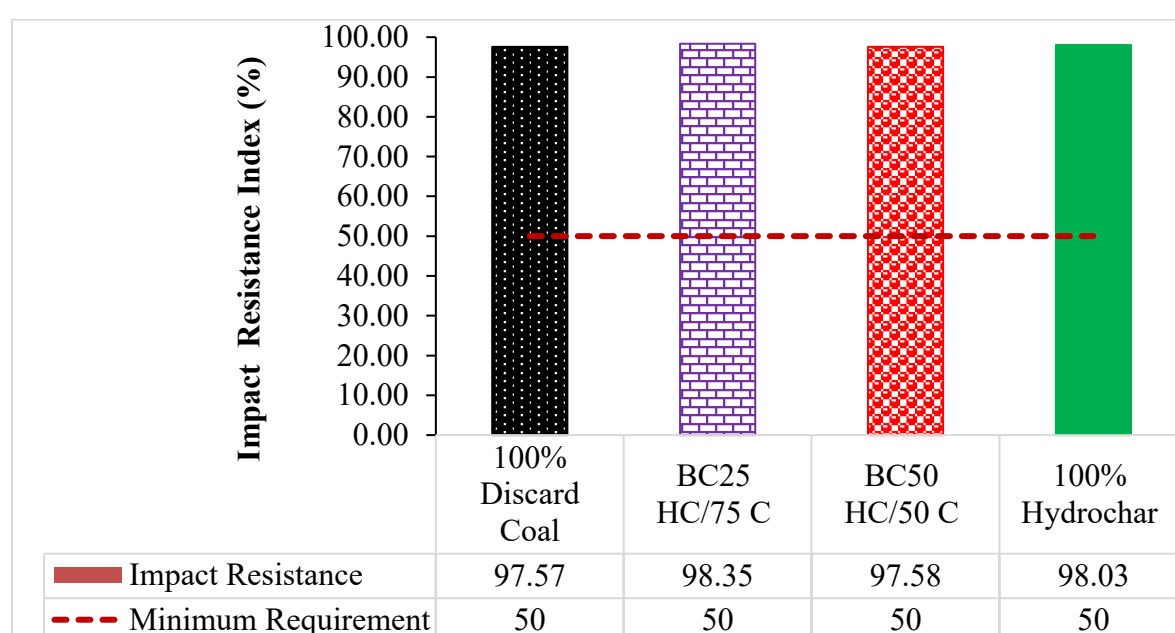


Figure 4-12: Effect of hydrochar inclusion on the impact resistance of pellets.

4.8.3. Effect of Hydrochar Inclusion on Moisture Resistance of Pellets

The amount of water absorbed by the pellets after immersion in water for 30 minutes ranged from 11.13 moisture % to 31.53 moisture % as seen in Figure 4-13. All the samples did not meet the water-resistance index (WRI) standard of 95 % after 30 minute submersion according to (Richards, 1990). The WRI is proportional to the moisture uptake in that a pellet that absorbs the least amount of water will have a higher WRI than its counterparts. However, the BC₂₅ HC/75 C absorbed the least amount of water at 11.13 moisture % and by extension had the highest WRI of 88.87 %. It was also observed in this

study that although the 100 wt. % discard coal pellets absorbed less water than the 100 wt. % hydrochar, it disintegrated to a certain level while the 100 wt. % hydrochar appeared to have grown. This is an interesting phenomenon in how hydrochar and discard coal are different in their interaction with water.

Hoekman et al. (2014) reported that torrefied pellets formed at temperatures below 200 °C swelled and were less durable, while those produced from HTC had highly stable, water-resistant pellets. However, the authors did not report exact figures in terms of percentages. Shuma (2018) and Gaqa and Watts (2018) all reported that none of their pellets survived the 30-minute submersion test. This calls for further research on improving the quality of the pellets to ensure its stability in contact with excess moisture. Fosnacht et al. (2018) reported that higher percentage inclusions of hydrochar led to briquettes becoming more moisture resistant however, an opposite effect was observed in this research.

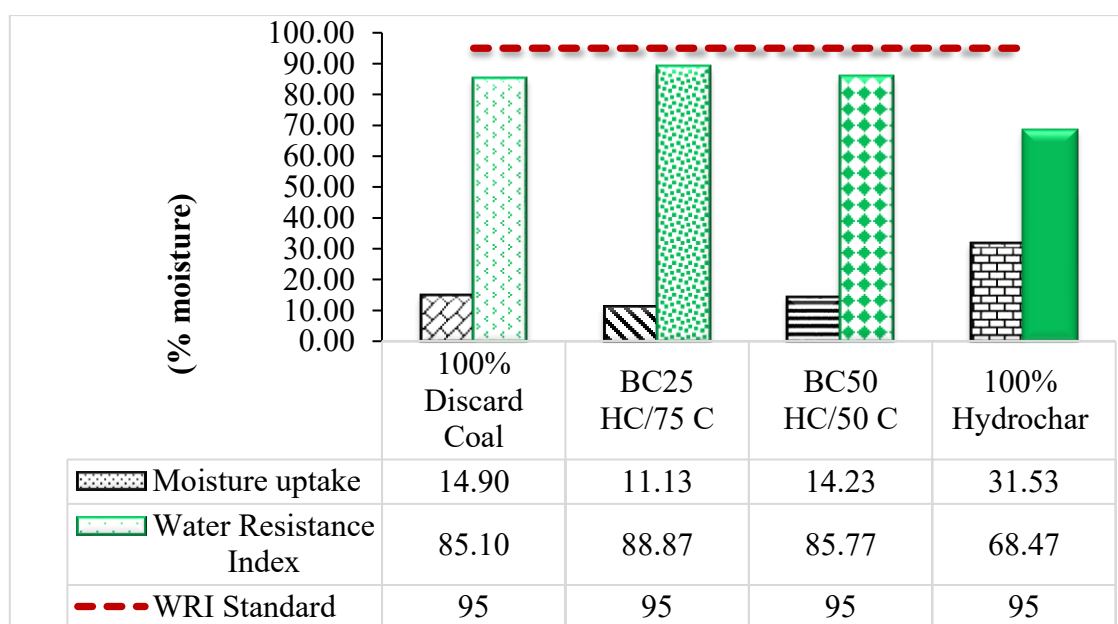


Figure 4-13: Effect of hydrochar inclusion on the water resistance index of pellets.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1. OVERVIEW

The increase in human population will inevitably require increasing the energy output, which will necessitate more resources such as fossil fuels and biomass to be added to the world's total energy mix. The current global energy landscape including that of South Africa is still largely dependent on fossil fuels, accounting for 78.4 % of total energy resources making them the most widely used resources for energy production. The overwhelming dominance of coal might seem impossible to break as coal is not only a relatively cheap source for energy production but also a key economic driver. However, its mining, production, and subsequent use as a fuel in power plants has had and continues to have significant environmental and health effects. One of the by-products formed in the coal processing industry is the discard coal generated in the country from the washing plants, and from the fines generated during mining or screening, which are disposed of as the ultra-fines in the slurry ponds. These resources are considered uneconomical, environmentally hazardous, and difficult to process. In addition, the handling, storage, and disposal operations of these coal-fines present significant and unproductive expenses to the mining industry.

Biomass waste, particularly from trees used in the treatment of acid mine drainage in most mines, is readily available and abundant. The conversions of lignocellulosic biomass into carbonaceous solids of high value through HTC have received quite a broad interest worldwide. HTC can be used on different biomass resources such as those from agriculture, forestry, industrial and municipal solid waste with the aid of reducing environmental pollution and creating feedstock for thermal energy. With the application of thermal pre-treatment processes such as HTC coupled with densification, the environmental challenges posed by these trees can be minimized.

The aim of this research study was to produce a renewable solid fuel blend of hydrochar from raw biomass obtained via HTC and South African discard coal fines. This was achieved by investigating the physicochemical, combustion and mechanical properties of raw biomass, hydrothermally carbonised and biocoal pellets to establish their potential as suitable fuel source in combustion boilers. Five specific objectives were outlined and followed successively to address the research questions in section 1.4. Response Surface Methodology was used for investigating temperature and time, which allows the optimised

processing conditions for hydrochar production to be recognised by considering the interactions between the different variables involved. This chapter presents the major findings of this research and provides recommendations for further study.

5.2. KEY FINDINGS OF THIS RESEARCH

I. Analysis of the physicochemical characteristics of the raw biomass and coal revealed the following:

- The physicochemical characterisation showed that *Tamarix usneoides* possess a high percentage of moisture and ash content (26.87 %), particularly in the leaves and bottom compartments of the trees tested (roots, rootball, and stump). The *Searsia lancea* had a superior fixed carbon content with lower ash content across all plant sections, with higher calorific value than *Tamarix usneoides*. Thus, the *Searsia lancea* was used for further analysis and as the raw biomass blend in producing the hydrochar.
- The discard coal reported the highest sulphur content of 1.34 % along with nitrogen (1.15 %), and a high ash content of 41.95 %.

II. Analysis of the physicochemical characteristics of hydrochar and biocoal resulted in the following:

- The ash content and volatile matter of the hydrochars produced showed a decreasing trend with an increase in temperature and residence time while fixed carbon increased significantly over the same conditions. The highest energy content of 29.71 MJ/kg was obtained at the HTC process conditions of 280 °C and residence temperature of 90 minutes.
- The regression equations developed in this study indicated that the values obtained experimentally agree with the predicted values from the models via correlation coefficients (R^2) which are given as 0.9537, 0.9525, 0.9789 for mass yield, calorific value, and ash content, respectively.
- The BC_{50 HC/ 50 C} (50 wt. % hydrochar + 50 wt. %) had better physicochemical properties than the BC_{25 HC/75 C} (25 wt. % hydrochar + 75 wt. %) pellets. However, BC_{25 HC/ 75 C} pellets were seen to be more compatible with the discard coal pellet, in terms of combustion reactivity

and similar burnout temperature as well as better mechanical properties (compressive strength and impact resistance).

III. The ash chemistry analysis on raw biomass, hydrochar, and biocoal pellets, along with the analysis of organic matter dissolved in process water revealed that:

- The samples contained both major and trace elements. The trace elements, nonetheless, met the disposal standards and can be used in the fertiliser, agriculture, and forestry applications as soil ameliorants.
- The process water contained both dissolved organic compounds, major and potentially toxic trace elements. Further clean up may be necessary to allow for safe disposal.

IV. The biocoals that were produced yielded fuel products of high calorific value than the discard coal and raw biomass, better physicochemical and mechanical properties therefore the results obtained in this research study supported the hypothesis.

5.3. RECOMMENDATIONS FOR FUTURE WORK

This section provides recommendations for further investigations. The suggestions are based on the findings and observations of this research. These are as follows:

- I. Investigate the effect of additional variables such as different feed particle size, pressure, water-to-biomass ratio and process water recirculation on the hydrochar quality.
- II. Investigate the impact of cold versus hot forming for pellets and impact on the mechanical stability of pellets.
- III. Testing the pellets in a domestic sized stove and comparison to be made on their flame stability.
- IV. A pilot-scale plant on HTC may be set up to determine the cost-benefit analysis of the systems.
- V. Investigate further value-added products including its marketability from the 100 wt. % hydrochar and biocoal pellets.

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APPENDICES

Appendix A: Figures

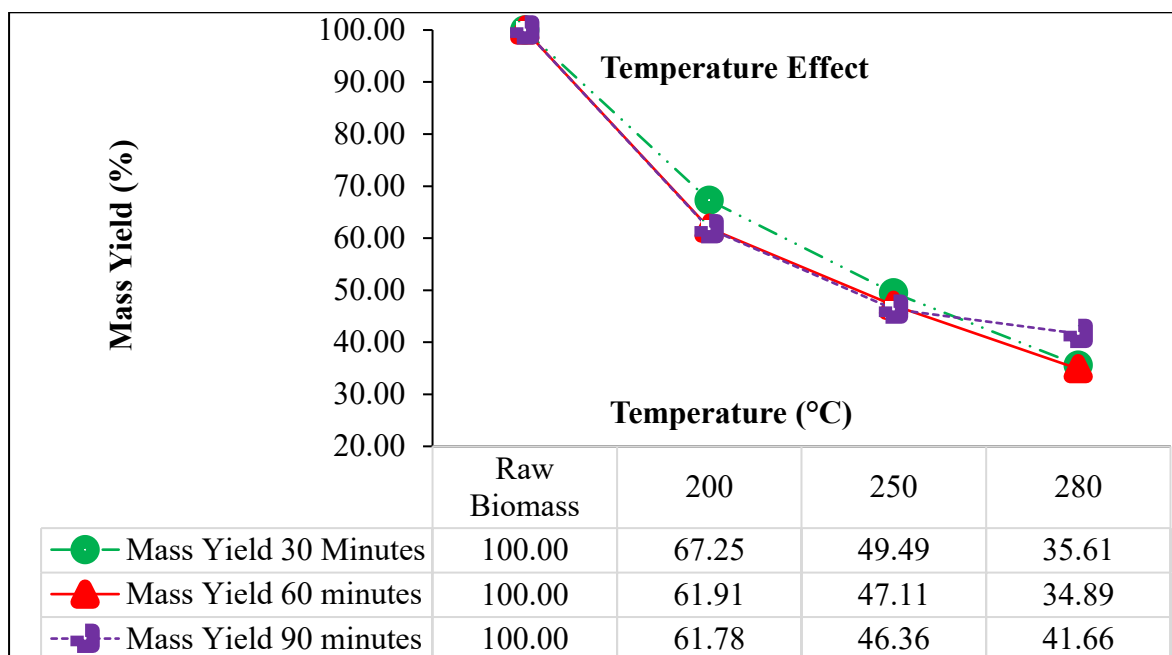


Figure A1: Individual effects of temperature on the mass yield of the produced hydrochars.

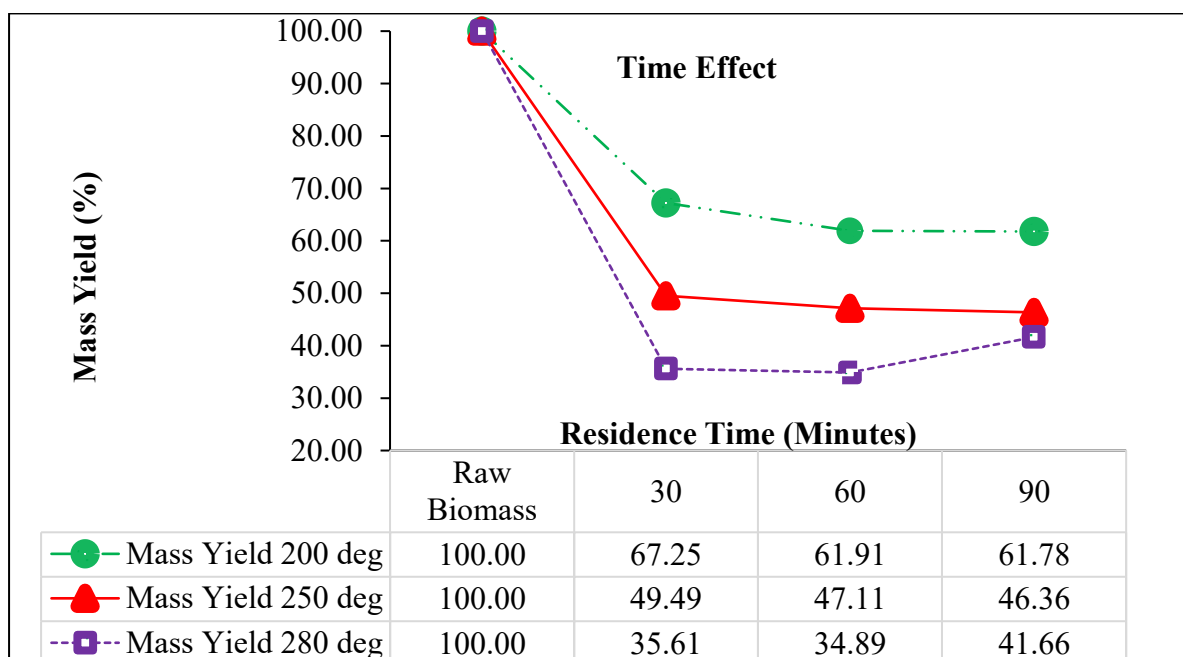


Figure A2: Individual effects of residence time on the mass yield of the produced hydrochars.

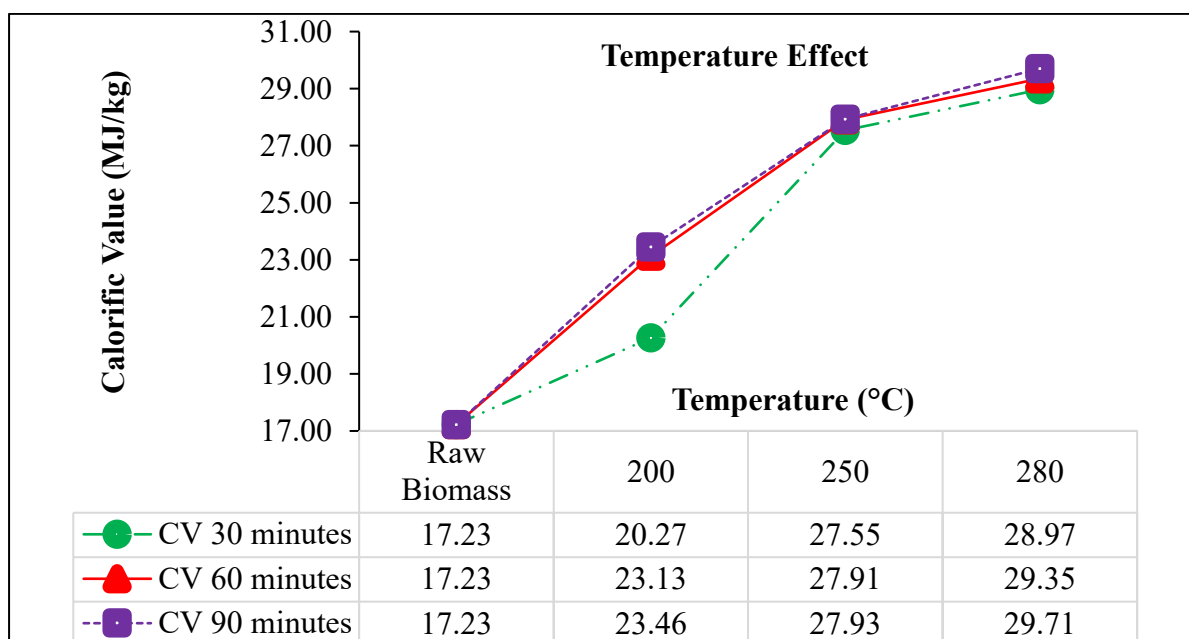


Figure A3: Individual effects of temperature on calorific values of the produced hydrochars.

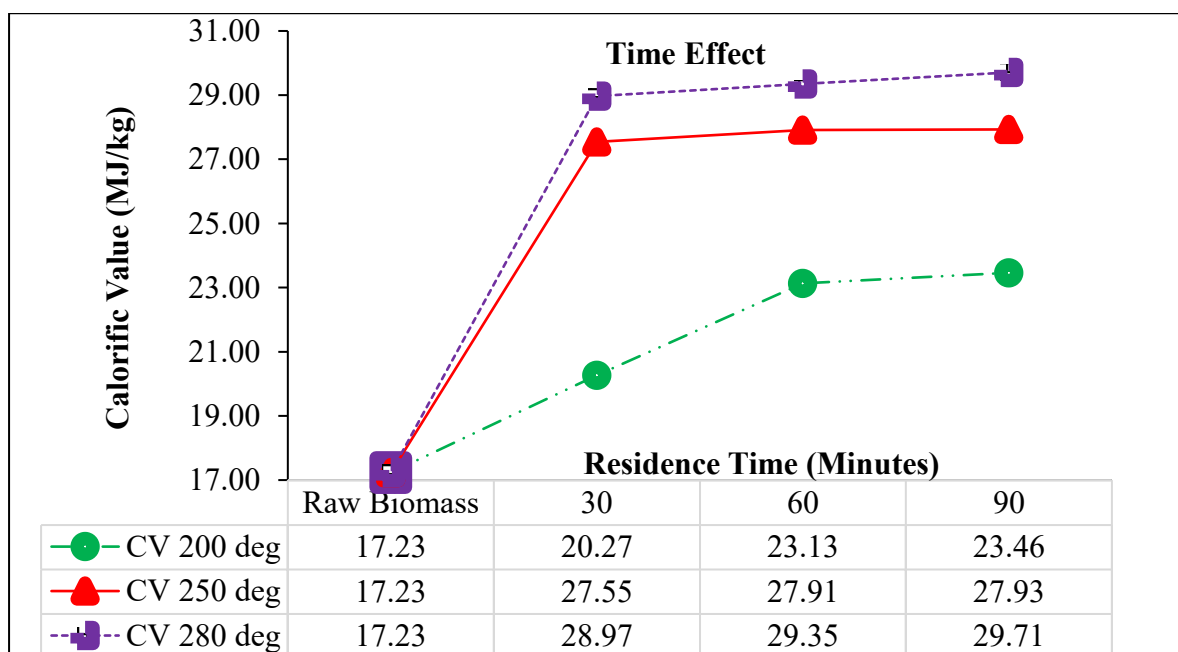


Figure A4: Individual effects of residence time on calorific values of the produced hydrochars.

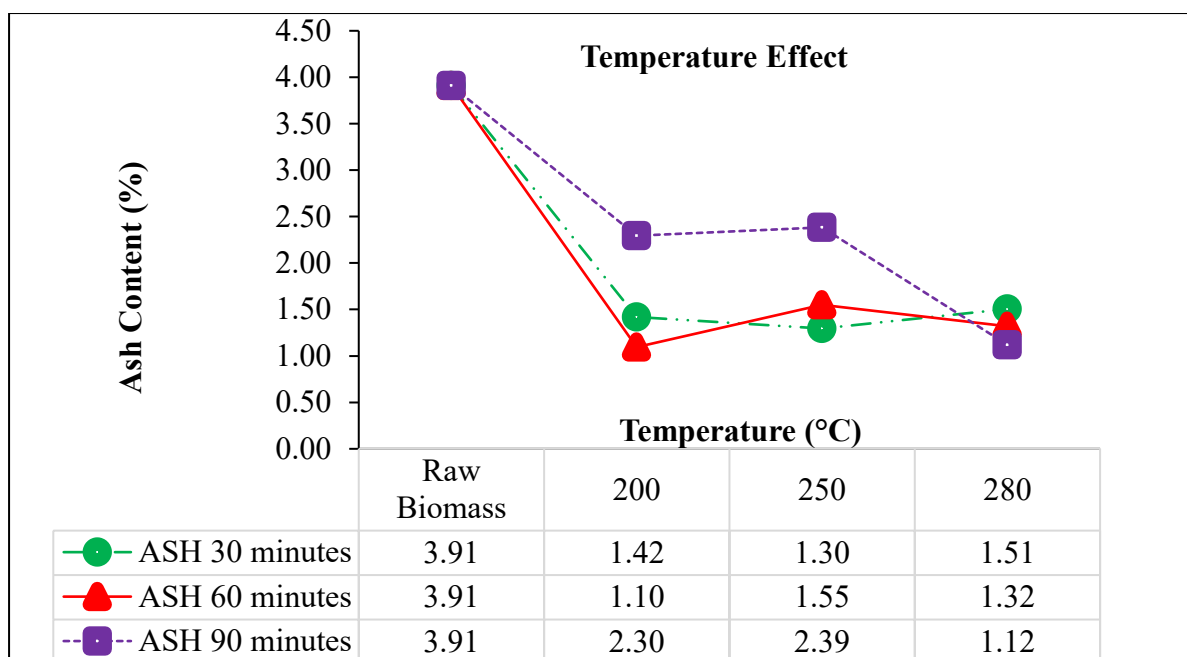


Figure A5: Individual effects of temperature on the ash content of the produced hydrochars.

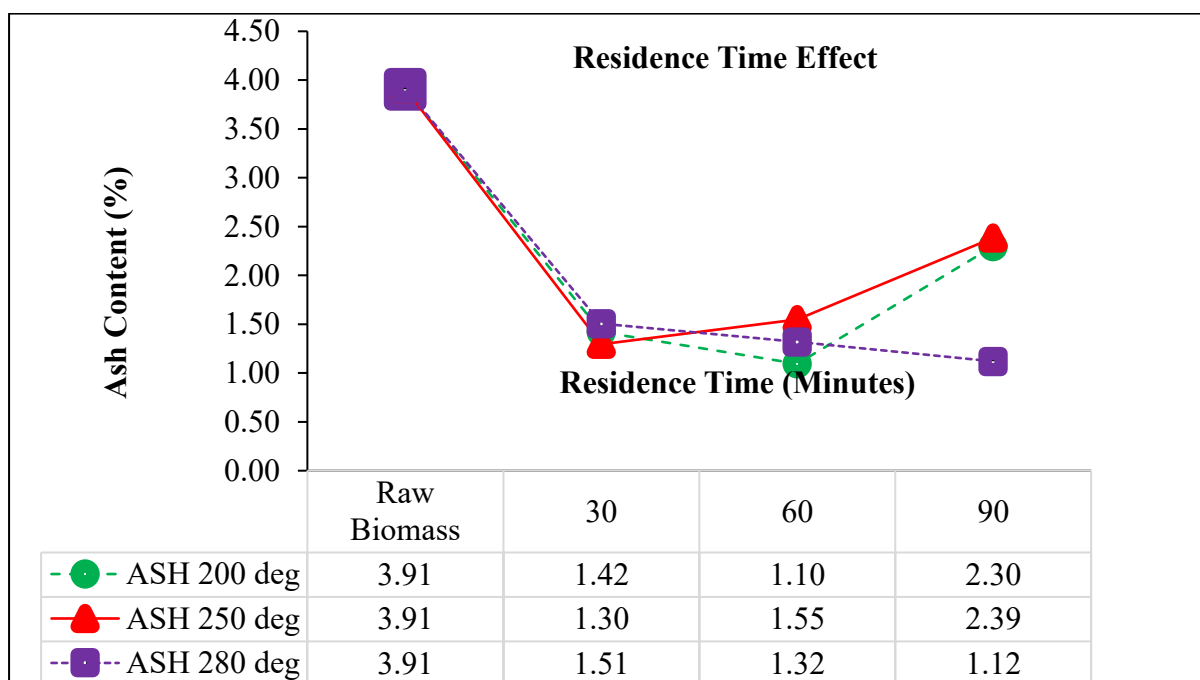


Figure A6: Individual effects of residence time on the ash content of the produced hydrochars.

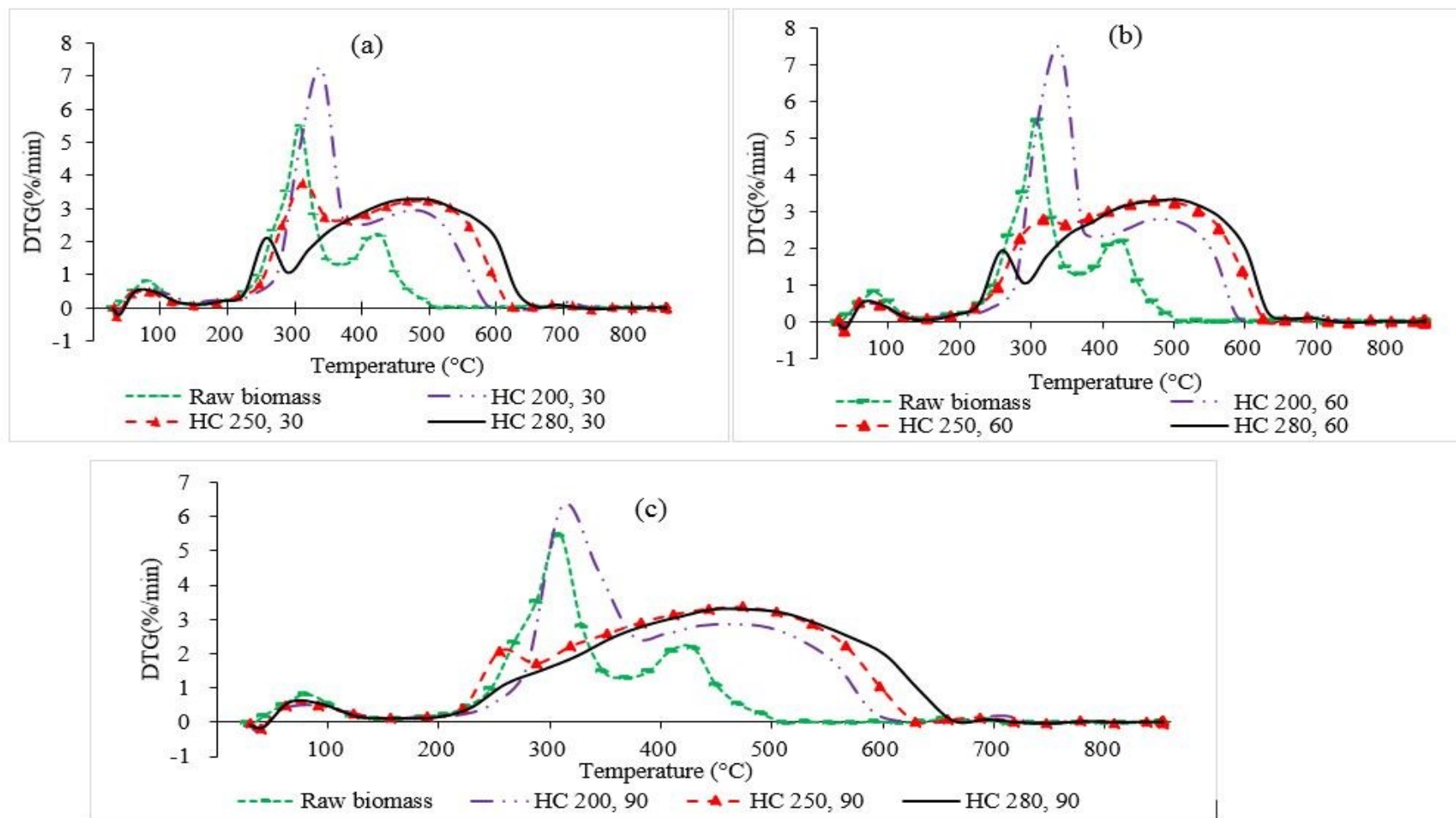


Figure A7: Combustion Properties for HTC 200, 250, 280 °C compared on time basis (a) 30 minutes, (b) 60 minutes, and (c) 90 minutes.

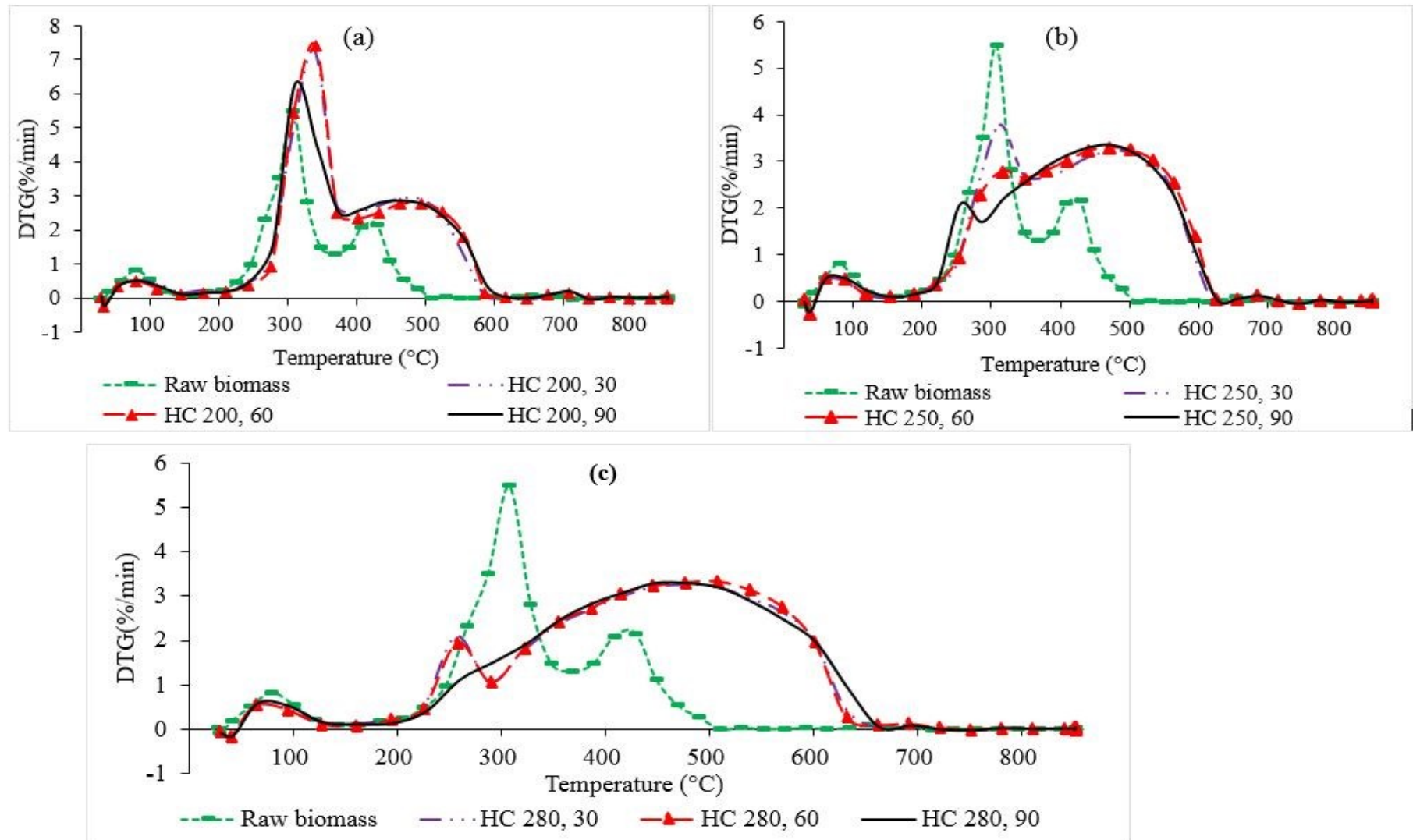


Figure A8: Combustion properties for HTC hydrochars compared on temperature basis (a) 200 °C, (b) 250 °C, and (c) 280 °C.

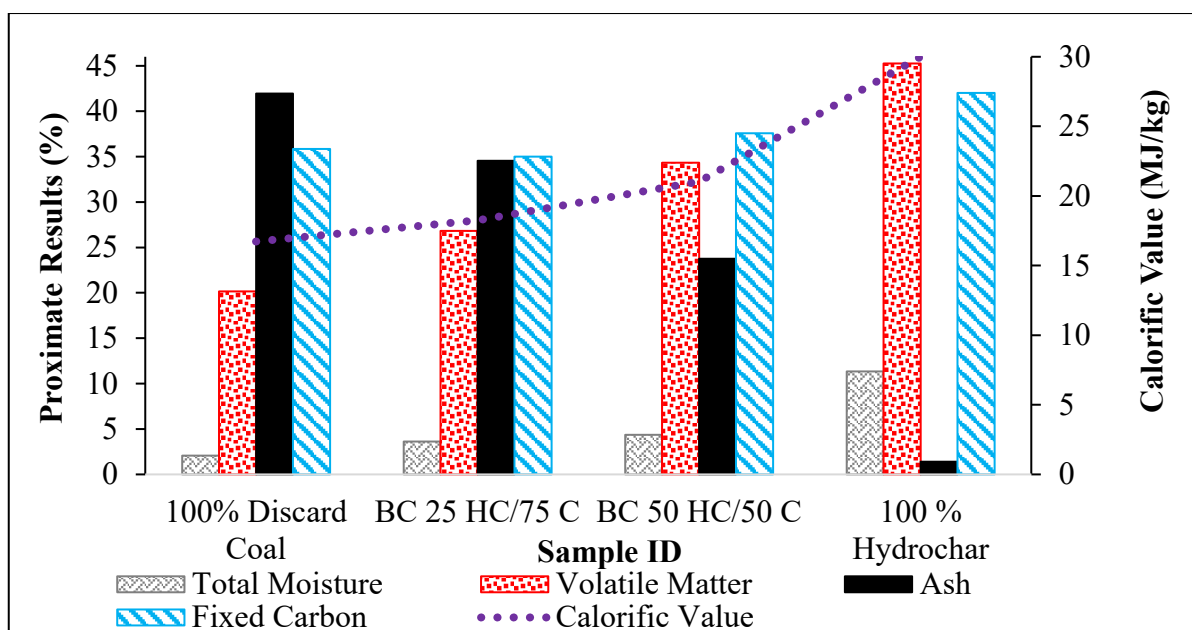


Figure A9: Physicochemical analysis results and calorific values of the discard coal, biocoal blends and hydrochar.

Appendix B: Tables

Table B1: Physicochemical characterisation of blends obtained from raw samples.

Sample ID	Blends	TM (%)	VM (%)	Ash (%)	FC (%)	CV (MJ/kg)
T1	Blend 1 ^b	7.57	68.14	9.13	15.17	
	Blend 2 ^c	7.59	69.46	7.25	15.71	16.23
T3	Blend 1 ^b	6.87	69.25	9.87	14.02	
	Blend 2 ^c	7.24	69.96	9.12	13.69	15.89
S1	Blend 1 ^b	8.03	66.57	4.54	20.86	
	Blend 2 ^c	8.14	67.00	4.33	20.54	17.75
S3	Blend 1 ^b	7.64	68.25	5.34	18.79	
	Blend 2 ^c	7.61	63.19	9.74	19.46	16.48
T4	Blend 2 ^c	7.93	65.63	9.70	16.75	16.71
T6	Blend 2 ^c	7.34	63.69	11.41	17.57	16.57
S4	Blend 1 ^b	6.09	70.27	2.81	20.84	17.32
	Blend 2 ^c	6.94	70.76	2.49	19.83	17.33
S5	Blend 1 ^b	5.94	70.17	2.94	20.96	
	Blend 2 ^c	7.34	69.00	3.64	20.04	17.34
T7	Blend 1 ^b	7.06	69.03	9.79	14.12	
	Blend 2 ^c	7.37	68.10	8.84	15.69	16.36
T9	Blend 1 ^b	6.56	69.50	9.80	13.64	
	Blend 2 ^c	7.32	68.32	8.16	16.21	16.49
S7	Blend 1 ^b	6.92	65.63	4.94	22.53	
	Blend 2 ^c	7.22	65.34	5.40	22.05	17.28
S8	Blend 1 ^b	7.28	68.06	3.20	21.48	
	Blend 2 ^c	7.93	68.52	3.00	20.56	17.29
T11	Blend 1 ^b	8.20	63.22	15.45	13.15	
	Blend 2 ^c	7.91	62.84	15.63	13.64	16.31
T12	Blend 1 ^b	8.20	63.22	15.45	13.15	
	Blend 2 ^c	7.91	62.84	15.63	13.64	16.31
S11	Blend 1 ^b	7.72	67.28	4.99	20.03	
	Blend 2 ^c	7.42	68.42	4.73	19.43	17.59
S12	Blend 1 ^b	8.15	66.41	5.82	19.64	
	Blend 2 ^c	8.12	67.01	5.72	19.15	16.60

b: Comprises of all the tree compartments; c: Comprises of all the tree compartments excluding the sections with elevated ash levels; a: Dry Biomass; TM: Total Moisture; VM: Volatile Matter; FC: Fixed Carbon; CV: Calorific Value.

Table B2: Dissolved organic matter in process water.

ID No.	Compound	Retention time (minutes)	Area (%)
1	Furan,2,3,5-trimethyl	4,892	1,27
2	Phenol, 2,6-dimethoxy	5,331	2,93
3	3,5-Methano-2H-cyclopenta[b]furan-2,4)	7,26	2,39
4	Ethanone, 2-azido-1-(4-methyl-3-furazanyl	7,401	5,04
5	1-hydroxylinalool	7,45	2,61
6	Pentadecane	7,532	4,72
7	Tetradecane	9,688	9,32
8	Heptadecane	12,043	2,06
9	4-Oxo-beta-isodamascol	14,232	2,85
10	2-Bromotetradecane	14,53	1,82
11	1-Butanethiol,3-methyl	14,935	1,84
12	3-Oxo7,8-dihydro-alpha-ionol	18,42	1,8
13	Pentadecanoic acid	18,83	6,34
14	1,1-Dichloro-2-propylcyclopropane	18,97	2,07
15	Dimethylmalonic acid, 2-isopropoxypheny	19,05	2,29
16	3-(aminomethyl)-5-tert-butyl-2	19,463	2,7
17	10-Oxocyclodec-2-enecarboxylic acid, meth	20,27	1,97
18	1,8-Diethyl-3,6-diazahomoadamantan-9-ol	20,45	1,28
19	9,12-Octadecadienoic acid, (Z)	20,671	2,56
20	9,17-Octadecadienal, (Z)	21,072	6,28
21	1,5-Anhydro-2,6-di-O-di-O-methyl	21,579	1,41
22	Bicycol[2,2,1]heptan-2-amine,N,N,1,7,7-P	22,028	1,32
23	Decanoic acid	23,621	2,58
24	Heptadecanoic acid, ethyl ester	24,405	1,21
25	11-Bromo-1,1-Dideuterioundecane	25,183	1,37
26	2H-Pyran-2-acetic acid,tetrahydro	25,327	1,67
27	8-Nonynoic acid	27,14	1,55
28	Dimethyl2-methylsuccinate	27,35	1,61
29	Decanedioic acid, diethyl ester	27,53	1,35
30	Octadecanoic acid,2-(2-hyxyethoxy)ethyl	27,626	1,25
31	cis-p-mentha-1(7),8-dien-2-ol	27,94	1,7
32	(1Alpha,3beta,4beta)-p-menthane-3,8-diol	28,189	4,06
33	Hexadecanoic acid, 2,3-bis[(trimethylsilyl)]	28,708	11,87
34	Germacyclopenten-3	29,04	1,47
35	Hexadecane, 1,16-dichloro	29,134	1,44