



**PRODUCTION OF BIOCOAL FROM WASTEWATER SLUDGE-
BIOMASS FEEDSTOCK**

By

Zinhle Mkhwanazi

20900634

Thesis submitted in fulfilment of the requirements for the degree of Master of
Engineering: Chemical Engineering

Faculty of Engineering and the Built Environment

Durban University of Technology

Durban, South Africa

Supervisor: Yusuf Makarfi Isa

Co-supervisor: Shadana Thakor Vallabh

June 2022

Declaration

I, Zinhle Mkhwanazi declare that the work reported in this thesis is my own unaided work. The work presented is original, except where otherwise indicated and specifically acknowledged as being sourced from other researchers. This thesis is being submitted for the degree of Master of Engineering at Durban University of Technology, South Africa. Furthermore, this work has not been submitted for any other degree or diploma.

05 June 2022

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Date

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Certification

This is to certify that the work contained in the thesis entitled “**Production of biocoal from wastewater sludge-biomass feedstock**”, submitted by **Zinhle Mkhwanazi (Student No.: 20900634)** for the award of the degree of **Master of Engineering (MEng)** to the **Durban University of Technology, South Africa** is a record of original research works carried out by her under my direct supervision and guidance.

I considered that the thesis has reached the standards and fulfilling the requirements of the rules and regulations relating to the nature of the degree. The contents embodied in the thesis have not been submitted for the award of any other degree or diploma in this or any other university.

Prof. Yusuf Makarfi Isa (Supervisor)

Chemical Engineering Department,
University of the Witwatersrand.

11 August 2022

Date

Ms. Shadana Thakor Vallabh (Co-Supervisor)

Chemical Engineering Department,
Durban University of Technology

12 August 2022

Date

Abstract

The increasing volume of wastewater sludge and sugarcane bagasse from wastewater treatment and sugarcane facilities is becoming a prominent concern globally. The disposal of sludge is particularly challenging and poses severe environmental hazards due to the high content of organic, toxic, and heavy metal pollutants among its constituents. The emissions from burning sugarcane bagasse are known to have an impact on respiratory health. At the same time, the availability of energy supply is in demand. The reliance on fossil fuels in the 21st century is unsustainable as the world's reserves are limited and are continually depleting. This depletion of reserves demonstrates the need for alternative energy sources. To minimize the reliance on fossil-based energy sources, a renewable resource such as biomass can be optimized as an energy source. Wastewater sludge and bagasse have the energy potential to produce high calorific value biocoal, this will contribute to the supply of energy in South Africa. South Africa is a major consumer of coal, to produce electricity therefore the development of renewable energy is essential to reduce fuel shortage as concerns for clean and sustainable energy grows. The synthesis of biocoal from wastewater sludge and bagasse through an artificial synthetic coal production process, i.e., hydrothermal carbonization (HTC) is preferred over other thermal conversion techniques as HTC is capable of handling feed having a high (75-90%) moisture content. This study focuses on the production of biocoal from wastewater sludge and sugarcane bagasse as an alternative to sustainable bioenergy supply and is one of the potential solutions for reducing net CO₂ greenhouse gas (GHG) emissions from fossil-fuel power plants.

This study followed the application of the HTC process, with the purpose to convert wastewater sludge and sugarcane bagasse into valuable biocoal. The wastewater sludge and sugarcane bagasse were subjected to hydrothermal carbonization in stainless steel batch reactors, where the effect of temperature, solid loading (solid-liquid wt. %), and biomass type were investigated, while other process parameters were kept constant. The effect temperature was explored at 180 °C, 210 °C, 240 °C, and 260 °C. A ratio variation of 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 dry sludge to bagasse(SB), and the composition of solid to liquid (solid loading wt. %) of 1:10, 2:10, 23:10, 2 and 4:10 (SB:H₂O) corresponding to 9.09%, 16.67%, 23.08% and 28.57% loading were investigated. The process yielded gaseous, solid, and aqueous phases. Calcium hydroxide was used as a binding medium of the produced biocoal.

The results obtained in this study revealed that solid loading, temperature, biomass type, and ratio variation had a substantial impact on the yield and calorific value of biocoal produced. The highest biocoal yield of 23.36 wt. % was achieved at 210°C and derived from

sludge/bagasse (S/B) with a sludge content of 20%. Across all runs, the highest calorific value of 20.21MJ/kg was achieved at 260°C when pure bagasse was employed (0% sludge content).

Keywords: hydrothermal carbonization; biocoal; sugarcane bagasse; wastewater/municipal sludge

Acknowledgements

The work in this thesis could not have been accomplished by just one person, but with great support and guidance from many other individuals.

I wish to express my utmost gratitude to the Lord Almighty, the creator of heaven and earth. My strong tower, the giver of life who has sustained me, gave me strength, and hope throughout my postgrad studies. I give all glory and praise to you Lord.

Special thanks go to my family, my strong pillar, my mother Ntombifuthi Mkhwanazi. My ever-caring grandmother Jetty Mkhwanazi, and my beautiful sister Slindile Mkhwanazi. There can never be another family I could ask for, your love, constant prayers, and support have brought me thus far. You have given me the ability to achieve anything I set my mind to and have been my role model.

This thesis would not have been possible without the help, support, and patience of my supervisor Prof. Yusuf. M. Isa and co-supervisor Ms. S. Vallabh. The tireless support of your supervision towards this master's degree is highly appreciated. Thank you for your indispensable guidance and advice. I admire your excellent work and I am grateful for being under your supervision.

Lastly, I would like to acknowledge all those who contributed to this project that I cannot name individually. I am thankful and appreciate everyone, without you all this project would not have been successful. I will not fail to acknowledge the BRICS project, this work was based on research funded partly by the National Research Foundation of South Africa (NRF), (BRIC190321424123).

Dedication

I wish to dedicate this thesis to my love, Mhlengi Jibreel Zuma. Thank you for supporting me and being my strength in good and challenging times. No words can ever express how much I love you. I will forever remember the beautiful moments we shared together as a blessing from God. I thank you for the most precious gift you gave me of unconditional love. May your soul rest in eternal peace. Phumula sthandwa sami, Phumula Nxamalala, Msholoz! I love you.

Publications and presentations

Publications:

1. Z Mkhwanazi, Y.M Isa. Production of biocoal from wastewater sludge and sugarcane bagasse using hydrothermal carbonization. *Manuscript submitted to Biofuels, Bioproducts, and Biorefining Journal.*
2. Z Mkhwanazi, S Vallabh, Y.M Isa. Production of biocoal from wastewater sludge-biomass feedstock: A Review. *Manuscript submitted to Chemical Engineering Transactions.*

Presentations:

1. Z Mkhwanazi. Y.M Isa, (2021). Production of biocoal from wastewater sludge and biomass feedstock. **Oral presentation.** Sustainable Bioenergy and Processes Conference 2021, 13th – 15th December, Cape Town, South Africa.
2. Z Mkhwanazi. Y.M Isa, (2022). Valorization of wastewater sludge and sugarcane bagasse biomass to biocoal. **Oral presentation.** 1st Postgraduate BRICS Project Workshop 2022, 15th January, China.

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List of abbreviations

Abbreviations	Meaning
HTC	Hydrothermal carbonization
T	Temperature
VM	Volatile matter
FS	Feedstock sludge
FB	Feedstock bagasse
FSB	Feedstock sludge & bagasse
PS	Pure sludge (not filtered)
D1	Solid loading (solid: liquid) @ 9.09wt. %
D2	Solid loading (solid: liquid) @ 16.67wt. %
D1	Solid loading (solid: liquid) @ 23.08wt. %
D1	Solid loading (solid: liquid) @ 28.57wt. %
S0-100	Sludge percentage
FC	Fixed carbon
S	Sludge
B	Bagasse
Daf	Dry ash-free

CHAPTER 1

1. Introduction

Current energy crises are the consequence of a rising world population and a tremendous amount of pressure on the demand and consumption of fossil fuels, especially in countries, for energy generation (Kambo, 2014). Worldwide concerns about global warming and the emission of greenhouse gases (GHGs), of which carbon dioxide has a major impact, have prompted a profound review of developing energy policies. The world's total energy consumption was estimated at 524 exajoules per year (EJ/y) and has been predicted to increase by 65 percent by 2040 (British, 2013; EIA, 2013). Sulfur oxide (SO_x) emissions that are released during the combustion of fossil fuels are the primary cause of acid rain. Significantly increasing emission rates of CO₂ are posing climactic disasters (Kambo, 2014). A continuous increase in these emissions can result in serious environmental threats such as excessive rainfall, floods, droughts, and large climatological variations. One of the most effective approaches for dealing with these issues would be to reduce the consumption of fossil fuels with a clean-green, sustainable and renewable energy resource.

The rapidly increasing population and urbanization growth have resulted in higher demands on finite resources such as land space, water, food, and energy. It has also intensified environmental challenges, which include pollution and waste management issues (Oladejo et al., 2018). Environmental pollution and climate change are two increasingly important problems that the world is facing currently. Some of the major contributors include wastewater sludge, agricultural waste disposal, and emissions of greenhouse gases, mainly carbon dioxide (CO₂) into the atmosphere. Many industries produce massive quantities of wastewater sludge, bagasse, and carbon dioxide, such as wastewater treatment plants, sugarcane industries, and the combustion of fossil fuels for the generation of electricity. These issues are quite detrimental to the global goal of sustainable development and, hence, have ignited global interest in sustainable strategies for energy utilization, production, and waste management. Therefore, the production of biocoal from sludge and bagasse is significant, as these sources of waste could be readily used as biomass.

The disposal of sludge and the burning of bagasse are harmful to plants, animals, and human life as it contains organic pollutants and toxic elements. Industries that deal with the combustion of fossil fuels have contributed to climate change, which has become the world's most important problem. This is due to emissions of greenhouse gases, mainly carbon dioxide

(CO₂), into the atmosphere. Therefore, the need to utilize renewable energy resources such as biomass for bioenergy is of great importance.

South Africa is facing environmental sludge and bagasse disposal problems and is severely crippled by an energy crisis, with widespread inaccessibility to clean energy still being an issue. In Africa, only about 30% of the sub-Saharan African population has access to electricity and roughly 70% must gather fuel wood (Maqhuzu et al., 2019). Therefore, the conversion of biomass energy sources such as sludge and bagasse to bioenergy can provide a solution to these problems. This may not only solve environmental sludge and bagasse disposal problems, but it will also reduce CO₂ emissions in the atmosphere, which is the main source of climate change and global warming by the greenhouse effect (Hauchhum & Mahanta, 2014). The modern use of biomass is notable for its conversion into high-quality energy carriers such as electricity. Energy recovery from waste and sustainable sources like sludge and bagasse can play a role in mitigating energy shortages and diversifying the energy supply.

South Africa's energy needs are provided by fossil-based coal, and 53% of the coal produced in South Africa is used to generate electricity (Eskom Power Generation, 2011). According to the World Bank Development Indicators (2015), electricity production from coal in South Africa was reported at 92.7%. While the industry (Eskom) is beneficial in providing electricity, substantial CO₂ emissions occur during the process. This study focuses on research and evaluation of the HTC process to produce biocoal from wastewater sludge and sugarcane bagasse. The main objective is to produce biocoal and examine the use of HTC operating parameters as a sustainable development approach in converting biomass to bioenergy.

Hydrothermal carbonization (HTC) is a thermochemical process that converts organic feedstock into a high-carbon-rich solid product. The process is especially suitable for biomass waste with a high moisture content (75–90%). This singular advantage of the HTC process eliminates the pre-drying requirement of wet biomass, which is a huge energy-intensive process and a financial load in biomass pre-processing, especially when performed under conventional thermal pre-treatments like slow-pyrolysis or dry torrefaction (Martínez, 2019).

This process operates within a short period (1–12 hrs) at a relatively low-temperature range (130–250°C) and corresponding pressures (up to 20 bar) (Libra et al. 2011; Titirici 2013). Biomass can be used without expensive pre-drying, and the process is feasible for a very wide range of biomass types. In addition, problematic wastes that currently require expensive

disposal, low investment, and maintenance costs, operation at moderate pressure and temperature, and that are environmentally friendly can be safely treated (Vuuren, 2018).

The main products of the HTC process are a solid (hydrochar), a liquid fraction (also referred to as HTC liquor or HTC process water (PW)), which could contain up to 15% of the initial carbon present in the feedstock (Danso-Boateng et al., 2015), and a gas phase mainly formed by CO₂ (> 90%) and small amounts of CH₄, H₂, and CO (Cha et al., 2016, and Basso et al., 2016). Usually, moderate temperatures promote liquid yield, whereas higher temperatures generate gas and char, mainly (Martínez, 2019).

1.1. Problem Statement

The disposal of sludge and the burning of bagasse are harmful to plants, animals, and human life as it contains organic pollutants and toxic elements. Industries that deal with the combustion of fossil fuels have contributed greatly to climate change, which has become the world's most important problem. This is due to emissions of greenhouse gases, mainly carbon dioxide (CO₂), into the atmosphere. The management of sludge and bagasse in an economically and environmentally acceptable manner is one of the critical issues facing modern society due to the extremely fast increase in sludge and bagasse production as a result of the implementation of Directive 1991/271. This is accompanied by increased challenges in complying with waste legislation (Directive 1999/31 for landfilling and Directive 2000/76 for incineration). On the other hand, many farmers are reluctant to accept land utilization of sewage sludge (Martínez, 2019). As being wakened by the fact that conventional fossil fuels are depleting in South Africa at a rapid rate and the environmental pollution related to the use of these conventional fossil fuels has created an interest in biomass, using it as a substitute fuel for coal is gaining significant attention (Bridgeman et al., 2010; Pimchuai et al., 2010). The hydrothermal treatment of wastewater sludge and bagasse, in particular hydrothermal carbonization, has been discovered to be an alternative route to facilitate the transformation of this carbon-rich organic matter into valuable energy and fuel (Martínez, 2019). Therefore, the need to utilize renewable energy resources such as biomass for bioenergy is of great importance.

1.2. Research aim and objectives

The aim of this study was to produce biocoal from wastewater sludge and biomass feedstock (sugarcane bagasse).

The objectives were:

- Characterize wastewater sludge and sugarcane bagasse.
- Investigate the effects of temperature and solid loading on the heating value and yield of the biocoal.
- Characterize biocoal using relevant analytical techniques.

1.3. Research questions

This study addressed the following questions:

1. How effective will the hydrothermal carbonization process be in the production of biocoal from sludge and bagasse?
2. What is the effect of the operating parameters including, temperature, biomass type, and solid loading wt. % on the production of biocoal?
3. What process conditions are to achieve the valorization of sludge and bagasse?

1.4. Delineation of study

The scope of this research was based on the conversion of wastewater sludge and sugarcane bagasse to biocoal by the hydrothermal carbonization process. And the investigation of the effect of temperature, solid to liquid composition (solid loading wt. %), and the biomass type on the valorization of sludge and bagasse. The following were not considered:

- The effect of heating rate
- The effect of particle size
- The effect of catalyst
- The effect of residence time

1.5. Thesis Structure

The research presented in this thesis was carried out at the Durban University of Technology (DUT), Durban, South Africa. The outline of this dissertation is provided below:

➤ Chapter 1: **Introduction and background of the study**

The introduction, which highlighted the background of this study was presented, the problem statement, the research aim, objectives, and questions, and the delineation of the study.

➤ Chapter 2: **Literature review**

This chapter presents a comprehensive literature review that covers the history of renewable and sustainable resources. It further outlines the various biomasses available for alternative energy sources and focuses on wastewater sludge and sugarcane bagasse. The chapter also reflects on the various thermochemical methods for the valorization of biomass and the effects of various process parameters on the calorific value and the biocoal yield. The chapter then proposes hydrothermal carbonization as a process to be used in conducting this study.

➤ Chapter 3: **Materials and experimental procedure**

Details of the materials, equipment, and experimental method that were applied are discussed, and a schematic diagram of the experimental procedure is presented.

➤ Chapter 4: **Analysis of results and discussion**

Results and discussion of the effects of operational parameters on the production of biocoal are presented in this chapter.

➤ Chapter 5: **Conclusions and recommendations**

Presents various conclusions and recommendations that were drawn from the results demonstrated in this thesis.

CHAPTER 2

2. Literature review

This chapter reviews the history of conventional fuels and the challenges pertaining to their application. It further outlines the diverse biomasses that are potential renewable energy sources and focuses on wastewater sludge and sugarcane bagasse as alternative energy sources. The chapter also considers various thermochemical methods, particularly hydrothermal carbonization, as well as the effects of process parameters on calorific value, biocoal yields, and biocoal production (Taylor, Govindarajalu, Leven, Meyer, & Ward, 2008).

2.1. Introduction

Energy is well recognized to be the lifeline of all human activities, and the world we live in today has undoubtedly been shaped by the global energy system. However, the very energy system that humanity has become so dependent on is increasingly becoming less sustainable as the energy demand continues to grow at exponential rates.

Furthermore, many human activities during the last two centuries have led to a sudden increase of greenhouse gases in the atmosphere, which raises the average temperature of the earth (Swedish Society for Nature Conservation, 2016). These activities include the combustion of fossil fuels, burning biofuels such as wood without planting new trees, and emissions from agriculture. In 2010, the activity with the largest share of greenhouse gas emissions (70 %) was the energy sector (IEA, 2015). In this sector, 90% of the emissions were in the form of CO₂ (IEA, 2015). As a result, the fear of environmental threats has fuelled the desire to investigate potential alternative renewable energy sources to contribute to South African energy (Valenti, 2015).

Biomass-derived fuels are considered “carbon-neutral” and are seen as one option for mitigating climate change (Kirkinen, 2010). Biomass is a non-edible renewable energy resource derived from living or recently living organic matter such as wood, wood waste, and agricultural residues. Biomass is the world’s fourth-largest source of energy, and its billion-ton availability can meet sustainable energy demand and production (Kambo, 2014).

Biomass waste can be valorized utilizing well-established thermochemical processes such as pyrolysis, dry torrefaction, hydrothermal carbonization, and gasification (Martínez, 2019). HTC is a thermochemical process for the treatment of high moisture content biomass that can

convert biomass to biocoal at a wide range of temperatures (180-350 °C) and autogenous pressure (2–6 MPa) for variable periods (5 min–24 h) (De la Rubia et al. 2013).

2.2. Conventional energy

Conventional energy refers to the dominant energy sources that currently generate electricity. These dominant sources are classified as fossil fuels and are widely considered non-renewable. The three main forms of fossil fuels are coal, and gas (Valenti, 2015).

Fossil fuels have been formed when plants and animals sink to the bottom of seas and lakes. The remains of these plants and animals have then been covered by more and more sediment. Over millions of years, they have been subjected to high pressures and temperatures and have been transformed into carbon and hydrogen compounds, such as oil, coal, and natural gas (Swedish Energy Agency, 2014).

According to the US Department of Energy (2013), coal has been used for heating for thousands of years. Coal was also the first fossil fuel used on a wide scale in England in the 1700s. Due to rising energy demand, coal is becoming more popular (Areskoug & Eliasson, 2007). Improvements in steam engines, powered by coal, meant that more water could be pumped out of coal mines and the mines could become deeper, producing more coal. The increased supply of coal could also be used for other purposes, such as clothing factories, transportation, and the production of steel (White, 2016).

Oil, commonly called petroleum, was made available in the middle of the 19th century. Its first use was for lighting, where the fuel was refined and used in paraffin lamps. At the end of the century, the internal combustion engine was invented, which marked the beginning of the automobile, and since then the use of oil has only increased (Areskoug & Eliasson, 2007). The Swedish Energy Agency (2016) states that 80 % of the current worldwide supply of energy is derived from fossil fuels, and of this amount, oil makes up almost one-third of the supply.

2.2.1. Effects of using fossil fuels

Fossil fuels are considered non-renewable because the rate at which humans consume them exceeds their natural regenerative capacity. In addition, the use of fossil fuels raises serious environmental concerns (Valenti, 2015). According to Swilling and Annecke (2012), the burning of fossil fuels produces roughly 21.3 billion tonnes of CO₂ per year; only half of this is naturally absorbed by the atmosphere. The combustion of these fossil fuels produces more greenhouse gases, which causes the earth to warm due to the greenhouse effect. The negative

consequences of using fossil fuels are numerous and exist on both a local and global scale. Emissions with local effects include carbon monoxide (CO) and nitrous oxides (NO_x). Carbon monoxide is formed during incomplete combustion and inhaling it can cause, among other things, headaches, nausea, dizziness, and even death (US Consumer Product Safety Commission). Nitrous oxides (NO_x) can form at high combustion temperatures and generate ground-level ozone, which is harmful to respiratory systems and crops (Areskoug & Eliasson, 2007).

Coal and oil also contain sulfur, which forms sulphuric acid when in contact with moisture in the air. This is called acid rain, and it caused many forests and lakes to die in Europe in the 1960s and 70s. Several measures can be taken to reduce acid rain, and a concerted effort has resulted in an 80 percent reduction in sulfur levels in Sweden from 1990 to 2013 (Swedish Environmental Protection Agency, 2016). It should also be noted that fossil fuels are not the only energy carriers that can have adverse environmental effects (Areskoug & Eliasson, 2007).

Arguably the most important emissions from fossil fuels are greenhouse gases. These gases prevent heat from leaving space and redirect it to the earth. Their contribution to global warming is known as the greenhouse effect, and without it, the earth's surface temperature would be too low to support all life. This effect is sometimes referred to as a blanket around the earth, keeping it warm (Swedish Society for Nature Conservation, 2016).

Of all the greenhouse gases, the most important one is carbon dioxide (CO₂), which is formed from the combustion of fuels containing carbon. Other examples of greenhouse gases include methane (CH₄), laughing gas (N₂O), and many refrigerants. When used for comparison, the effect of other gases is commonly calculated as the equivalent of the greenhouse effect of CO₂, which is called their carbon dioxide equivalents (Swedish Society for Nature Conservation, 2016).

As a consequence of the negative impacts of human emissions and activities, several energy and environmental targets have been set. The European Union has climate and energy goals for 2020, 2030, and 2050. For 2020, these include a 20% reduction in greenhouse gas emissions compared to 1990 levels, having 20% renewable energy, and using energy 20% more efficiently. These same levels are projected to be 40%, 27%, and 27% in 2030, respectively. By 2050, the goal is to have a low-carbon economy, which means that greenhouse gas emissions should be 80% lower than they were in 1990 (European Commission, 2016).

2.2.2. Climate change

The United Nations Framework Convention on Climate Change (UNFCCC) defines climate change as "*a change in the climate that is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and which is in addition to natural climate variability observed over comparable time periods*". Climate change is a naturally occurring phenomenon that has occurred throughout history. However, it has recently been associated with the induced effect of anthropogenic activities that have increased levels of greenhouse gases in the earth's atmosphere, stimulating an enhanced greenhouse effect, known as global warming (Mokheseng, 2010). The global consensus is that human activities on earth have a greater than realized influence on the global climate (Intergovernmental Panel on Climate Change (IPCC, 2013). Over the last century, the average global temperature has risen by 0.7°C (Seifred & Witzel, 2010).

2.2.3. Greenhouse gas

According to the IPCC (2013:22), greenhouse gases (GHGs) are "*those gaseous constituents of the atmosphere, both natural and anthropogenic, that absorb and emit radiation at specific wavelengths within the spectrum of infrared radiation emitted by the Earth's surface, the atmosphere, and the clouds.*" Increases in global GHGs give rise to the greenhouse effect, a process in which the absorption of infrared radiation by the atmosphere warms the Earth (IPCC, 2013). GHGs include water vapour (H₂O), carbon dioxide (CO₂), nitrogen oxide (N₂O), methane (CH₄), and ozone (O₃).

2.2.4. South African energy sector

Fossil fuels overwhelmingly dominate the South African energy system, with coal the largest contributor. Coal combustion at coal-fired power plants provides approximately 90% of electricity needs (Smit, 2009). The remaining 10% is split between other energy sources, including nuclear (5%), and renewable energy (2%). In terms of overall energy consumption (not specifically electricity production), fossil fuels also dominate, with coal, oil, and natural gas making up over 95 percent of total consumption (Valenti, 2015). Figure 2.1 illustrates the total primary energy consumption in South Africa

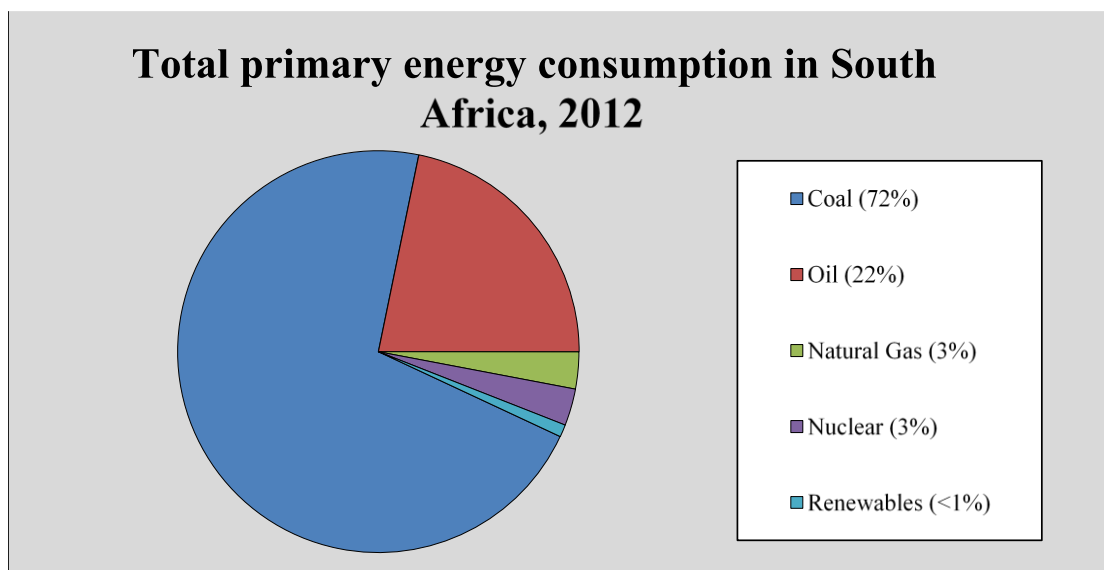


Figure 2.1 Total primary energy consumption in South Africa, 2012. Adapted from DOE (2012)

As a result, South Africa has one of the world's most energy-intensive economies (Swilling & Annecke, 2012). The primary reason South Africa uses coal as an energy source for over 90 percent of its energy needs is due to the fact that the country has extremely large coal reserves. At nearly 50 billion tonnes, South Africa has the sixth largest recoverable coal reserves in the world (McDaid, 2009). In addition, coal is of particular importance to the South African economy as it provides over 70 percent of the country's primary energy supply, supports over 90 percent of electricity generation, and provides feedstock for nearly a quarter of the nation's liquid fuels via Sasol's coal-to-liquid process (Swilling & Annecke, 2012).

The combustion of coal releases high levels of GHG gases into the atmosphere, carbon dioxide in particular. Due to its dependency on coal for its energy demands, South Africa ranks as one of the worst emitters of GHGs in the world. In 2011, South Africa emitted 367,6 million tonnes of CO₂, accounting for 1.17 percent of global emissions, making it the world's most carbon-intensive developing country (Swilling & Annecke, 2012).

Not only does South Africa rank near the top of the list in terms of absolute CO₂ emissions, but so too do South Africa's per capita emission statistics. South Africa has one of the highest per-capita CO₂ emissions in the world – currently 11th on the global list. The average South African emits 7.27 tonnes of CO₂ per year-significantly greater than the global average of 4.50 tonnes of CO₂ (EIA, 2013). In addition to this, the average South African emits an overwhelming 7.8 times more CO₂ than the average person in Africa, which has an average of

0.93 tonnes of CO₂ per capita (Valenti, 2015). Figure 2.2 illustrates South Africa's CO₂ emissions per capita compared to the global and African averages.

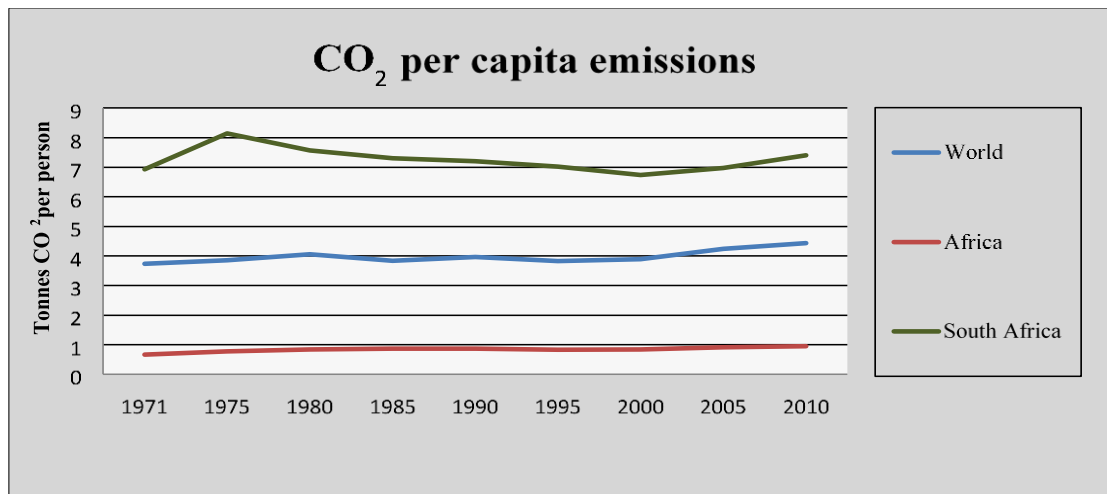


Figure 2.2 CO₂ per capita emissions. 1971-2010. Redesigned from EIA (2013)

South Africa also faces the inevitable challenges associated with increases in electricity demand resulting from rapid population and urbanization growth. The projected electricity demand based on the Gross Domestic Product (GDP) and population growth forecasts, as presented in the Long-Term Mitigation Scenarios (LTMS), shows an expected electricity demand of 430 TWh by 2030 upstream of transmission (Edkins et al., 2010). This demand is almost double the current demand, as can be seen in Figure 2.3 (Valenti, 2015).

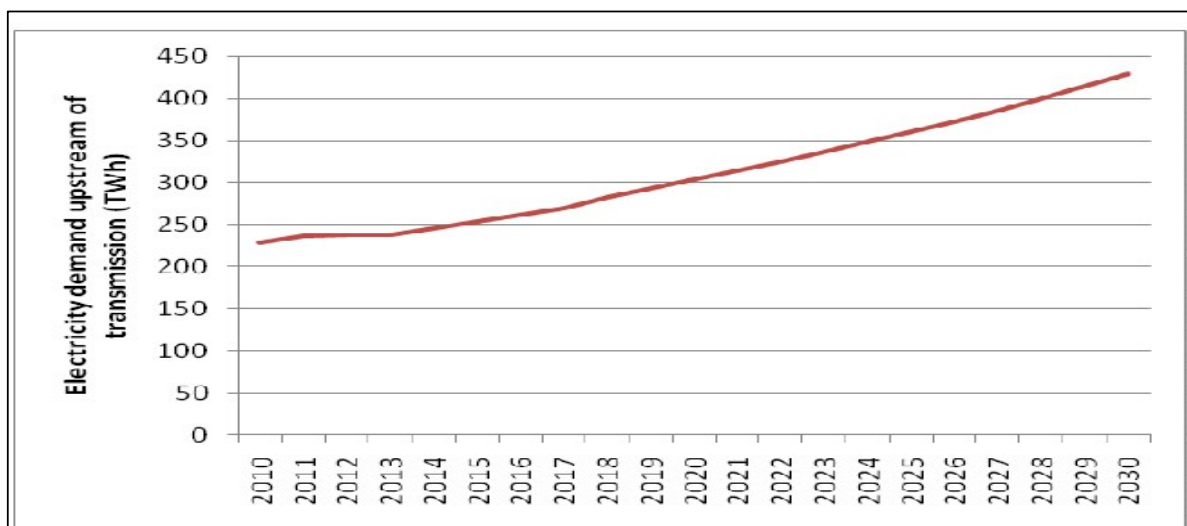


Figure 2.3 Electricity demand projections in South Africa, 2010 – 2030. Adapted from Edkins et al. (2010)

2.3. Biomass as an alternative energy resource

The importance of energy for a nation's development cannot be overemphasized. This is because energy is the cornerstone of economic and social development. Globally, 140 billion metric tons of biomass are generated every year by agriculture (Ganeshraj et al. 2015). This volume of biomass can be converted into an enormous amount of energy. Agricultural biomass is waste that, when converted to energy, can replace fossil fuels, reduce greenhouse gas emissions, and provide renewable energy. Biomass takes the form of residual stalks, roots, leaves, husks, shells, and animal waste. Waste biomass is a valuable resource. It is widely available, renewable, and virtually free.

2.3.1. Biomass

Biomass is a lignocellulosic material derived from living or recently living organic materials such as wood and agricultural residuals. In a broad vision, non-lignocellulosic materials, like animal and municipal solid wastes (MSWs), are also termed biomass (Demirbaş, 2001). Biomass is the fourth largest source of energy, followed by coal, oil, and natural gas, and provides about 14 percent of the world's total energy consumption (Saxena et al., 2009; Tumuluru et al., 2011). Biomass is the only renewable energy resource that can be converted into any form of fuel, including solid, liquid, and gaseous (Özbay et al., 2001). Biomass is widely used to meet a wide variety of energy requirements, such as heat and electricity generation, and producing biofuels for fuelling vehicles. Moreover, its non-edible nature, ability to grow relatively quickly even on infertile land, and abundant availability on earth nominates it as a potential energy resource for sustainable energy production, which is the overall goal of the vision of bioenergy development (Perlack et al., 2005). Using biomass as a fuel can also be an opportunity to empower rural communities.

As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting to various forms of biofuel. There are two major biomass groups, and the sub classifications are presented below (Basu, 2010):

1. Virgin
 - Terrestrial: Cultivated crops, Forest biomass, Energy crops, and Grasses.
 - Aquatic: Water plants and Algae.
2. Waste
 - Municipal: MSW, Bio-solids, Sewage, and Landfills.
 - Agricultural: Livestock and manure, Agricultural crop residue.

- Forestry residues: Bark, Leaves, and Floor residues.
- Industrial wastes: Demolition wood, Sawdust, and Waste oil or fat.

2.3.2. Chemical structure of biomass

Biomass cannot be defined as a specific reactant due to its high degree of chemical complexity and heterogeneity. Lignocellulose (plant) biomass consists mainly of three carbohydrate polymers: cellulose, hemicellulose, and lignin. The chemical structures of these compounds are shown in Figure.2.4. Small quantities of pectin, protein, extractives, and ash have also been detected, and the composition of all constituents varies among plant species. Cellulose is the main constituent of the plant cell wall, and chains of 20–300 monomers group together to form microfibrils. Hemicellulose is the second most abundant polymer that is not chemically homogeneous and contains branches with short lateral chains of different sugar types (xylan is presented in Figure. 2.4). Lignin is the third most abundant polymer in nature. Its molecular structure contains cross-linked polymers of phenolic monomers (Bevan et al. 2020). The physical and chemical properties of these components are discussed in Table 2.1.

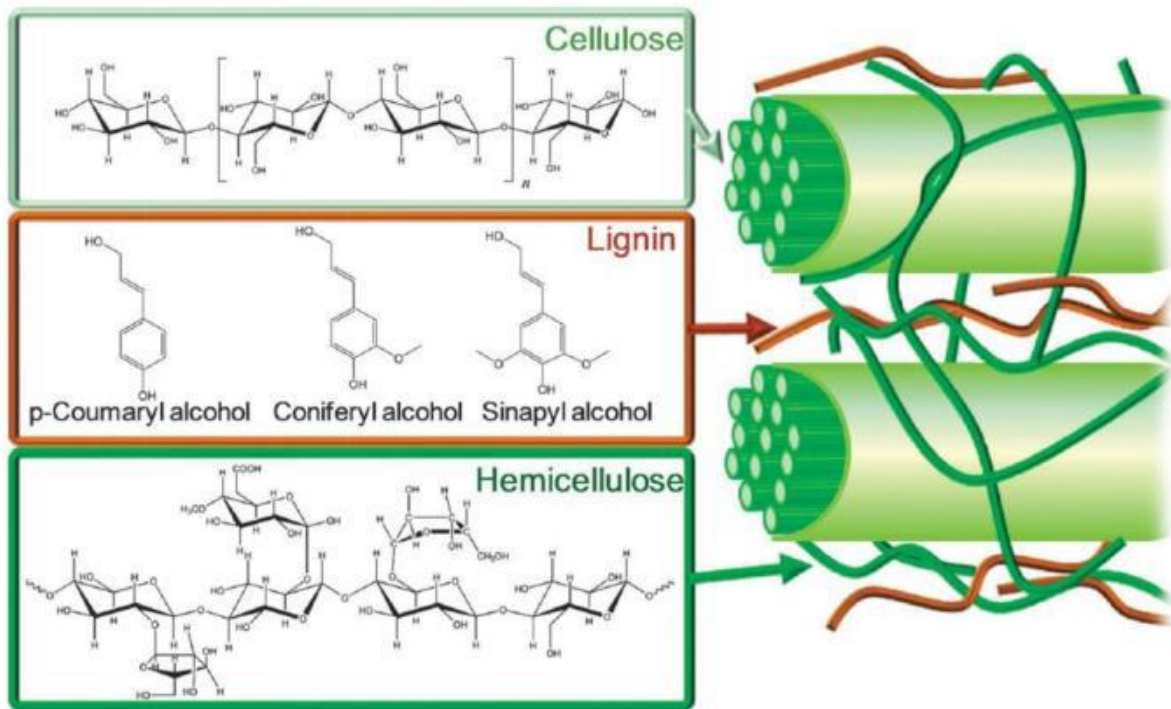
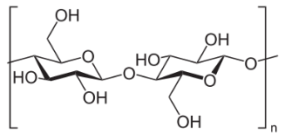
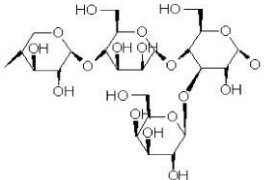
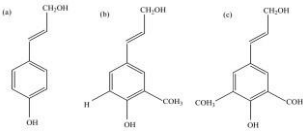


Figure 2.4 Structural representation of Lignocellulosic biomass with cellulose, hemicellulose, and building blocks of lignin. Adapted from (Alonso et al., 2012)

Table 2.1 Physical and Chemical Properties of Lignocellulosic biomass composition. Redesigned from (Demirbaş, 2005; Ebringerová, 2005; Fengel & Wegener, 1983; Garrote et al., 1999; Glasser & Sarkanen, 1989; Grønli et al., 2002; Janshekar & Fiechter, 1983; Kumar, 2010; Saha, 2003; Sun, 2010; Thielemans et al., 2002)

Compound	Cellulose	Hemicellulose	Lignin
Chemical Structure	 <p>Cellobiose (D-glucose) Unit</p>	 <p>Xylose - $\beta(1,4)$ - Mannose - $\beta(1,4)$ - Glucose - $\alpha(1,3)$ - Galactose</p>	 <p>Lignin monomers (a) trans-p-coumaryl alcohol, (b) coniferyl alcohol, and (c) sinapyl alcohol</p>
Molecular Formula	$(C_6H_{10}O_5)_n$	$C_5H_{10}O_5$	(a) $C_9H_{10}O_2$, (b) $C_{10}H_{12}O_3$, and (c) $C_{11}H_{14}O_4$
Typical Composition in Biomass	(i) Hardwood:39-54% (ii) Softwood:41-50% (iii) Agricultural:24-50%	(i) Hardwood:15-36% (ii) Softwood:11-27% (iii) Agricultural:22-35%	(i) Hardwood:17-29% (ii) Softwood:27-30% (iii) Agricultural:7-29%
Structural Formation	A homopolymer of D-glucose subunits. Cellulose is linked by β -1,4 glycosidic bonds forming long chains	A heteropolymer of Xylose, Mannose, Glucose, and Galactose. Xylan, the dominating component in hemicellulose, is linked by β -(1 \rightarrow 4)-glycosidic or α -(1 \rightarrow 2)-bonded 4-Omethylglucuronic acids. Also, may an contain acetyl group attached to it.	A heteropolymer is built up of three different phenylpropane monomers groups; p-coumaryl, coniferyl, and sinapyl alcohol. This complex polymer is oriented by different degrees of methoxylation of the above-mentioned monomers forming a large molecular structure(s).
Hydrophobicity	Medium	Low	High
Calorific Value	17-18 MJ/Kg	17-18 MJ/Kg	23.3-26.6 MJ/Kg

Thermal stability and Solubility in Water	Cellulose is nonsoluble in water under standard conditions. It can be hydrolyzed in subcritical water around 180°C and around 300-400°C in standard conditions.	Owing to its amorphous structure, the thermal breakdown of hemicellulose is relatively easier. It can be hydrolyzed in the water around 160°C and around 200-300°C under standard conditions.	Lignin is the most thermochemically stable component in wood and highly insoluble in water. Its degradation/hydrolysis starts in near or supercritical water or around 600°C in ambient conditions.
Applications	Paper manufacturing, textiles, biofuels, chromatography, binding/composite materials, etc.	Mainly includes animal feed, food packaging, health care, and the biorefinery industry.	Manufacturing of adhesive compounds and bioenergy

2.3.3. Cellulose

The cellulosic composition of the woody biomass varies from 39 to 54%; generally, hardwood contains a higher percentage of cellulose content in it compared to softwood and agricultural biomass (Garrote et al., 1999). Cotton fiber is the purest and naturally occurring form of cellulose (Kumar, 2010). It is composed of D-glucose (C₆H₁₀O₅) subunits linked by β-1, 4 glycosidic bonds forming long chains (called elemental fibrils) linked together by the hydrogen bonds and van der Waals forces. The β-linkage linear chains in the cellulose are highly stable and are resistant to chemical attack because of the presence of a high degree of intra and intermolecular hydrogen bonding (Jarvis, 2003). The presence of strong hydrogen bonding provides a strong and rigid structure to a polymer. In addition, due to the crystalline structure, the thermal degradation of cellulose starts at a temperature range of 300-400°C (Grønli et al., 2002; Pérez & Samain, 2010).

2.3.4. Hemicellulose

Unlike cellulose, hemicellulose is a low molecular weight polymer and is made up of 23–32% of raw biomass. Hemicellulose has a complex carbohydrate structure consisting of diverse types of polymers like pentoses, hexoses, mannose, glucose, and sugar acids. Xylan is the most dominating component of hemicellulose in hardwood and agricultural plants, like grasses and straw, whereas glucomannan is dominant in softwood (Fengel & Wegener, 1983; Saha, 2003). Due to the low molecular weight and amorphous structure, hemicellulose is a highly soluble

polymer in water. Among all three lignocellulosic polymers of biomass, hemicellulose is the least thermally stable polymer, followed by cellulose and lignin. The thermal degradation of hemicellulose starts at a temperature range of 200–300 °C (Gronli et al., 2002). However, its solubilization in the water (mainly due to hydrolysis) starts at about 180 °C under hydrothermal conditions (Bobleter, 1994; Garrote et al., 1999).

2.3.5. Lignin

After cellulose and hemicellulose, lignin is the most abundant polymer in nature and is present in the cell wall of biomass. Lignin is a complex, cross-linked, and amorphous heteropolymer that is made up of three different phenyl-propane groups: (i) p-coumaryl, (ii) coniferyl, and (iii) sinapyl alcohol, forming a large molecular structure (Hendriks & Zeeman, 2009; Kumar, 2010). Generally, softwoods contain a higher percentage of lignin than hardwoods and agricultural biomass (Garrote et al., 1999). The main functions of lignin in plants are to provide structural strength, impermeability, and resistance against microbial attack (Fengel & Wegener, 1983).

2.3.6. Biomass Materials

Agro-residues and forestry wastes are currently becoming another primary energy source to reduce the dependence on fossil fuels (coal, oil, and natural gas). To date, as one of the major globally applicable renewable energies (RE), carbon-neutral biomass energy contributes nearly 10% of annual energy consumption (Chao He et al. 2018). Due to the rapid depletion and relatively high cost of non-renewable fossil fuels as well as the resulting severe environmental concerns, more efforts have been made to explore alternative, inexpensive, and renewable energy sources (RE) with fewer or no environmental impacts to meet dramatically increasing energy demand worldwide.

2.4. Sugarcane Bagasse

The selection of feedstock for energy production purposes is dependent upon certain criteria such as potential yield per hectare, feedstock properties, and potential uses. However, the value of sugarcane bagasse as a fuel for energy production largely depends on its calorific value, which in turn depends on its composition, especially its moisture content, and the calorific value of the sugarcane plant, which mainly depends on its content of sucrose.

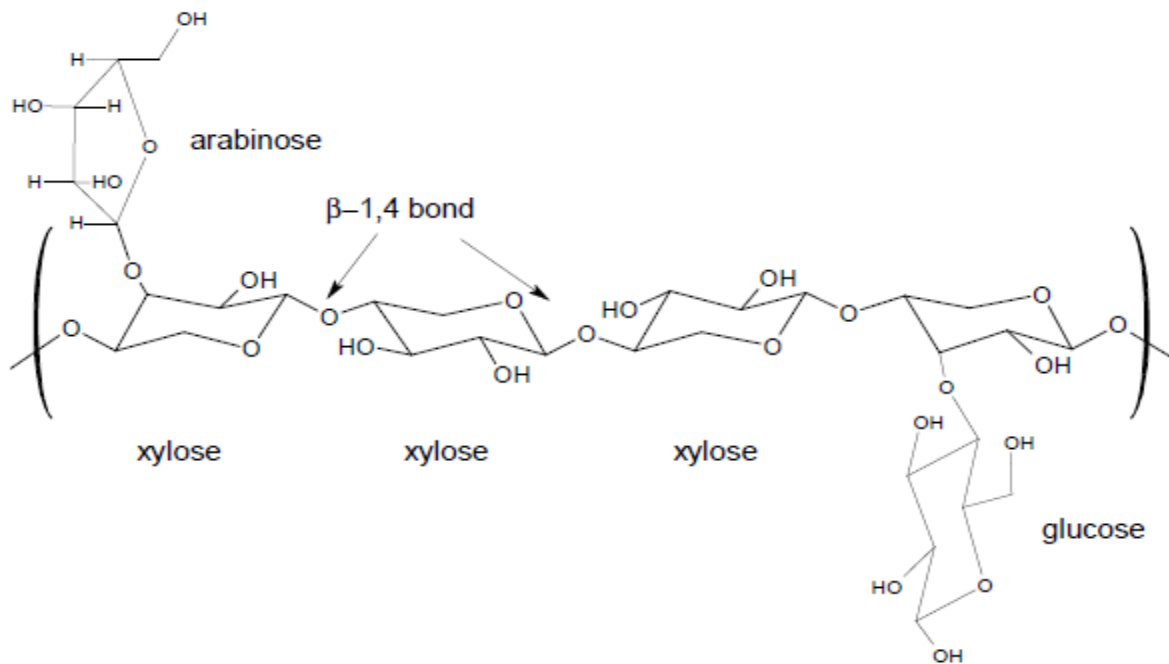


Figure 2.5 Simplified structure of bagasse (Wazeer, 2017)

Sugarcane bagasse is a solid waste obtained after the crushing of the sugarcane in the sugarcane mills as demonstrated in Figure 2.6. It proves to be a very efficient raw material in the production of renewable energy. In comparison with the other agricultural crop residues, sugarcane bagasse is the most abundant and high-yielding material. In general, 1 ton of sugarcane generates 280 kg of bagasse. About 54 million dry tons of bagasse are produced annually throughout the world. In South Africa, approximately 6 million tons of raw bagasse are produced annually (Wazeer, 2017). Most large and medium-sized mills can use up to 75% of this bagasse onsite to generate heat and electricity. Sugarcane bagasse proves to be a great source of fuel for the downward gasifier to produce electricity. Sugarcane bagasse is one of the most important lignocellulosic, or plant biomass, materials utilized in the field of power generation. Lignocellulosic materials do not contain readily accessible monosaccharides and chemicals, but rather polymers that need to be hydrolyzed to release the desired compounds. Lignocellulosic material is determined by its fibrous nature and the structural framework of

which the plant cell is composed. Figure 2.5 illustrates a simplified structure of bagasse. Bagasse has its ash content and a correspondingly high heating value of the order of 4400 Kcal/kg (Ganeshraj et al. 2015).

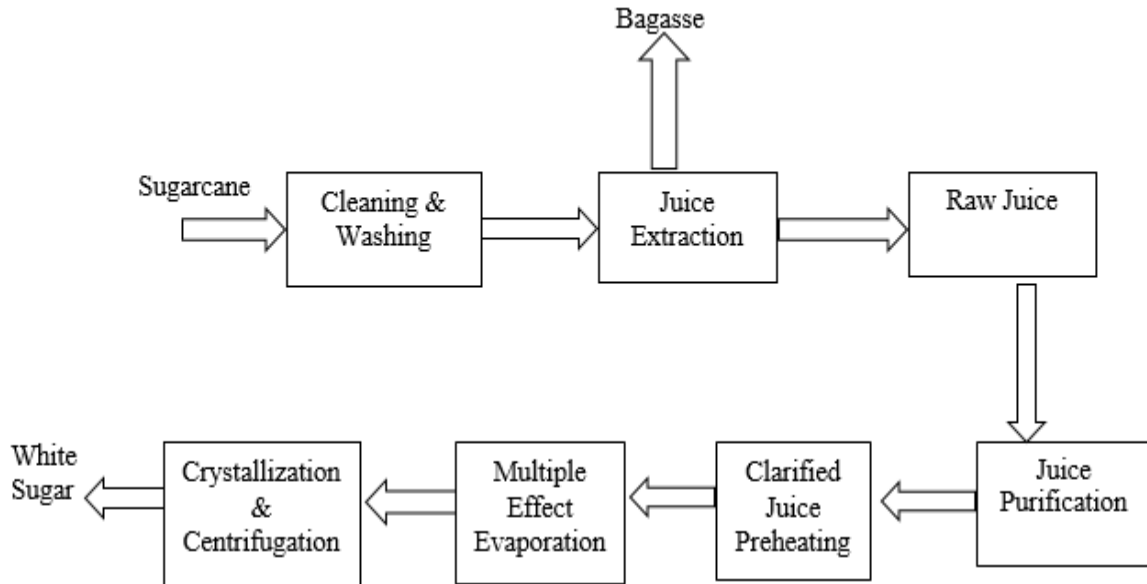


Figure 2.6 A simplified process diagram for the generation of sugarcane bagasse (Wazeer, 2017)

2.4.1. Composition of Sugarcane Bagasse

Sugarcane bagasse is a fibrous material consisting of the framework of plant cell walls. The main composition of sugarcane bagasse consists of carbohydrates obtained from two types of polysaccharides, namely cellulose and hemicellulose, lignin, protein, and moisture.

- Carbohydrates: The major source of carbohydrates in sugarcane bagasse is cellulose and hemicellulose.
- Cellulose: It is the most abundant constituent and is a homo – polysaccharide composed entirely of β -1, 4 - glucosidic linked glucose monomers. There is the formation of hydrogen bonds between and within the molecules i.e., inter and intramolecular hydrogen bonds due to the presence of linearity in the structure of cellulose. Approximately 50-90% of the total cellulose is crystalline, depending on the biomass source.
- Hemicellulose: It is the heterogeneous polysaccharide composed of D – xylose, D – glucose, D – mannose, D – galactose, D – arabinose, D – glucuronic acid, and 4 – O –

methyl – D – glucuronic acid (Walford, 2008). Bagasse hemicellulose is composed of a backbone of xylose, branched with glucose and arabinose units.

- Lignin: Lignin is a three-dimensional polymer with three different phenyl – propane precursor’s monomers: p – coumaryl, coniferyl, and sinapyl alcohols.
- Protein: The protein is determined as a nitrogenous compound.
- Moisture: It is one of the main contents of the sugarcane bagasse.

Table 2.2 Composition of sugarcane bagasse

Component (%)	Bagasse 1	Trash 2
Cellulose	41.1	39.8
Hemicelluloses	26.4	28.6
Lignin	21.7	22.5
Ash	4.0	2.4
Extractives	6.8	6.7

1. Average of measurements for South African bagasse.
2. Composition taken Oliveira et al., 2013

2.4.2. Calorific value of sugarcane bagasse

For measuring the heating value of biomass, two common equations are used to estimate this value. These are the Dulong equation and the Boie equation. The Dulong equation is given by:

$$HV \text{ (MJ/Kg)} = 33,823xC + 144,250 \left(\frac{H-O}{8} \right) + 9419xS \quad \text{Equation 2.1}$$

Where HV is the heating value of the material in MJ/kg, and C, H, O and S are the elemental mass fractions of the material as shown in equation 2.1 (Wazeer, 2017).

The Boie equation is given by:

$$HV \text{ (MJ/Kg)} = 35,160xC + 116225xH - 11090xO + 6,280xN + 10465xS \quad \text{Equation 2.2}$$

Where, C, H, O, N and S are the elemental mass fractions of the biomass material as presented in equation 2.2 (Channiwala and Parikh, 2002).

2.5. Production of Municipal Sewage Sludge

Municipal wastewater, or sewage, refers to water that has been used in urban and suburban areas for washing, bathing, and flushing toilets. Municipal wastewater may also include water from industrial sources. To remove chemicals or pollutants resulting from industrial processes, industrial contributors to municipal wastewater systems must pre-treat their wastewater before

it is discharged into the sewerage system. The wastewater is conveyed via the sanitary sewerage system to a centralized wastewater treatment plant (sometimes called a “publicly owned treatment works,” or POTW). At the POTW, the sewage passes through a series of treatment steps that use physical, biological, and chemical processes to remove nutrients and solids, break down organic materials, and destroy pathogens (disease-causing organisms) in the water. The rejuvenated water is released into streams and rivers or maybe sprayed over large areas of land (Stehouwer, 2010).

2.5.1. Treatment methods for municipal sewage sludge

There are four types of treatment that wastewater can be subjected to:

- Preliminary treatment – removal of grit, gravel, and larger solids.
- Primary treatment – settling out of any solid matter (removes approximately 60% of solids and approximately 35% of BOD).
- Secondary treatment – the use of digestate bacteria to break down organic substances (removes approximately 85% of BOD and solids).
- Tertiary treatment – disinfecting/denitrification of the treated effluent (to protect sensitive water environments from eutrophication).

Primary, secondary, and tertiary sludge is normally combined, and the resulting mixture, which contains from 1 to 4% solids, is called "raw" sewage sludge. Because of its pathogen content and its unstable, decomposable nature, raw sewage sludge is a potential health and environmental hazard. However, several treatment processes are now used to stabilize sewage sludge, decrease its pathogen content, and increase its solids content. Some of the more commonly used processes for stabilizing and reducing pathogen levels in sewage sludge are listed and briefly described in Table 2.3 (Stehouwer, 2010).

Table 2.3 Common methods for treating and stabilizing sewage sludge. Adapted from (Stehouwer, 2010).

Treatment method	Description	Effects on sludge
Thickening	Sludge solids are concentrated either by settling due to gravity or by introducing air, which causes sludge solids to float.	Sludge retains the properties of a liquid, but solids content is increased to 5 to 6%
Dewatering	<p>Several processes are used:</p> <ul style="list-style-type: none"> • air drying on sand beds • centrifugation • belt pressing (filtration) 	<ul style="list-style-type: none"> • Increases solids content to 15 to 30% • Air drying reduces pathogens • Centrifugation and filtration result in some loss of nutrients
Anaerobic digestion	One of the most widely used methods for sludge treatment. Sludge is held in the absence of air for 15 to 60 days at temperatures of 68 to 131°F. Anaerobic bacteria feed on the sludge, producing methane and carbon dioxide. In some treatment plants, the methane is collected and burned to maintain the treatment temperature.	<ul style="list-style-type: none"> • Increases solids content • Reduces odors • Decreases volatile solids • Decreases viable pathogens • Conserves plant nutrients
Aerobic digestion	Sludge is agitated with air or oxygen for 40 to 60 days at temperatures of 59 to 68°F. Aerobic bacteria feed on the sludge, producing carbon dioxide.	<ul style="list-style-type: none"> • Increases solids content • Reduces odors • Decreases volatile solids • Reduces viable pathogens • Some loss of nitrogen usually occurs
Alkaline stabilization	Sufficient alkaline material, most commonly lime (CaO), is added to the sludge to increase its pH to at least 12 for 2 hours. The pH must remain above 11.5 for an additional 22 hours.	<ul style="list-style-type: none"> • Decreases volatile solids • Reduces viable pathogens • Loss of ammonia (NH₃)

		<ul style="list-style-type: none"> • Phosphorus may be converted to forms not readily available to plants
Composting	Sludge is dewatered to increase the solids content to around 20%, then mixed with a high-carbon organic material such as sawdust. The mix is composted under aerobic conditions at temperatures of at least 131°F for several days during the composting process.	<ul style="list-style-type: none"> • Volume reduction of sludge • Reduces odors • Decreases volatile solids • Stabilizes organic matter • Eliminates most pathogens • Decreases plant nutrient value

Most of these processes are highly technical and have very specific requirements for variables such as holding time, temperature, pH, and solids content.

Typically, sewage water contains less than 0.1% solid matter. And once separated in the primary treatment, the resulting "sludge" contains organic matter, dead bacteria from the treatment process, and particulates. It is this biomass-rich sludge that can be processed in an HTC reactor (Bevan et al., 2020). Therefore, primary sludge is preferred over anaerobic-digested sludge. The selected sludge undergoes a pre-thickening process where the moisture content is 96.8% and total solids are 3.1%. The characteristics of municipal sewage sludge are shown in Table 2.4.

Table 2.4 Characteristics of municipal sewage sludge. Adapted from Gao et al., (2020); Tyagi & Lo (2013)

Parameter	Sludge Type		
	Primary Sludge	Activated sludge	Secondary sludge
Total dry solids, TS (%)	2-9	6-12	0.8-1.2
Volatile solids, VS (%)	60-80	30-60	59-68
Grease and fats (%)	7-35	-	5-12
Protein (%)	20-30	15-20	32-41
Cellulose (%)	8-15	8-15	7-9.7
Phosphorus (%)	0.8-2.8	1.5-4	2.8-11
Nitrogen (%)	1.5-4	1.6-6	2.4-5
Potassium (%)	0-1	0-3	0.5-0.7
pH	5-8	6.5-7.5	6.5-8
Energy MJ/kg	23-29	-	19-23

2.5.2. Efficient methods of sludge to energy recovery

The importance of energy recovery in contemporary waste management practices remains assured due to its impact on global waste minimization, resource optimization, and alternative energy generation. Focus energy conversion technologies have been highlighted in Figure 2.7, which shows the conversion pathways of sludge to syngas, liquid fuel, chemicals, heat, and/or electricity.

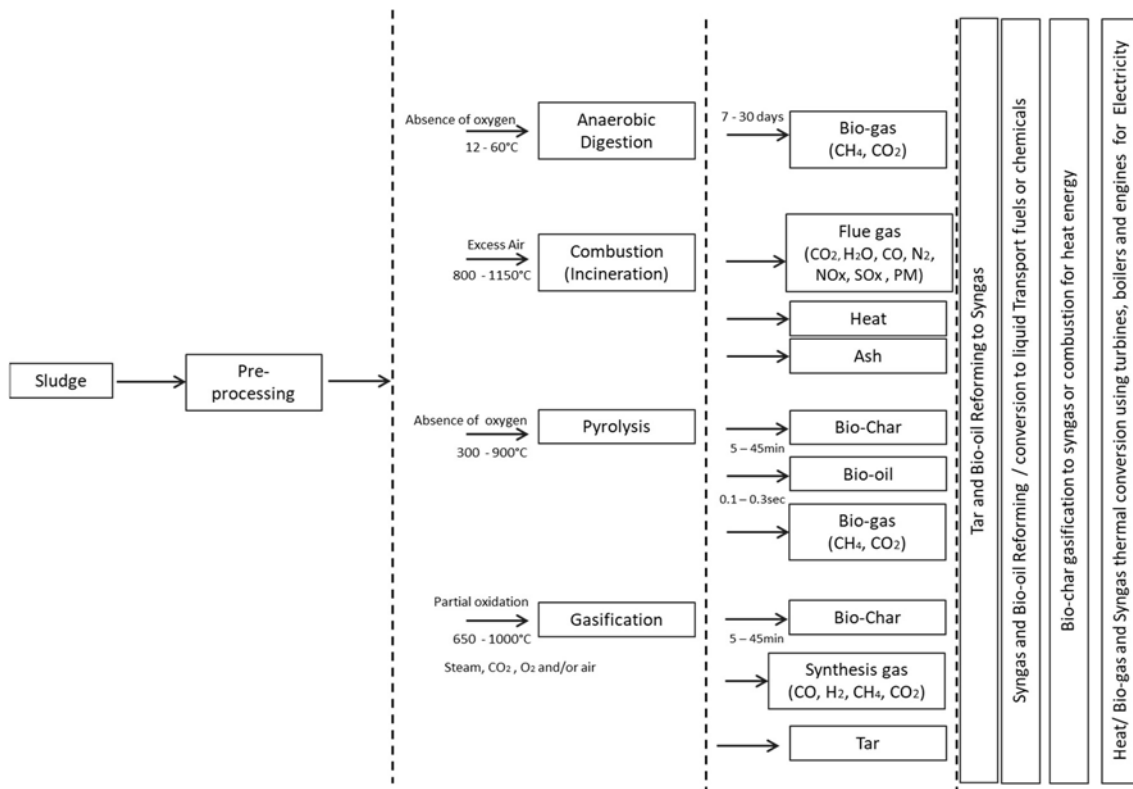


Figure 2.7 Potential Sludge-to-Energy Recovery Routes. Adapted from (Seiple et al., 2017; Syed-Hassan et al., 2017; Magdziarz et al., 2016; and Mulchandani & Westerhoff, 2016) Anaerobic digestion is a biological conversion method that is widely used due to its low cost and ability to utilize organic waste with high moisture content without reducing the high calorific value of the produced biogas (a combination of methane and carbon dioxide). The biogas obtained from the digester can be cleaned and further upgraded to produce bio-methane, which can be a direct substitute for natural gas, or the biogas can be converted to heat and electricity via cogeneration using thermal reactors. Biochemical processes traditionally occur in an inert environment at mesophilic temperatures for sludge stabilization with process residues used for agricultural purposes (Syed-Hassan et al., 2017; and Ruffino et al., 2017). However, the reaction time is long, with a duration ranging from 7 days to 5 weeks, and the conversion efficiency of organic matter is low, with 40–70% of organic constituents unconverted after reaction completion. This results in digested sludge with poor biodegradability and high organic content diverted for agricultural applications, which is inappropriate.

On the other hand, thermochemical conversion routes such as combustion, pyrolysis, and gasification are characterized by shorter reaction times, which range from seconds to minutes. Unfortunately, these processes require sludge with lower moisture content, and the drying of sludge requires enormous energy inputs. The rapid and controlled decomposition of 80% of

the organic matter in inert, partially oxidizing, or oxidizing atmospheres is one of the main benefits of these thermal processes in comparison to anaerobic digestion (Ruffino et al., 2017).

2.6. Wastewater Sludge (primary sludge)

A direct and easily overlooked consequence of increasing waste globally is the escalating volume of urban wastewater, especially sewage sludge (Oladejo et al., 2018). Sludge can be described as any solid, semi-solid, or liquid waste generated by a wastewater treatment facility. This waste can be sourced from municipal, commercial, or industrial processes. The solid phase in sludge is made up of a homogenous mix of proteins, carbohydrates, oils, inorganic matters, and micro-organisms. This combination of organic, inorganic, and living organisms produces an unstable, volatile, and putrid matter containing toxic elements. Its volatile organic contents, range from 21-48%, and the energy content of dried sewage sludge reported in past literature varies between 11.10-22.10 MJ/Kg which indicates higher calorific values in comparison to lignite and various biomass samples (Oladejo et al., 2018). This heating value is one of the core determinants of the suitability of sludge as a solid fuel, as well as the need to effectively eliminate the high organic matter from sludge before disposal. Energy recovery from sludge is regarded as the most attractive for utilizing the increasing quantity of sludge for eliminating volatile organic matter, reducing waste volume with the possibility of recovering nutrients, and providing bioenergy.

2.6.1. Composition of Wastewater Sludge

Sludge has been detected to be composed of high-water content, potentially toxic elements (PTEs) such as cadmium (Cd), chromium (Cr III and Cr VI), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn), organic pollutants, pathogens and microbiological pollutants. These heavy metals are mostly pollutants from physiochemical and biological processes such as industrial waste, corrosion in pipelines, food, medicine, textile materials, and cosmetics. Other pollutants of interest are metalloids, arsenic, selenium, and the metal silver. The sources of metal pollution in the wastewater system can be classified into three main categories:

- Domestic,
- Light industrial (connected to the WWTS) and commercial,
- Urban runoff (which also encompasses lithospheric and atmospheric sources).
(Thornton et al., 2001)

The typical elemental analysis of sewage sludge with a moisture content of 75.8% according to Prestigiacomo et al. (2019) is presented in Table 2.5.

Table 2.5 Elementary analysis of sewage sludge. Adapted from Prestigiacomo et al. (2019)

Elemental Analysis	Value
C (wt. %)	43.39
H (wt. %)	6.48
N (wt. %)	5.04
S (wt. %)	0.86
HHV (MJ/kg)	16.13
Cd (mg/kg)	<0.1
Cu (mg/kg)	150
Ni (mg/kg)	17.4
Pb (mg/kg)	55.4
Zn (mg/kg)	331
Hg (mg/kg)	<0.1
Cr (mg/kg)	24.3
Organic content	89.1

Figure 2.8 demonstrates a summary of the various inputs, outputs, and pathways followed by water and associated contaminants from both natural and anthropogenic sources encountered in urban environments (Thornton et al., 2001).

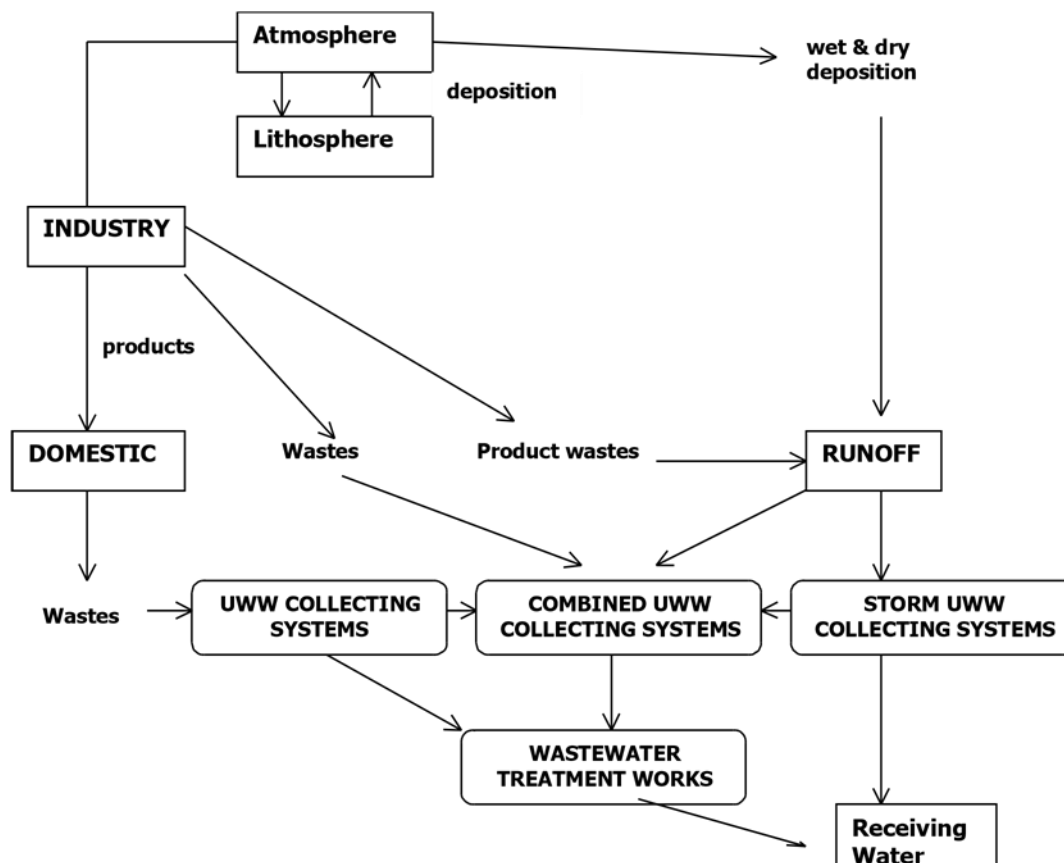


Figure 2.8 Sources of pollutants in wastewater (Lester, 1987)

2.6.2. Wastewater Sludge Disposal Practice in South Africa

The statistics regarding the use and disposal of wastewater sludge were presented by Snyman (2007). Half of the approximately 970 wastewater treatment plants in South Africa treat less than 500 m³/day (less than 0.5 Ml/day) and a further 11% treat between 500 and 2000 m³/day. There is little information on the sludge handling practices of these small plants, although it is suspected that most of the sludge is accumulated on-site. A survey of 72 wastewater treatment plants (Snyman et al., 2004) which focused mainly on plants larger than 2000 m³/day revealed that most of the sludge that is used or disposed of is anaerobically digested sludge (primary and humus sludge). Final disposal methods employed by the wastewater treatment plants surveyed in South Africa are still dominated by on-site disposal methods. This includes direct land application and stockpiling of the sludge on-site (Snyman and Herselman 2006). Therefore, alternative methods of utilizing sludge as a renewable source of producing bioenergy are of great importance.

2.7. The Importance of Binders on Biocoal Pellets

Several studies using different pre-treatment methods and binders have been conducted to address pellet quality using various feedstocks (Lu et al. 2013; Agu et al. 2017; Emadi et al. 2017; Soleimani et al. 2017; Tilay et al. 2015; Kaliyan and Morey 2006). According to Emadi et al. (2017), binders in pellets are employed to improve binding, lubrication, and abrasion characteristics by forming a matrix that improves intermolecular bonding within the contact area of the biomass during pelletizing. A binder can be in liquid or solid form to facilitate strong inter-particle bonding. Many types of binders have been investigated and applied at different densities of biomass. The selection of a binder additive in any process is dependent on the binder-temperature reaction (Yoo and Jo 2003). Also, during binding reactivity, preheating or steam conditioning is important to add heat and moisture to activate the added binder; the choice of binder depends on cost and environmental sustainability (Kaliyan and Morey 2006). Tumuluru et al. (2011) reported that binders reduce the wear on production equipment and increase the abrasion resistance of the fuel. According to Tarasov et al. (2013) on EU standards, binder additives that improve fuel quality, decrease emissions, or improve burning efficiency constitute a maximum of 2% of the total mass of the biomass pellets.

Binders can be categorized into three types:

- Organic binders such as molasses, corn or potato flour, maize, and rye flour; bio-solid, microalgae, walnut, and peanut shell, woody plants, coffee meal, bark, hydrothermal carbonize biochar, softwood residue, and sawdust.
- Inorganic binders include lignosulfonate, recycled polymer plastic, bentonite, colloids, lubricant, sodium hydroxide, calcium hydroxide, potassium hydroxide, dolomite, lime, cement, and alkaline lignin; and
- Complex binder like coal tar residue (Soleimani et al. 2017; Yoo and Jo 2003; Lu et al. 2013; Kaliyan and Morey 2006; Emadi et al. 2017).

Organic binders can be classified as biological additives which are rich in starch content, free of ash and unwanted elements like nitrogen and sulfur, two elements that can be sources of gas emissions. Inorganic and complex binders are referred to as "commercial binders" and are rich in minerals like lignosulfonate (a water-soluble anionic polyelectrolyte polymer) or bentonite (clay) or coal tar residue (coal). The main advantage of using inorganic binders in biomass pellets is that they achieve satisfactory mechanical strength (Kaliyan and Morey 2006; Tarasov 2013). The complex binder can improve the mechanical strength and calorific value of pellets

while reducing the energy consumed during the granulation process. The disadvantage is environmental pollution. There is an insufficiency of research studies on the pollutant emission performance of biomass pellets with coal tar residue as a binder (Si et al. 2017). As a result, in this study, calcium hydroxide Ca(OH)_2 is preferred over other binders because it can improve mechanical strength, promote combustion performance, and exhibit acceptable moisture uptake (Hu et al., 2015).

2.7.1. Densification

Densification of biomass is accomplished by applying mechanical force to compact biomass into uniformly sized solid particles such as pellets, briquettes, logs, and cubes (Veal 2010; Chen et al. 2015). A densification process may be achieved through palletization (Veal 2010). The palletization process shows high productivity, density, strength, and pellets formed from herbaceous biomass that do not have enough strength due to a lack of natural binding components between the particles. Utilization of such pellets will be expensive, dusty, and difficult to manage (Lu et al. 2013). Densification aims to increase bulk density, improve storability, lower handling, and transportation costs, and lower the moisture content of biomass (Mani et al. 2003; Chen et al. 2015). In addition, the densification process is affected by material properties (e.g., particle size, shape, moisture content, and composition) and processing conditions (e.g., compressing speed, temperature, pressure, and die size and shape) (Hu et al., 2015). Generally, the densification of herbaceous biomass depends on the strength and durability of the particle bonds, and these are the main desirable parameters used to describe biomass pellets (Tumuluru et al. 2011; Agu et al. 2017).

Densification of biomass into the compacted regular-shaped product(s) like pellets, briquettes, or cubes is one of the optimal solutions and has aroused a great deal of interest worldwide in recent years as a most efficient technique in improving the logistics of biomass. Densification of agricultural (straw and grasses) and woody (chips) biomass into pellets can increase the bulk density from 40-200 to 600-800kg/m³ (Kaliyan & Vance Morey, 2009). Thus, the process can significantly reduce the overall transportation and handling costs associated with the biomass processing industry (Kambo, 2014). Densification in combination with thermal pre-treatments like torrefaction is often proposed as an alternative to improve the physicochemical properties of biomass (Bergman, 2005; Pimchuai et al., 2010).

2.8. Thermochemical Energy Conversion Processes

As global energy demands grow exponentially with time, the number of research projects into various large-scale biomass processes also increases. Biomass is being converted into a renewable energy source through the global application of numerous industrial technologies and processes as shown in Figure 2.9. Besides thermal conversion of biomass (combustion), there are currently three main process technologies available: bio-chemical, thermo-chemical, and physio-chemical. Bio-chemical conversion encompasses two primary process options: anaerobic digestion (to biogas) and fermentation (to ethanol), where enzymes or microorganisms break down the biomass into liquid fuels. The physiochemical conversion consists principally of extraction (with esterification), where oilseeds are crushed to extract oil. Thermochemical conversion processes include gasification, pyrolysis, and hydrothermal carbonization (wet pyrolysis). The main reason behind the recent interest in bioenergy production is the potentially unlimited supply of biomass available due to its renewability. Thus, biomass is the only naturally occurring carbon resource that is available in large enough quantities to substitute for the world's primary energy-containing resources (fossil fuels) (Bevan et al., 2020).

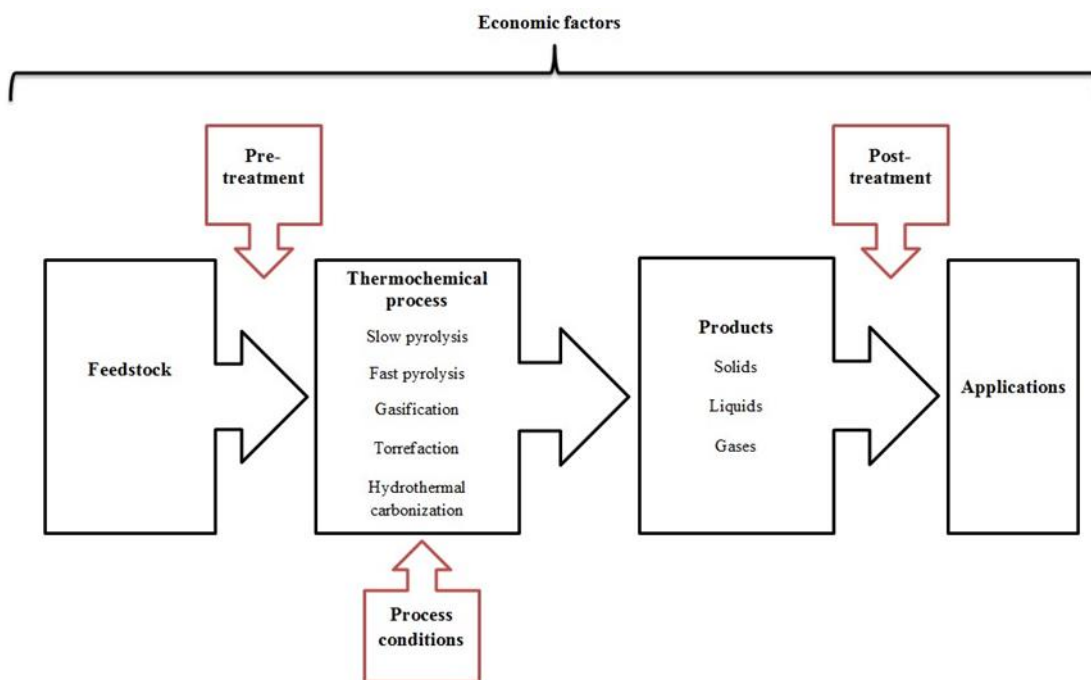


Figure 2.9 Factors influencing the production and application of char. Adapted from Libra et al., 2011

The research presented in this review literature first details the different thermochemical processes alongside the possible reaction mechanisms that occur in the reactor. But the focus is hydrothermal carbonization (HTC), which was first studied by Friedrich Bergius (1913).

2.8.1. Conventional Pyrolysis

This process describes the thermal decomposition of organic material under anaerobic conditions. During a pyrolysis operation, the biomass feed decomposes under high temperatures and pressures to produce an energy-dense and carbon-rich stream (Bevan et al., 2020). Slow pyrolysis is a process that has been traditionally used for thousands of years to produce charcoal. Organic material is heated over relatively long periods at temperatures of around 400°C. Slow pyrolysis is more tolerant at a moisture content of 15–20%. The main yield is solid char, although tar-like substances and gases are also produced (Demirbas & Arin, 2002). Reaction temperatures and residence times can be adjusted to promote the desired product yield. In general, lower temperatures and longer residence times will yield higher amounts of solid products. As temperatures rise and residence times decrease, higher yields of gaseous and liquid products are achieved (Michael Child, 2014). However, the main concern associated with slow pyrolysis is the effect of longer residence time on the process energy requirement.

2.8.2. Fast Pyrolysis

Fast pyrolysis involves rapid heating (500 °C–1000 °C) and devolatilization of organic fuels by thermochemical processes in the presence of little or no oxygen. The products of the process are primarily small amounts of char and relatively large amounts of vapour, which contain tars and volatile gases that are rapidly quenched into liquid form. These liquids can then be further refined as useful fuels (Michael Child, 2014).

2.8.3. Gasification

Gasification is similar to pyrolysis in that it involves the heating and devolatilization of organic fuels. In this case, enough oxygen is present so that partial combustion may occur. Temperatures remain high (approximately 800°C) throughout the process to encourage high yields (up to 85%) of gaseous products, or syngas, which are typically used directly. Alternatively, they can be purified and used as gaseous fuels, such as synthetic natural gas (SNG), or in the subsequent production of liquid fuels. As temperatures are generally higher

than during pyrolysis and residence times are generally short (10-20 seconds), gasification yields very little char (10%) and even less liquid product (5%) (Libra et al., 2011).

2.8.4. Torrefaction

Torrefaction is a thermal process that involves the processing of biomass in a torrefied to produce a "charred" product that can be used as a fuel. Torrefaction is the heating of an input material within an engineered reactor where heat is added from an external fuel source that is directly or indirectly applied to the input biomass undergoing conversion into a "torrefied product" (Barskov et al., 2019). It is also known as "mild pyrolysis" and occurs at relatively low temperatures (200–300 °C) over moderate residence times (1-3 hours). Importantly, the torrefaction process begins with stages of initial heating, pre-drying, post-drying, and intermediate heating designed to facilitate evaporation of water and attain a target torrefaction temperature. These stages may involve the consumption of external energy or the auto-consumption of gaseous products to generate heat. The main products of torrefaction are fairly high levels of char (70%) and torrefaction gas (30%). It can yield char that has an improved mass and energy balance over the original feedstock, resulting in improved heating values (Michael Child, 2014).

2.8.5. Hydrothermal carbonization Process

Hydrothermal carbonization (HTC) is a thermochemical conversion technique that uses sub-critical liquid water as a reaction medium for the conversion of wet biomass and waste streams into a valuable carbon-rich solid product called biocoal. Figure 2.10 demonstrates the schematic of the HTC reactor. Biocoal is a stable, hydrophobic, friable solid product that has a fuel value similar to that of lignite coal. It is usually performed at temperatures ranging from 180°C to 280°C, at pressures slightly higher than water saturation pressure to ensure water is in a liquid state, and under an inert atmosphere (Reza et al. 2014). HTC temperatures aid the decomposition of biopolymers and the reformation of new compounds. The metamorphosis starts at 100 °C with the dissolution of water-soluble compounds, followed by hydrolysis where monomeric bonds are broken-this occurs at temperatures greater than 150°C (Durak & Genel, 2020). Reactions occur within the first 20 min to several hours (1–12 hrs). Reaction time plays a role in increasing carbon and ash content while decreasing oxygen (Libra et al. 2011). Wet biomass and water may be used in this process. During hydrothermal pre-treatment, hemicelluloses and cellulose are hydrolyzed into oligomers and monomers, while lignin is mostly unaffected.

The HTC process has increased recently because of its many advantages (general technological simplicity, versatility, and applicability to wet feed to yield a fuel with properties comparable to lignite). The main advantages of HTC over other thermochemical conversion technologies (such as pyrolysis, gasification, and incineration) are its ability to convert wet feedstock to become carbonaceous solid products (hydrochar) at relatively high yields without preliminary dewatering and drying (Libra et al. 2011; Lu et al. 2012) and, consequently, requiring less energy. The energy required for the HTC process is expected to be substantially lower than that required for pyrolysis of such wet feedstock (moisture content of 75–90%) (Libra et al. 2011).

HTC technology provides a sustainable and eco-friendly approach to producing biocoal from wastewater sludge and bagasse. This process is cost-effective (costly drying processes are not required), environmentally friendly (net CO₂ emissions released to the atmosphere are reduced), and capable of producing biocoal with characteristics approaching those of low-rank natural coal. HTC products are mostly in the solid phase, accompanied by gaseous (mainly CO₂) and aqueous (containing bio-oil) by-products. The percentage and properties of final products of HTC processes are affected considerably by process conditions, mainly temperature, which is the main parameter (Roman et al., 2018).

HTC has been applied to a great variety of lignocellulosic biomass, with variable composition in hemicellulose (20–40%), cellulose (40–60%), and lignin (10–25%), and non-lignocellulosic ones, such as animal manure, food, sewage sludge, and municipal solid wastes, among others, which have significant differences in composition (Martínez, 2019). The most important advantages of this technology are:

No previous waste drying requirement.

1. Reduction of waste volume to landfills (90-95%) (Munir et al., 2017).
2. High stability of treated feedstock.
3. Improvement of cost-effectiveness compared to conventional thermal drying.
4. Obtaining hydrochar with high energy density.
5. Decrease nitrogen content by 50%, reducing NO_x emission compared with feedstock combustion (Zhao et al., 2014; and Zhao et al., 2013).
6. Efficient pelletization compared to biochars, diminishing transport cost and handling difficulties (Reza et al., 2012).

7. Improvement of surface properties of hydrochar by chemical activation (Jain et al., 2016; and Saqib et al., 2018).

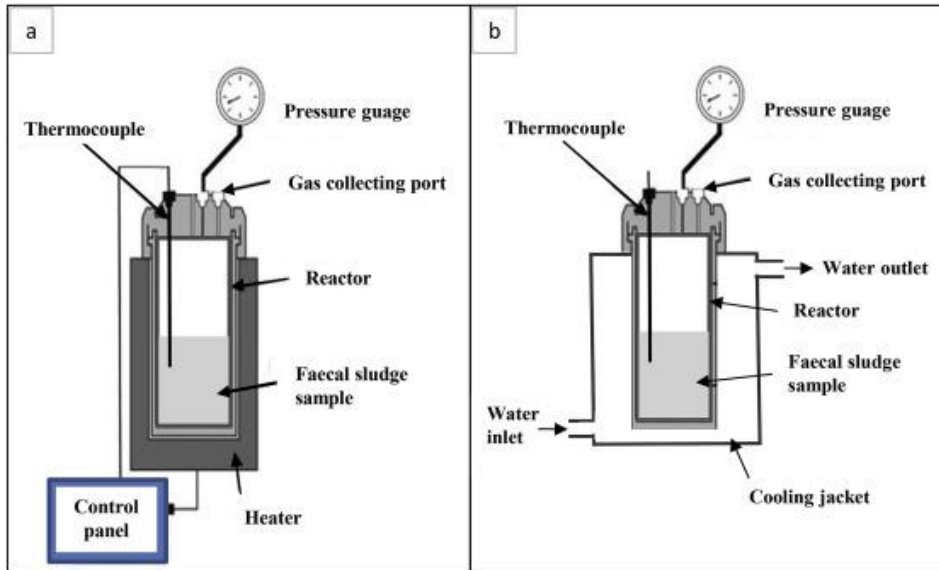


Figure 2.10 Schematic of HTC reactor: (a) heating system; (b) cooling jacket. Adapted from (Fakkaew et al., 2015).

Table 2.6 Comparison of thermochemical treatments and typical product yields. Adapted from Michael Child, 2014

Process	Process conditions						Approximate product yield (weight %)		
	Temperature range (°C)	Heating rate	Residence time	Pressure	Surrounding medium	Cooling rate	Char	Liquid	Gas
Slow pyrolysis	250-450	Slow _b	Hours to weeks	Low _c	Little or no O ₂	Slow	35	30	35
Fast pyrolysis	450-550	Fast _b	Seconds	Variable _c	Little or no O ₂	Rapid	12	75	13
Gasification	900-1500	Fast _c	10-20s	Variable _c	Lightly reducing atmosphere	-	<10	5	>85
Torrefaction	200-300	Moderate _a	Several hours _a	Atmospheric _a	Little or no O ₂ _a	None _a	70 _a	0 _a	30 _a
Hydrothermal carbonization	180-250	Moderate	No vapour residence time. processing time from minutes to several hours	High Autogenous	Water	Slow	50-80	5-20	2-5

All values are approximations provided by Libra *et al.* (2011) unless denoted otherwise.
a (Van der Stelt *et al.*, 2011) b (Demirbas & Arin, 2002) c Values are highly variable and depend on the desired distribution of product yield. Values expressed are generalizations by the author.

In the 21st century, research on biomass being converted into a renewable energy source through the global application of numerous industrial technologies and thermochemical processes is being conducted as shown in Table 2.6. Cruz (2012) assessed the slow pyrolysis of different biomasses (maple wood and birch bark) to produce a solid pyrolysis product (biocoal) with promising properties and potential use in traditional fossil-coal applications. Batch pyrolysis experiments were carried out in a Mechanically Fluidized Reactor (MFR) having an inside diameter of 9 cm, a height of 13 cm, and a volume capacity of 815 ml. Experiments were conducted at various reaction temperatures (143 °C, 190 °C, 238 °C, 285 °C, 333 °C, 380 °C, 428 °C, 475 °C, 570 °C, and 665 °C), with a heating rate of 12 °C/min and holding times of 30, and 50min.

The results showed a decrease of 35% in mass yield between 190 and 238 °C, followed by a decrease of 26–21% between 238 and 285 °C. At 285 °C, the biocoal mass yield decreased by 6 % to 3 %, reaching a final value of 22.3% at the highest evaluated reaction temperature of 665 °C. The decrease in biocoal mass yield resulted from the fact that further reactions occurred at an increased holding time of 30 to 50 min. The effect of reaction temperature on the high heating value (HHV, on a dry basis) of the biocoal produced with a holding time of 30 min showed that HHV increased with reaction temperature up to 380 °C, while the percentage energy recovery in the biocoal (i.e., energy yield) decreased with increasing reaction temperature. Energy recoveries for biocoal produced at 238 and 665 °C were 83.7% and 32.8%, respectively. The biocoal produced was characterized by ultimate (elemental) analysis, ash analysis, calorific analysis (high heating value), Fourier transform infrared spectroscopy (FTIR), and hygroscopicity. All tests were done after pre-drying samples for over 2 hours in an oven at 100 °C.

Fialho et al. (2019) also investigated the potential use of four agroforestry biomasses (sugarcane bagasse (*Saccharum sp.*), bamboo (*Dendrocalamus giganteus*), straw bean (*Phaseolus vulgaris*), and eucalyptus wood chips (*Eucalyptus sp.*)) to produce biocoal. The pyrolysis of biomass was conducted in an electric laboratory oven using a container with approximately 0.003 m³ volume capacity. The heating control was conducted manually in increments of 50 °C every 30 minutes, which corresponds to an average heating rate of 1.67 °C/min. The initial reaction temperatures were 100 °C, with the final temperatures being 400, 550, and 700°C. Findings revealed that at 700 °C bamboo and eucalypts biocoal had the highest heating values, 30.43 and 29.33 MJ.kg⁻¹ whereas sugarcane bagasse and straw bean had the

lower heating values, 27.37 and 28.25 MJ.kg⁻¹, respectively. It was observed that bamboo and eucalyptus contained high lignin content, which resulted in them having a high heating value when compared to the other biomasses. Cheng et al. (2020) also recorded high heating values (25.4 to 28.2 MJ.kg⁻¹) of biocoals from representative biomasses that were comparable to those of commercial coals. Five common renewable biomass wastes (rice husk, sawdust, wheat straw, bagasse, and soybean straw) were selected as representatives to produce biocoals. The renewable biomass was first fast pyrolyzed at 500°C in an anaerobic atmosphere in a quartz tubular reactor to produce bio-oil and biochar. Then, the bio-oil was distilled under an air atmosphere from room temperature to approximately 240°C to obtain the liquid chemicals and biocoal. Results demonstrated the five types of biocoals obtained from the different biomass wastes exhibited yields derived from the bio-oil of 45.2, 37.2, 33.9, 41.8, and 34.3%, respectively. In addition, the estimated mass-energy densities of the rice husk, sawdust, wheat straw, bagasse, and soybean straw-derived biocoals were 25.4, 28.0, 28.2, 26.3, and 27.6 MJ.kg⁻¹, respectively.

Muhammad et al. (2020), developed a modified vacuum pyrolysis reactor to convert sugarcane bagasse to syngas. The pyrolysis of bagasse was conducted in a stainless-steel fix batch reactor (lab-scale reactor) using a modified-vacuum pyrolysis reactor. Experiments were conducted at reaction times (20, 30, 40, 50, and 60 min) and reaction temperatures (210, 230, 250, 270, and 290 °C). An electromagnetic field was applied as a function of current, starting from 1, 2, 3, 4, and 5 Ampere (A) in the second method. The results showed that 0.12 ng/μL, 0.85 ng/μL, and 0.31 ng/μL of hydrogen (H₂), carbon dioxide (CO₂), and carbon monoxide (CO) gases, respectively, started forming in the first 20 min at 210°C. At 60 min and 290 °C 20.98, 14.86, 14.56, and 15.78 ng/μL of H₂, CO₂, CH₄, and CO were generated, respectively. The application of electromagnetic field demonstrated a significant improvement, in which applying current 3A improved the gas product to 33.76, 8.71, 18.39, and 7.66 ng/μL of H₂, CO₂, CH₄, and CO, respectively, with an H₂/CO ratio above 2.

Research by (Manyuchi et al. 2019) to produce a high calorific value biocoal from sugarcane bagasse as an alternative use of coal was experimentally investigated using a stainless-steel reactor with a length of 200 cm and a width of 150 cm. Bagasse was subjected to carbonization at 250-400°C for 1-7 days. The findings indicate that the amount of ash content in the biochar produced significantly decreased by about 69%. The amount of moisture content in the biocoal decreased as high as 49%. As the carbonizing temperature increased from 250 °C to 400 °C,

the fixed carbon content in the biochar increased by 385%. The biocoal had a calorific value of 28.2 MJ/kg, moisture content of 6.3%, a fixed carbon of 74.6%, and an ash content of 1.4%. The biocoal also had carbon dioxide and carbon monoxide emissions of less than 0.9% and 0.02% respectively.

Tan et al. (2017) used microwave-induced torrefaction to synthesize and characterize biocoal from lemongrass (*Cymbopogon citrates*) residue. A modified benchtop microwave oven (model R374AST, Sharp, Malaysia) was purged with nitrogen gas to maintain an inert environment as well as to prevent combustion (Kambo and Dutta, 2014; Kishor et al., 2014). The microwave power level (100, 300, 500, 800, and 1000 W) and reaction time (30 and 40 min) were varied to obtain the desired torrefaction temperature. Findings revealed that changes in elemental composition were most significant at a torrefaction temperature of 300°C. The C content increased by 0.49, 2.29, and 3.96%. At torrefaction temperatures of 200, 250, and 300 °C, H content decreased by 3.12, 8.77, and 8.92%. The O content also experienced a reduction in amount by 2.08, 1.84, and 58.79%, respectively, at the three torrefaction temperatures, studied. A high heating value of 19.37 MJ/kg was achieved by lemongrass residue torrefied at 300°C. The H/C and O/C ratios were reduced by 14.3% and 60.0%, respectively. Mass and energy yield of the torrefied lemongrass residue was 61.20–81.50% and 66.11–83.85%, respectively.

In the study of processing and valorizing elephant dung by torrefaction to produce fuel with improved qualities for cooking. Stepien et al., (2019) conducted lab-scale experiments at six different temperatures (200, 220, 240, 260, 280, and 300°C), and three process durations of torrefaction (20, 40, 60 min) using a muffle furnace (Snol, model 8.1/1100, Utena, Lithuania) with CO₂ gas supplied to the furnace, ensuring non-oxidative conditions occur. Results showed a downward trend in the mass yield (MY) for elephant dung biocoal with the increase in process temperature. The highest mass yield value of 90% was obtained at 200°C. The lowest MY value of 66% was achieved at 300°C. In this case, the mass yield decreased. The energy yield (EY) of the biochar from elephant dung also decreased with the increase in temperature and did not change with time. When compared to raw material, the biocoals produced at 200 °C yielded more than 105% EY. However, the EY dropped below 68% due to torrefaction at 300 °C. The decrease in the HHV of the biocoals produced from the elephant dung was observed along with the increase in temperature and time. The highest average HHV_{daf} of 27.20 MJ.kg⁻¹ for the biocoal generated was obtained at 280 °C for 60 min.

Chen et al. (2012) analyzed the torrefaction of sugarcane bagasse at 200-300 °C for 1 hour using a reaction tube which was situated in a tube furnace. Nitrogen was continuously blown into the reaction tube to keep the samples in a non-oxidizing environment and to remove volatiles produced from the thermal degradation of bagasse. The flow rate of nitrogen was controlled at 100 mL.min⁻¹ (25 °C). Results from the research showed solid and energy yields go down with increasing heating time, and the solid yield is always lower than the energy yield. In examining the HHV, the value rises from 17.1 (raw bagasse) to 22.3 MJ/kg (torrefied at 290 °C). To produce torrefied pellets, Agar (2017) assessed European beech wood using a torrefaction temperature of 270 °C and a residence time of 40-45 min in a rotary-drum reactor. The data obtained revealed a low heating value of 18.28MJ/kg, moisture content of 5.0%, and an energy density of 12.84 GJ/m³.

Van der Stelt et al. (2011) investigated wood biomass upgrading by torrefaction to produce biofuels at a temperature range of 250-300 °C and a reaction time of 30-10 min. Thus, results showed that at 250 °C and 30 min, carbon 51.3%, hydrogen 5.9%, oxygen 40.9%, nitrogen 0.4%, ash 1.5%, and LHV 17.6 19.4 MJ/kg. At 300 °C and 10 min, carbon 55.8%, hydrogen 5.6%, oxygen 36.3%, nitrogen 0.5%, ash 1.9%, and LHV 21.0 MJ/kg, respectively. Kambo and Dutta (2015) assessed lignocellulosic biomass to produce a solid biofuel. The experiment was carried out in a reactor which consists of a small, perforated basket made of stainless steel fitted with a ceramic crucible attached to the balance to hold the sample at 260 °C with a heating rate of 10°C /min for 30 min. The reactor was continuously purged with nitrogen gas at a rate of 10 ml/min to maintain an inert atmosphere as well as to prevent the combustion of feedstock. Findings showed at 260 °C and 30 min, hemicellulose (%) 21.5 ± 3.1, cellulose (%) 36.2 ± 3.2, lignin (%) 35.1 ± 3.9 and ash (%) 0.94 ± 0.04.

Barskov et al. (2019) studied the torrefaction of three types of biomasses (agricultural wastes, food wastes, and non-Lignocellulosic wastes). The experiments were conducted at 200-350°C. The results showed that the energy yield for agricultural waste was 71.9%, the oxygen/carbon (O/C) ratio was 0.60, the hydrogen/carbon (H/C) ratio was 0.10, and the heating value was 21.1MJ/kg. Food waste has an energy yield of 78.2%, an oxygen/carbon (O/C) ratio of 0.49, a hydrogen/carbon (H/C) ratio of 0.23, and a higher heating value of 24.5 MJ/kg. The non-lignocellulosic waste energy yield was 83.3%, the oxygen/carbon (O/C) ratio was 0.61, the hydrogen/carbon (H/C) ratio was 0.13, and the heating value was 22.2 MJ/kg.

A study conducted by Van der Stelt et al. (2011) on biomass (wood) gasification in a circulating fluidized bed (CFB) at operating temperatures of 950-1200 °C and atmospheric pressure to avoid problems with ash softening and melting. Air was used as a gasifying medium. The steam was exported at 280 °C and 45 bar. Results showed that the integration of torrefaction and gasification resulted in higher energy efficiency than stand-alone gasification. Torrefaction at 300 °C integrated with gasification at 1200 °C conserves the highest amount of chemical energy in the product gas. Couhert et al. (2009) carried out gasification experiments using torrefied beech wood in an Entrained Flow (EF) reactor. It was confirmed that torrefaction reduces the O/C ratio in biomass, and the quality of syn-gas is improved. The gasification of torrefied wood produces 7% more hydrogen, 20% more carbon monoxide, and approximately the same amount of carbon dioxide as the original wood.

2.9. Hydrothermal Carbonization Experimental Procedure

Hydrothermal carbonization reactions were performed in a reactor at a temperature range of 1280–260 °C. A ratio variation of dry sludge and bagasse material was mixed with a constant capacity of deionized water. Biomass solid loading lowers the solubility of the feedstock, increasing hydrochar yield, carbon content, and calorific value. The mixture was then transferred into an HTC reactor. Reactions were conducted at a reaction time of 1 h. Reaction time plays a role in increasing carbon and ash content and decreasing oxygen (Libra et al. 2011). Thereafter, the reactor was removed from the heater and cooled to room temperature. The solid and liquid products were separated using a filter paper of Grade 1 qualitative circles. The solid product was air-dried for 30 minutes and then oven-dried at 100°C for 8 hours to ensure dewatering of the product (Kiran et al. 2019). Figure 2.11 demonstrates the HTC Conversion Processes of biomass to biocoal.

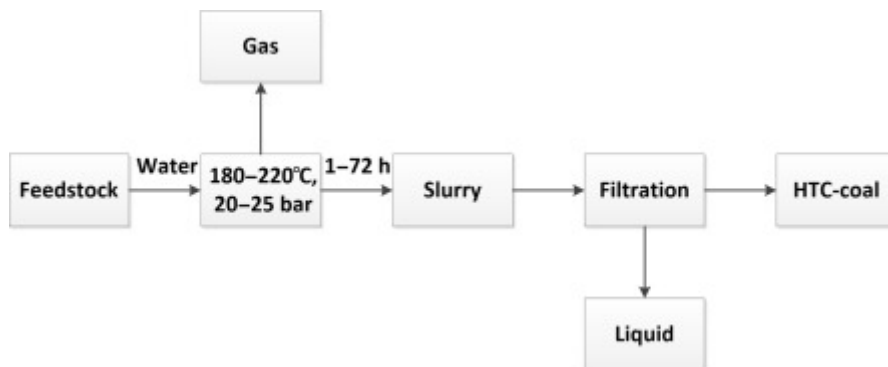


Figure 2.11 Hydrothermal carbonization process. Adapted from Kirtania, 2018.

2.10. Reaction Chemistry of Hydrothermal Carbonization Process

2.10.1. Hydrolysis

This is the first step of the HTC reaction, where water reacts with extractives, hemicellulose, or cellulose and breaks ester and ether bonds (mainly β -(1-4) glycosidic bonds), resulting in a wide range of products, including soluble oligomers like (oligo-) saccharides from cellulose and hemicellulose. Liquid water enters through surface pores and hydrolyses the components, after which the hydrolyzed products may proceed to exit through the same pore. Components like extractives, which are monomeric sugars (mainly glucose and fructose), along with various alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides, are very reactive in hydrothermal media. With increased reaction time, the oligomers further hydrolyze into simple monosaccharides or disaccharides. At HTC temperatures above 180°C, hemicellulose starts hydrolyzing, and cellulose hydrolysis starts above 230°C. Cellulose can degrade into oligomers, a portion of which hydrolyzes into glucose and fructose. The non-cellulolytic bacteria from the formed glucose produce hydrogen. The hydrolysis reaction pathway is shown in Figure 2.12. A very small portion of lignin reacts at a higher HTC temperature (200 to 260 °C) and releases phenol and phenolic derivatives. Furthermore, inorganic components are very stable and probably remain unchanged by HTC at 200–260 °C. However, the degradation of polymeric components might release inorganics from the solid structure into the liquid.

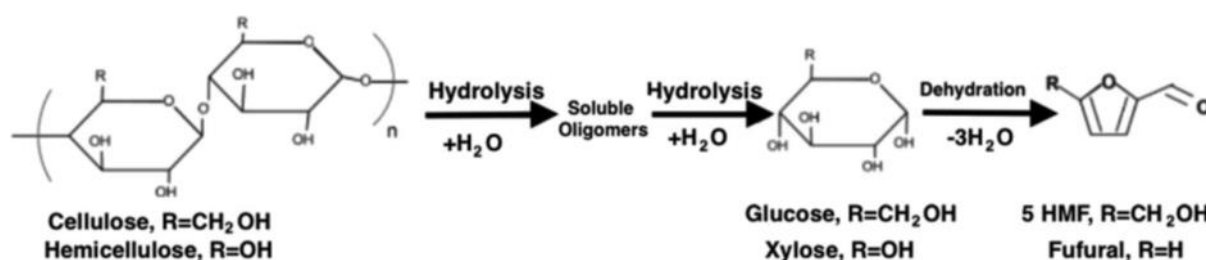


Figure 2.12 The hydrolysis reaction pathway from cellulose and hemicellulose to glucose and xylose. Adapted from (Bevan et al., 2020).

Dehydration and decarboxylation of hydrolyzed products likely take place immediately after hydrolysis and occur simultaneously. The reduction of carboxyl groups, mainly from extractives, hemicellulose, and cellulose, could be the main reason for the significant decrease in oxygen content. Under hydrothermal conditions, hydrolyzed products degrade into furfurals like 5-Hydroxyl Methyl Furfural (5-HMF), erythrose, and aldehydes, which further dehydrate and decarboxylate into CO_2 and H_2O .

2.10.2. Dehydration

This occurs in the HTC process as both residence time and temperature increase. Most macromolecules are made from single subunits, or building blocks, called monomers. The monomers combine via covalent bonds to form larger molecules known as polymers. In doing so, monomers release water molecules as by-products. This type of reaction is known as "dehydration synthesis," which means "to put together while losing water." It is also considered to be a condensation reaction since two molecules are condensed into one larger molecule with the loss of a smaller molecule (the water).

Dehydration of biomass is the formation of water molecules via the elimination of branched hydroxyl ($-OH$) groups, also known as dihydroxylation. This reaction produces hydrochar with a lower O/C and H/C ratio when compared to the feed and replicates the ratios present in natural coal. The ratio of O/C and H/C bonds is inversely dependent on the temperature, and more significantly so for O/C bonds. The products resulting from the hydrolysis of cellulose and hemicellulose are dehydrated to form 5-hydroxymethylfurfural (HMF) and furfural, respectively. At temperatures above $150^{\circ}C$ and $200^{\circ}C$, respectively, dehydration of water during the cleavage of both phenolic monomers and hydroxyl functional groups may occur during HTC (Bevan et al., 2020). The dehydration of catechol, formed from the hydrolysis of lignin, may also occur.

2.10.3. Decarboxylation

It is a chemical reaction that removes a carboxyl group and releases carbon dioxide (CO_2). Usually, decarboxylation refers to the reaction of carboxylic acids with carbon atoms, removing a carbon atom from a carbon chain. Degradation of carbonyl ($-C=O$) and carboxyl ($-COOH$) can be associated with the formation of carbon monoxide (CO) and carbon dioxide (CO_2), respectively. Carbonyl and carboxyl degradation occur rapidly at temperatures above $150^{\circ}C$ and produce minor concentrations of the gases mentioned previously. The carbonyl functional group is present on both 5-HMF and furfural molecules (Figure. 2.13), and the likely source of the carboxyl functional group is the formation of both formic acid and levulinic acid (the hydrolysis products of furfural and 5-HMF, respectively) (Bevan et al., 2020).

2.10.4. Aromatization

Lignin is naturally composed of many stable aromatic rings, as shown in Figure. 2.13. These aromatic structures exhibit high stability under hydrothermal carbonization conditions and are

the basic building blocks of the resulting hydrochar (Bevan et al., 2020). An experiment conducted by Bevan et al. (2020) measured the percentage mass of lignin in the raw biomass feed as 7%. Operating the pilot HTC reactor at 200°C for 1 and 6 hours, they found a percentage mass for pseudo lignin of 25.1 and 38.3%, respectively. Operating at 250°C for the same residence time found 44.4% and 58.3%, respectively. Therefore, conclusions have been drawn that the lignin-like substances that were formed (pseudo lignin) during HTC conditions resulted from the aromatization of cellulose and hemicellulose, despite there being linear carbohydrate polymer chains.

2.10.5. Carbonization

Carbonization is the conversion of an organic substance into carbon or a carbon-containing residue, in which the production of charcoal or char is the primary goal. Here, the biomass is heated slowly in the absence of air or oxygen at a relatively low-temperature range as shown in Figure 2.13. The process is conducted over an extended period. The carbonization temperature increase from 200 to 250 °C results in increased energy content of the produced hydrochar and the volatile matter (VM) content degrades while the fixed carbon (FC) content in the produced hydrochar increases (Fakkaew et al. 2015).

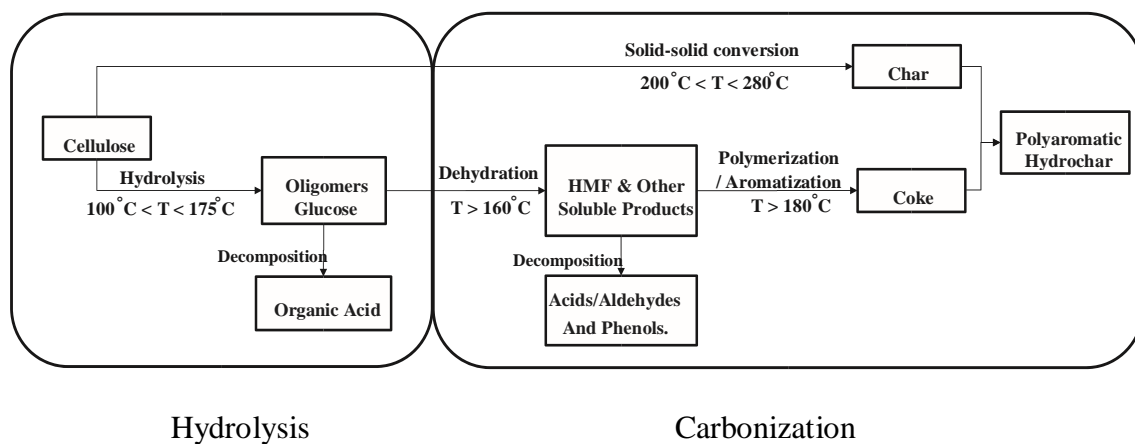


Figure 2.13 Two-stage HTC reaction pathways. Adapted from Fakkaew et al. 2015

2.11. Van Krevelen diagram

The Van Krevelen diagram presented in Figure 2.14 shows energy densification occurring at different temperatures (Kiran and Ross, 2019). The variation of the O/C and H/C atomic ratios indicates the degree of deoxygenation of biomass by decarboxylation, dehydration, or demethanation. The reduction of the O/C atomic ratio is mainly attributed to dehydration and decarboxylation, while that of the H/C atomic ratio is related to the dehydration and increased degree of aromatization. Materials with low O/C and H/C could avoid energy losses in combustion, so the closer a sample is to the 0 in the Van Krevelen diagram, the better fuel properties it has. The reduction of O/C and H/C atomic ratios illustrated the important improvements of hydrochar obtained by HTC through dehydration and decarboxylation. With an increase in the severity of the reaction (temperature and time), the produced biocoal samples move closer to exactly 0 on the van Krevelen diagram, and therefore have better thermal characteristics. Thus, the main reactions affecting the properties of biocoal are decarboxylation and dehydration (Khaskhachikh et al. 2019).

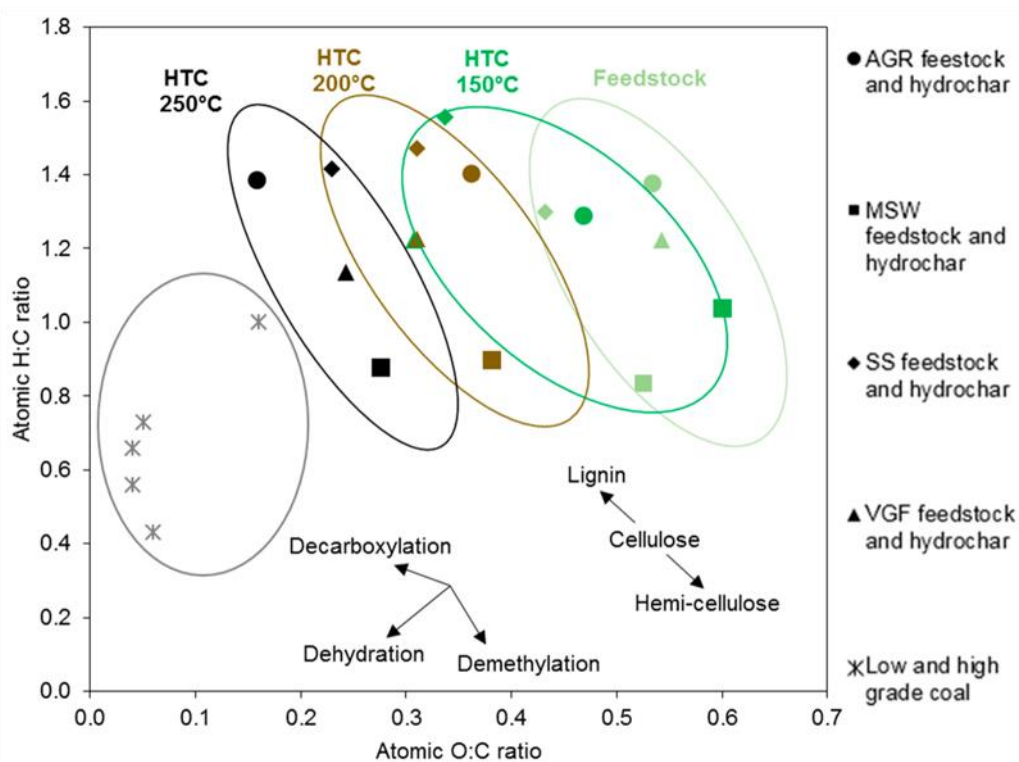


Figure 2.14 Van Krevelen diagram of hydrochar produced from various feedstock at 20% loading. Adapted from (Kiran et al., 2019).

2.12. The use of hydrochar

HTC technology is gaining attention for the potential applications of hydrochar in different fields, including soil amendment, water purification, energy storage, CO₂ sequestration, and catalysis, among others (Martínez, 2019).

HTC biomass can be a high-quality solid fuel with similar characteristics to coal (i.e., energy density), which makes it a suitable candidate to replace coal. The ratio of oxygen to carbon (O/C) decreases because of the release of volatiles during the carbonization processes. HTC produces biocoal with characteristics of low-rank natural coal and diverse applications such as modern carbon nanocomposites and hybrids. In some cases, solid products of HTC are reported to have high-value applications in catalysis, energy storage (in super-capacitors, batteries, and fuel cells), carbon nanotubes, carbon films, materials with high flexibility, carbon-based nanocomposites, porous carbon materials, bio-imaging and drug delivery, photo-catalysts and sensors, and adsorption (in some cases with superior properties than those of current technologies). Biochar has a higher adsorption capacity for both polar and nonpolar compounds and hence is a great candidate for pollution reduction (Martínez, 2019).

Hydrochar is a carbon-rich and energy-dense material that offers enormous potential as a solid fuel from a renewable source for energy valorization. Hydrochar has several advantages over other coal and carbonaceous materials obtained by thermal treatments including pyrolysis, activation, and others. To begin with, HHV has a relatively high energy density (<31 MJ/kg) and is comparable to low-rank brown coal and lignite, and it can be reached at relatively low temperatures (180-250 °C), improving energy efficiency (Saqib et al., 2018). Secondly, a significant environmental benefit associated with reducing pollutant emissions can be achieved thanks to the lower nitrogen and sulfur content of hydrochar compared with conventional chars obtained from activation and pyrolysis. Hydrochar energy content is affected by biomass carbon and hydrogen content and is also sensitive to biomass ash content, feedstock oxygen content, temperature, and reaction time (Li et al., 2018). It must be considered that the increases in biomass ash content (inorganic fraction) decrease the hydrochar energy content (Martínez, 2019).

2.13. Operating parameters on hydrothermal carbonization

2.13.1. Carbonization temperature

The carbonization temperature is the key variable in the HTC process (Román et al., 2018), having a great influence on the chemical composition (Wiedner et al., 2013), morphology (Sevilla and Fuertes, 2009), and energy content (Danso-Boateng et al., 2015) of the hydrochar and the carbon and nitrogen contents (He et al., 2015) and pH (Ekpo et al., 2016) of the aqueous phase. Falco et al. (2011) and Jamari and Howse (2012) observed an increase in the hydrochar carbon content with the temperature, related to biomass dehydration. A higher temperature increase, on the other hand, can result in a decrease in hydrochar yield due to gasification (Kang et al., 2012; and Nizamuddin et al., 2018). However, Hoekman et al. (2018) reported an increase in the hydrochar yield at higher temperatures as a consequence of the condensation and dehydration reactions and the formation of polymers. The morphology of hydrochar is affected by temperature as well. In this way, Sevilla and Fuertes (2009) obtained a hydrochar from cellulose carbonized at 210 °C with an irregular morphology similar to feedstock, whereas at 220 °C aggregates of microspheres (2-10 µm) were observed.

2.13.2. Effect of temperature on fixed carbon content on sugarcane bagasse

The carbonizing temperature has a positive effect on the fixed carbon content of the biochar produced. As the carbonizing temperature increased from 250 °C-400 °C illustrated in Figure 2.15, the fixed carbon content in the biochar increased by 38%. The increase was attributed to the bagasse being effectively converted to biochar at higher temperatures, resulting in a high calorific value for biochar (Manyuchi et al., 2019). In the literature, fixed carbon content values ranging from 72–86% have been reported (Pallavi et al., 2013).

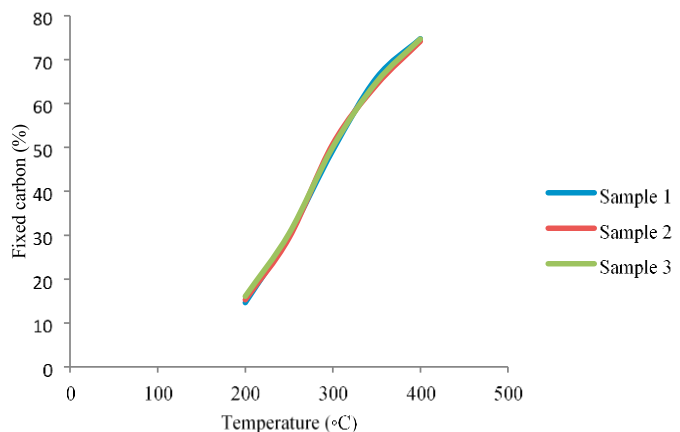


Figure 2.15 Effect of temperature on biochar fixed carbon. Adapted from Manyuchi et al., 2019

2.13.3. Effect of temperature on agricultural residue (AGR), municipal solid waste (MSW), sewage sludge (SS), and vegetable, garden, and fruit (VGF).

Figure 2.16 illustrates the effect of temperature on gaseous, liquid, and solid product yields, including the energy content of the hydrochar. As the temperature increases, the yield of hydrochar reduces for all the feedstocks. The most dramatic decrease is seen in Figure 2.16a for the AGR digestate, which contains the largest lignin content and the lowest ash content (Parmar and Andrew, 2019).

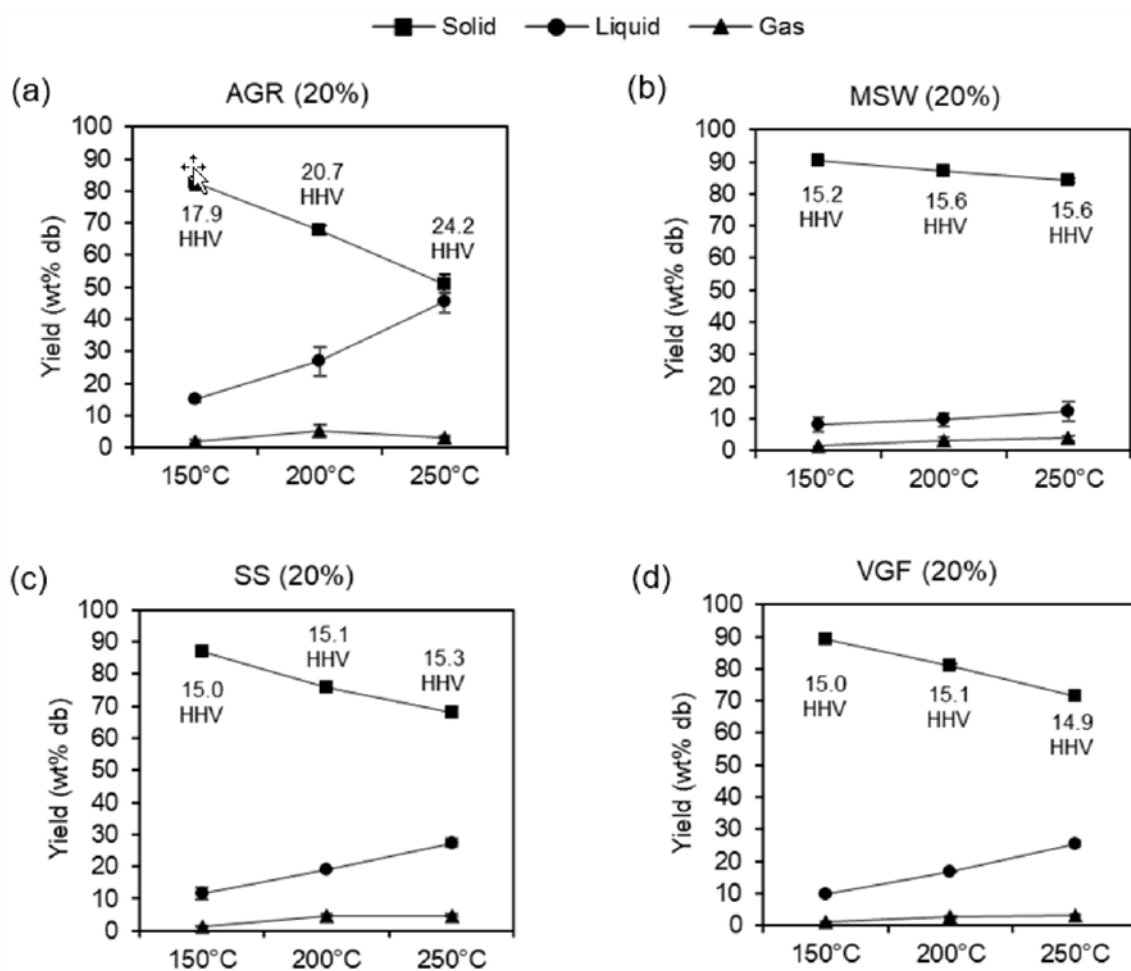


Figure 2.16 Influence of temperature on product yields including energy content of hydrochar at 20% loading for (a) agricultural residue (AGR), (b) municipal solid waste (MSW), (c) sewage sludge (SS), and (d) vegetable, garden, and fruit (VGF) on a dry basis (db). Adapted from Parmar and Andrew, 2019

2.13.4. Reaction time

Reaction time also has a significant role in the HTC process. Lu et al. (2013) determined an increase in the hydrochar carbon content of cellulose as the reaction time increased. Long-term HTC experiments show a decrease in hydrochar yield due to the polymerization of monomers and solved fragments in the aqueous phase (Hoekman et al., 2011; and Wang et al., 2018) and transference of carbon to the gas phase (around 7-9% of carbon content, mainly as carbon dioxide, butane, furan, ethylene, ethane, and propane in trace amounts). The hydrochar morphology is also affected by reaction time. Romero-Anaya et al. (2014) obtained spherical carbons after a long carbonization time of carbohydrates (12–24 h). Comparable results were reported by Gao et al. (2014), who observed an increase in the number of microspheres increasing the reaction time of water hyacinth.

In general, a high heating rate exerts a negative impact on hydrochar yield. Brand et al. (2014) determined a decrease in hydrochar yield on the carbonization of red pine sawdust and cellulose at subcritical conditions (250–300 °C) after increasing the heating rate from 2 to 20 °C/min. However, for low heating rates, the increase in temperature and reaction time resulted in a high degree of carbonization, related to the decrease of O/C and H/C atomic ratios. Therefore, high heating rates decrease the higher heating value (HHV) (Wang et al., 2018).

2.14. Sewage sludge derived biocoal characterization

Table 2.7 summarizes the operational conditions and main characteristics of the hydrochars obtained from the HTC of sewage biosolids. One of the main disadvantages of the HTC materials, including sewage sludge hydrochars, is that they present limited porosity and surface area (Parshetti et al., 2013; Alatalo et al., 2013; Saetea and Tippayawong, 2013). N₂ adsorption is not a proper method to characterize the textural properties of hydrochar since it only presents ultramicropores (<0.5 nm). Thus, the CO₂ adsorption isotherm could be a better option (Titirici, 2012).

Table 2.7 Main characteristics of the hydrochars obtained from HTC of sewage sludge under typical operational conditions. Adapted from Martínez, 2019

Feedstock	Solid (%)	Temperature (°C)	Time (min)	Solid yield (%)	C (% wt.)	HHV (KJ/kg)	Reference
Dewatered sewage sludge	20.1	190-220	300-420	60.2	25.9-41.1	11.02-19.1	Escala et al., 2013
Secondary sewage sludge	10	250	15	-	40.1	15.8	Parshetti et al., 2013
Digested sewage sludge	14.3	200	240-720	60.4	33.0	14.7-15.1	He et al., 2013
Dewatered sewage sludge	12.0	200	30	-	41.9	-	Zhao et al., 2013
Sewage sludge digested	3.6	180-280	30	80.4-93.9	40.0-48.4	16.5-22.4	Kim et al., 2014
Municipal sludge	20.0	190-260	60-1440	-	35.9-38.6	16.7-18.3	Zhang et al., 2014
Dewatered activated sludge	14.0	180-240	15-45	-	52.2-67.9	18.8-20.2	Zhao et al., 2014
Primary sewage sludge	4.3	140-200	15-240	60.5-81.1	37.2-39.2	17.0-19.0	Danso-Boateng et al., 2015
Sewage sludge	10.7	180-300	30-480	53.0-66.2	19.6-24.5	11.0-12.1	Peng et al., 2016
Dewatered biological sludge	14.4	120-210	60	43.4-93.7	35.1	22.7-28.2	Wang et al., 2016
Dewatered sewage sludge	17.5	200-300	20	-	39.9	-	He et al., 2016
Secondary sewage sludge	11.0	270	120	-	-	-	Zhai et al., 2016
Dewatered sewage sludge	10.7	220-300	60	48.2-57.7	22.3-23.2	9.6-10.3	Zhai et al., 2017
Sewage sludge	-	180-200	240-480	-	57.3-58.6	-	Breulmann et al., 2017
Digested sewage sludge	19.0	200	30	65.0-85.0	23.4	-	Liu et al., 2017
Dewatered sewage sludge	14.4	120-210	60	-	30.2-36.6	22.7-27.0	Wang et al., 2017
Digested sewage sludge	19.0	200	30	-	23.3	-	Liu et al., 2018

2.15. Physicochemical properties of bagasse and biocoal

From the study conducted by Manyuchi et al., 2019, a carbonizing temperature of 400 °C is recommended for biocoal production from sugar cane bagasse. At this temperature, the highest calorific value of 28.2 MJ/kg is achieved. A summary of both the sugarcane bagasse and the bio coal is given in Table 2.8. The biocoal also had carbon dioxide and carbon monoxide emissions of less than 0.9% and 0.02% respectively. The low pollutants emissions from the biocoal make them an eco-friendly fuel (Pallavi et al., 2013).

Table 2.8 Summary of the bagasse and biocoal physicochemical properties. Adapted from Manyuchi et al., 2019

Physicochemical property	Bagasse	Biocoal
Moisture content (%)	12.3±.2	6.3±0.2
Calorific value (MJ/kg)	14.8±0.4	28.2±0.3
Ash content (%)	4.5±0.3	1.4±0.1
Fixed carbon (%)	15.4±0.7	74.6±.3
Bulk density (kg/m ³)	875±5	1025±5
Ignition time (s)	-	10s
Burning time (minutes)	-	30 minutes

2.16. Production of biocoal using the hydrothermal carbonization process

Table 2.9 Product yields of solid, liquid and gas using hydrothermal carbonization process

Product yield (%)			Feedstock	Ref
Solid	Liquid	Gas		
50-80	5-20	2-5	Biomass, waste materials	(Libra et al., 2011; Lu et al., 2012)
20-50	-	-	Municipal Solid Waste, Paper, Food waste	(Lu et al., 2012)
75-80	15-20	5	Variety of organic waste materials	(Ramke et al., 2009)
36-66	-	-	Cellulose, peat, wood	(Funke & Ziegler, 2010)
30-50	-	-	Cellulose	(Sevilla & Fuertes, 2009)
50-69	12-14	5-12	Jeffery Pine and White Fir mix	(Hoekman et al., 2011)
35-38	-	-	Cornstalk, forest waste	(Xiao et al., 2012)
63-83	8-17	9-20	Loblolly Pine	(Yan et al., 2010)

In a study conducted by Bevan et al. (2020) on the HTC of paper sludge over an experimental range of 180–300 °C. The temperature of 210 °C produced the highest heating value (9.7 MJ kg⁻¹) and the highest energetic recovery efficiency (90.12%) in the experimental trials. This implies that the final application of the hydrochar as a fuel source would be most optimally produced at this temperature. However, this study further found that hydrochar had lower nitrogen and sulphur content as the reactor temperature was increased. This implies that a lower reactor temperature would be preferred for hydrochar that is to be applied as a soil conditioner (for a paper sludge feedstock). Furthermore, the nitrogen content in hydrochar has been shown to have a significant impact on its specific applications.

Research has shown that the ideal reactor conditions can be determined by identifying the application of the hydrochar and by analyzing the composition of the feedstock. Kiran and Ross (2019) recorded biocoal with fuel properties similar to those of lignite coal in the hydrothermal treatment of swine manure. Hydrothermal processing of the swine manure was performed in an unstirred 600-mL Parr reactor (Parr, Moline, IL, USA). At temperatures ranging from 120 to 250°C for 1 h in either water alone or reagents including 0.1 M NaOH, 0.1 M H₂SO₄, and 0.1 M organic acid (CH₃COOH and HCOOH). The heating rate was approximately 10 °C.min⁻¹. The findings revealed that pH has a strong influence on ash chemistry, with decreasing pH resulting in increased removal of ash. The reduction in mineral matter influences the volatile content of the biocoal and its energy content. As the ash content in the final biocoal reduces, the energy density increases. Treatment at 250°C results in a more "coal-like" biocoal with fuel properties similar to that of lignite coal and a higher heating value (HHV) ranging between 21 and 23 MJ/kg depending on pH. Processing at low pH results in favorable ash chemistry in terms of slagging and fouling. Operating at a low pH also appears to influence the level of dehydration during HTC. The level of dehydration increases with decreasing pH, although this effect is reduced at higher temperatures. At higher temperatures of processing (250°C), operating at a lower pH increases the yield of biocoal. However, the lower yields obtained below 200 in the presence of acid may be due to the acid hydrolysis of carbohydrates in the manure.

In the study of hydrothermal carbonization chemical sludge from a pulp and board mill at 180–260 °C, using a 0.28 L Büchi Limbo (Büchi AG) reactor fitted with a magnetic stirrer, by Mäkelä et al. (2018), Results indicated carbonization increased the carbon content of chemical sludge from 49% to 55–65% depending on the experimental conditions. Char solid and carbon yields were in the range of 63–77% and 64–81%, respectively, and showed an increase in the dissolution of organic compounds at higher temperatures and higher sludge moisture contents. Char ash contents were in the range of 43-53%, with respective ash yields of 75-86%. Filtrate properties were mainly governed by the moisture content of the sludge feed, as a higher moisture content generated a more diluted filtrate. Nonaka et al. (2011) found a more hydrophobic solid product and a 91% mass yield with an energy density of 140%. When forest mangrove (*acacia magium*) was hydrothermally treated at 300 °C for 30 min in a batch reactor, Reza et al. (2013) investigated the effects of HTC on the agricultural residues of corn. Stover and rice hulls at 200–260 °C with a 5-minute reaction time and reported mass yields of 75–90%. Chen et al. (2012) performed HTC on sugar cane bagasse at 180 °C for up to 30 min. The

mass yield was reported to range from 61% to 70%, but HTC had an insignificant effect on energy densification, which was 110%. Kambo and Dutta (2015) also assessed the potential of using hydrothermal carbonization (HTC) on miscanthus feedstock to produce a carbon-rich solid fuel, referred to as hydrochar, whose physicochemical properties are comparable to those of coal. HTC of biomass was conducted in a 600 ml Parr benchtop reactor (Moline, IL) fitted with the glass liner (762HC3), at different reaction temperatures (190, 225, and 260 °C), residence times (5, 15, and 30 min), and feedstock-to-water ratio (1:6 and 1:12). Results documented revealed that with an increase in the reaction temperature from 190 to 260 °C at a solid load ratio of 1:6, the mass yield of hydrochar decreases from 83.5% to 47.8% and from 72.5% to 44.9% at 5 min and 30 min residence time, respectively. Similarly, at the solid load ratio of 1:12, with an increase in the reaction temperature of 190 to 260 °C, the mass yield of hydrochar decreases from 82.8% to 44.9% and from 66.6% to 42.8% at 5 min and 30 min residence time. The effect of reaction temperature on the HHV of hydrochar was found to be more prominent than the effects of reaction time and feedstock to water ratio. At the solid load ratio of 1:6, with an increase in the reaction temperature from 190 to 260 °C, the HHV of hydrochar samples was increased by 29.1% (from 19.9 to 25.7 MJ/kg) and by 42.9% (21.2 to 30.3 MJ/kg) at reaction times of 5 min and 30 min, respectively. On the other hand, at the same solid load ratio, with an increase in reaction time from 5 to 30 min, the HHV of hydrochar samples increased by 6.5% (from 19.9 to 21.2 MJ/kg) and by 17.9% (25.7 to 30.3 MJ/kg) at 190 and 260 °C, respectively. This shows that the effect of reaction time on the HHV of hydrochar samples is more pronounced at a high reaction temperature (260 °C) compared to a low reaction temperature (190 °C).

Chao He et al. (2018) reported that the husks of nuts contained extremely high levels of lignin, e.g., about 61% for the husks of *Carya cathayensis* Sarg (HCCS). The HHV of hydrochars from the HTC of HCCS under 180–260 °C ranged from 22.0 to 28.2 MJ/kg, which is even higher than some commercial coals. When assessing the hydrothermal carbonization of sugarcane bagasse via wet torrefaction in association with microwave heating, Chen et al. (2012) also reported that the calorific value of bagasse can be increased by up to 20.3% from wet torrefaction. The mixture of bagasse, deionized water, or sulfuric acid solution was transferred into a cylindrical reactor (50 mm i.d. x 318 mm length), which was a Teflon vessel. The reactor was placed in a microwave oven which was operated at a frequency of 2.45 GHz. The maximum power of the microwave oven was 900 watts, and the current output from the power controller was fixed at 10 A. The reaction temperature was kept constant at 180 °C. Carbon

content in raw bagasse was 39.78 wt. %, but it could be increased to 52.35 wt. % under the conditions of $SLR = 0.1 \text{ g mL}^{-1}$ and 15 min heating time. This accounts for a 32% increment in carbon content. The values of atomic H/C and O/C ratios in raw bagasse were 1.605 and 0.961, respectively, and they were in the ranges of 1.003–1.325 and 0.528–0.824 when bagasse was pre-treated by wet torrefaction. This implies that the chemical formula of bagasse has transformed from $CH_{1.605}O_{0.961}$ to $CH_{1.003-1.325}O_{0.528-0.824}$. The HHV obtained was 16.495 MJ/kg.

Berge et al. (2004), for which food waste, paper, and municipal sewage waste (MSW) were hydrolyzed at 250°C for 20 hours in 160-mL stainless steel tubular reactors. Each reactor consisted of a one-inch diameter stainless steel pipe nipple and endcaps (McMaster Carr). One of the endcaps was equipped with a gas sampling valve (Swagelok, Inc.) to allow the controlled collection of gas samples. Findings indicate that at 250°C and 20 h, the HHV obtained for paper, food waste, and MSW was 23860, 29100, and 20010 KJ/kg_{db}, respectively. When assessing biocoal obtained upon hydrothermal carbonization of brewer's spent grain, Poerschmann et al. (2014) also recorded high calorific values, indicating significant energy densification of biocoals as compared to the input substrate. The hydrothermal process was performed in an autoclave with a capacity of 200 mL (Roth; Karlsruhe, Germany) filled with 50 g of BSG (23.5% w/w dry mass) and 50 mL of distilled water at an operating temperature of 200 and 240°C, a reaction time of 14 h, and 80 µg/mL of citric acid as catalyst. Results showed that increased HTC-temperatures resulted in lower coal mass yields but higher OC-content. The high yield of black-colored carbonaceous precipitates and the high carbon content of the biocoal point to the good suitability of BSG for the HTC process and are expected to be beneficial for a prospective energetic application. Due to decarboxylation, dehydration, and condensation reactions, both HTC coals showed distinctively higher HHV values (29.9 MJ/kg at 200°C and 31.8 MJ/kg at 240°C) compared to the input feedstock and the aqueous HTC phase. The energy density of the coalification process as expressed by the $HHV_{Biocoal}/HHV_{Feedstock}$ ratio amounted to 1.35 for the 200°C-biocoal and 1.43 for the 240°C-biocoal. The calorific values calculated for both aqueous product streams were 20.5 and 20.9 MJ/kg, respectively. Both biocoals had calorie data slightly higher than those of brown coal, lignin, and significantly higher than those of carbohydrates, but lower compared to those of anthracite and lipids. Findings demonstrate that the brewer's spent grain by-product is a good feedstock for hydrothermal carbonization to produce biocoal, the latter offering good prospects for energetic and soil-improving application fields.

In the study of hydrochar production from faecal sludge (FS) at temperatures of 180, 220, and 250°C and reaction times of 0.5, 1.0, 5.0, and 10.0 h, using a 1-L high-pressure reactor made of stainless steel, equipped with a pressure gauge, thermocouple, and gas collecting ports by Fackaew et al. (2015). The results from three replicates of batch experiments indicated high energy contents of 19.5 and 19.0 MJ/kg could be obtained when the moisture contents were varied at 80% and 90%. However, the energy content of the produced hydrochar was decreased to 17.6 MJ/kg when the moisture content was reduced to 70%. At 95% moisture content, the energy content of the produced hydrochar was also decreased to 18.0 MJ/kg. The range of energy content of the produced hydrochar was comparable to that of lignite and sub-bituminous (15.0 MJ/kg and 18.2 MJ/kg, respectively) (United States Environmental Protection Agency (U.S.EPA) 2008), which can be used as a solid fuel in conventional combustion. The highest energy content of 20.3 MJ/kg was achieved at a temperature of 250°C and a reaction time of 10 h, while the lowest energy content of hydrochar was found at a temperature and reaction time of 180°C and 0.5 h, respectively. From the experimental results, increasing temperatures from 180 to 220°C and from 220 to 250°C resulted in about 4% and 10% increases in the energy content of the produced hydrochar, respectively. Increasing the temperature in the HTC reactor would result in more dehydration and decarboxylation of the FS samples, resulting in increased energy content of the produced hydrochar. Concerning reaction times led to increased energy content, especially when operating the HTC at 250 °C. At HTC reaction times of 0.5 h, 1.0 h, 5.0 h, and 10.0 h, energy contents of 13.8 MJ/kg in the initial dried FS were increased to 18.2 MJ/kg, 18.8 MJ/kg, 19.7 MJ/kg, and 20.3 MJ/kg in the hydrochar, respectively. The normalized energy yields of the produced hydrochar were found to decrease with increasing reaction time, but the temperature of 250°C still produced a higher normalized energy yield than those at 220 and 180 °C. It can be deduced from the results that the reaction time of 5 h was optimum in producing the highest normalized energy yield of 13.8 MJ/kg.

In 2015, Fackaew et al. studied the effects of hydrolysis and carbonization reactions on hydrochar production. The research was conducted in a reactor at a low-energy HTC process known as "Two-stage HTC," which consists of hydrolysis and carbonization stages with faecal sludge as feedstock. The study stated that for the hydrolysis stage, increasing the hydrolysis reaction time from 20 to 200 min resulted in the increased energy content of the produced hydrochar. The energy content of the produced hydrochar was greater than 20 MJ/kg at hydrolysis temperatures and reaction times of 150–175°C and 150–200 min, respectively. The effects of the carbonization temperature and reaction time on the energy content of the

produced hydrochar indicated that increasing the carbonization temperature from 200 to 250°C resulted in the increased energy content of the produced hydrochar. The energy content of the produced hydrochar was greater than 20 MJ/kg at the carbonization temperature range of 230–250°C. Concerning the carbonization reaction time, the energy content of the produced hydrochar tends to decrease with increasing the reaction time. If the energy content of the produced hydrochar was expected to be greater than 20 MJ/kg, the carbonization reaction times should be 100–250 min. The experimental results indicated the optimum conditions of the two-stage HTC to be hydrolysis temperature of 170°C; hydrolysis reaction time of 155 min; carbonization temperature of 215°C; and carbonization reaction time of 100 min. The hydrolysis reaction time and carbonization temperature had a statistically significant effect on the energy content of the produced hydrochar. Therefore, the two-stage HTC could be considered a potential technology for treating FS and producing hydrochar.

Khaskhachikh et al. (2019) analyzed the influence of hydrothermal carbonization parameters on the biomass to produce biocoal obtained from peat. Experiments were conducted in a stainless-steel batch reactor at operating temperatures of 160, 190, 210, and 230 °C with reaction durations of 1 hour and 8 hours. Results from the research showed that the mass yield of hydrochar samples was reduced with an increase in the reaction time and temperature. Hydrothermal treatment of peat at a relatively low temperature (160 °C) increased the carbon concentration to 60.5% compared to the initial peat, and an increase in the treatment temperature (230 °C) made it possible to increase it to 68.17%. At the same time, a decrease in the oxygen content of the sample by almost 10% was observed. It was established that with an increase in temperature and reaction time, the yield of hydrochar oxygen in it decreases (from 33.1%-initial peat to 19.47%-hydrochar obtained at 230 °C), but carbon increases (from 52.09%-initial peat to 68.17%-hydrochar obtained at 230 °C). With an increase in the reaction time, carbon increases (from 55.91% at 1 h to 64.84% at 8 h) and oxygen decreases (from 33.51% at 1 h to 22.13% at 8 h). It was further discovered that heating values depend on the carbon and oxygen content present in the material. With increasing amounts of carbon and decreasing oxygen, the calorific value will increase. As a result, the high heating values (26.77-LHV, 28.03-HHV) were obtained for a sample at 230 °C.

Mikko Mäkelä (2015) investigated the carbonization of two different pulp and paper mill sludge residues (fiber reject and mixed sludge) with a laboratory-scale pressure reactor at reaction temperatures of 180-260 °C and retention times of 0.5–6.25 h. It was established that during the fiber reject experiments, the dry solids contents of filtered hydrochar samples were

in the range of 39–65%, with respective solid yields of 59–98% dry basis (db). The reaction temperature was correlated with the increasing ash content of dried hydrochar, ranging from 48 to 67% (db). The ash recoveries obtained ranged from 82 to 102% (db), with an inverse relationship with increasing reaction temperature. Carbon content, O/C-ratio, higher heating value, and calculated energy densification of obtained fiber reject hydrochar did not change with reaction temperature, retention time, or liquid to solid-ratio until respective corrections for increasing ash contents were made. The resulting corrected, dry ash-free carbon content ranged from 37-87% with respective O/C-ratios of 0.05–1.2. Heating values and energy densification ratios for the dry-ash free hydrochars varied in their respective ranges of 19.9-30.7 MJ kg⁻¹ and 1.0-1.6. In addition, the corrected dry ash-free solid yields were in the range of 37-95%. Energy yields, derived from hydrochar mass yields and energy densification ratios, were in the range of 54–98%.

Results for the mixed sludge experiments indicated the dry solids content of filtered hydrochar samples was in the range of 23-53%, with respective solid yields of 64–96% (db). The reaction temperature was correlated with the increasing ash content of dried hydrochar, ranging from 35 to 48% (db). The recovered ash ranged from 81 to 99% (db), with an inverse relationship with increasing reaction temperature. Similar to fiber rejects, the carbon content, O/C-ratio, higher heating value, and calculated energy densification of attained mixed sludge hydrochar showed no apparent change with reaction temperature, retention time, or liquid to solid-ratio until respective corrections for increasing ash contents were made. The corrected, dry ash-free carbon content ranged from 43–84%, with O/C-ratios ranging from 0.01-0.9. Heating values and energy densification ratios for the dry-ash free hydrochars varied in their respective ranges of 24.2-33.1 MJ/kg and 1.0-1.3. In addition, the corrected dry ash-free solid yields were in the range of 54–95%. Energy yields, derived from hydrochar mass yields and energy densification ratios, were in the range of 65–97%.

Zvimba and Musvoto (2018) investigated calorific values using a hydrothermal carbonization process, such as the Polymeric Carbon Solid (PCS) process, at short processing times of 1 hour and temperatures ranging from 180 °C to 240 °C. The results revealed that an optimal temperature of 210 °C is required to produce a high-quality product. The process increases the calorific value of primary sludge (18 MJ/kg) and waste activated sludge (16 MJ/kg) to the level of low-grade coal (lignite and sub-bituminous), which makes the product a clean, useful biofuel with very low emissions compared to coal. However, the calorific value of digested sludge (11 MJ/kg) is generally low due to anaerobic digestion. The process reduces volatile and total solids

by 62–40% and 37–22%, respectively, when processing sludge only. Nonetheless, the processing of combined sludge and screenings increased the calorific value of the product by up to 35%. In this regard, the process not only provides a single solution for sludge and screening handling at wastewater treatment plants, but it also offers the possibility of co-processing wastewater sludge with other biomass (e.g., municipal solid waste, food waste, agricultural waste, and so on). Scale studies have demonstrated that PCS technology can convert wastewater sludge into useful biofuels and commercial products.

Yang et al. (2018) investigated hydrothermal carbonization for the conversion of organic residue from solid-state anaerobic digestion (SS-AD) of livestock waste to solid fuels. The experiments were performed using a 2,000 mL reactor consisting of a reactor body, a heater, and a steam condenser that operated under nitrogen gas. The operating temperatures of the HTC reactor were 180–240 °C, and the reaction time was set to 30 min, with a 200-rpm agitation speed. The raw organic residue of SS-AD indicated 10.9% of fixed carbon content and 68.5% of volatile matter content. After the HTC process, the fixed carbon content increased to 13.5% and 14.8%, and the volatile matter content decreased to 59.3% and 54.2% at 200°C and 220°C, respectively. As a result, the fuel ratio (fixed carbon/volatile matter) increased due to the hydrothermal carbonization reactions of 0.16, 0.23, and 0.27 at 200 °C and 220 °C, respectively. Results also demonstrated that the carbon content of the hydrochar increased from 44.9% to 47.1% and 48.0% as the HTC reaction temperature increased at 200 °C and 220 °C. The nitrogen content decreased from 1.4% to 0.8%, respectively. Furthermore, the atomic H/C and O/C ratios decreased from 1.3 and 0.5 to 1.1 and 0.3, respectively, as the reaction temperature increased from 180°C to 240°C. Moreover, the results of hydrochar showed properties approaching those of lignite and sub-bituminous coal as the HTC reaction temperature increased. The calorific values of the hydrochar from the organic residue of SS-AD were improved from 19.4 to 20.4 MJ/kg at 180 °C, 22.4 MJ/kg at 200 °C, 22.5 MJ/kg at 220 °C, and 23.1 MJ/kg at 240 °C, respectively. Therefore, these results confirm that the HTC process can improve the properties of hydrochar from the organic residue of SS-AD and that the elevated carbon and fixed carbon contents can be said to have a strong influence on the calorific value. As a result, the hydrothermal carbonization process can be said to be an advantageous technology in terms of improving the properties of organic waste as a solid-recovered fuel product. To produce solid hydrochar and process water rich in organic carbon, Kiran and Ross (2019) compared the treatment of four dissimilar digestates from anaerobic digestion (AD) of agricultural residue (AGR); sewage sludge (SS); residual municipal solid

waste (MSW), and vegetable, garden, and fruit waste (VGF). Hydrothermal reactions were performed in a 600-mL stainless steel Parr 4836 bench-top reactor (Parr, Moline, IL, USA) at 150, 200, and 250°C for 1 h using 10%, 20%, and 30% solid loadings of a fixed water mass. The results obtained for feedstock characterization indicated digestate samples contained high levels of ash, ranging from 40–55 wt. %. The exception was the AGR digestate, which had a lower ash content of 16 wt. % and a corresponding higher carbon content. The calorific value of the dewatered digestates ranged from 15 to 17 MJ/kg, with the lower ash content (AGR) having the higher calorific value. The protein content was highest in the SS digestate (24.3 wt. %), followed by the AGR digestate (17.7 wt. %), then VGR (9.8 wt. %), and MSW (6.8 wt. %). It was recorded that as the temperature increases, the yield of hydrochar reduces for all the feedstocks, but the most dramatic decrease was seen in the AGR digestate, which contains the largest lignin content and the lowest ash content. At 250 °C, there is significant energy densification from the feedstock of 17.8 MJ/kg to 24.2 MJ/kg. Energy densification is not observed for the other digestate samples, largely due to their high ash content. However, the yields of MSW, SS, and VGF hydrochar are higher, although the carbon contents of the hydrochars are significantly lower than that of AGR (44–57 wt. % for AGR to 24–34 wt. % for all other hydrochars).

The results showed that the effect of solid loading on solubilization is feedstock dependent. Increasing solid loading lowers the solubility across all feedstocks treated, increasing hydrochar yield. The greatest reduction in solubility was found with AGR treated at 200°C. However, an increase in temperature has been shown to favor an increase in carbon content and HHV. The AGR digestate produced the greatest higher heating value (HHV) of 24 MJ/kg at 250°C. The effect of energy densification was greater with AGR due to its larger lignin content. SS hydrochar carbon content is uniform, therefore there was little benefit to hydrochar quality when processed over 150 °C. Ash content in the hydrochar increased with both higher temperatures and solid loading, resulting in a decrease in inorganic content in the process water.

CHAPTER 3

3. Materials and Experimental Procedure

This chapter includes details of the materials, experimental equipment, and experimental procedures that were followed to obtain results for this work. The equations high heating value (HHV) and biocoal yield are presented as well as the list of equipment and materials used. A schematic diagram of the entire experimental procedure of the HTC of sludge and bagasse is presented.

3.1. Source and Preparation of Materials

This project will focus on the hydrothermal treatment of wastewater sludge and sugarcane bagasse for the potential production of waste-derived biocoal. Laboratory-scale Hydrothermal Carbonization (HTC) experiments were performed on sludge and bagasse provided by the Umgeni wastewater treatment plant and a sugarcane industry based in Kwa-Zulu Natal in South Africa. Important HTC process parameters, such as reaction temperature, biomass type, and solid-liquid ratio (solid loading) were investigated. Properties of the initial sludge, bagasse, and biocoal such as elemental composition and heating values were determined.

3.1.1. Equipment

The following equipment was used:

- Refrigerator
- Knife furnace: heavy mild steel sections and plate, lining of 114mm insulating firebrick backed up by 50 mm of calcium silicate board
- Oven: hot air-drying laboratory oven
- Grinder
- Measuring scale: HCB 602H- capacity 600g, readability and repeatability of 0.01g
- Beakers 250ml X5
- Funnels X5
- Filtering paper 110mm X90
- Mechanical sieve shaker: electrical sieve shaker equipped with a digital timer and motor
- HTC Reactors X4: 60 ml hydrothermal autoclave reactors
- Cylindrical metal clay extruder

3.1.2. **Materials**

Calcium hydroxide $\text{Ca}(\text{OH})_2$ that was used as a binder during the HTC of sludge and bagasse was purchased from Sigma-Aldrich (Pty) LTD in Johannesburg. All experimental apparatus such as beakers, thermometers, timers, furnace, oven, funnels, crucibles, sieving pans, mechanical sieve shaker, and deionized water were obtained from the university laboratory. The equipment used for analysis in this study includes an ultimate analyzer.

3.2. **Experimental Procedure**

3.2.1. **Preparation of wastewater sludge**

Supply of pre-thickened sludge sample was received from Darville Umgeni wastewater treatment plant, Kwa-Zulu Natal. The sample was collected following the thickening of primary sludge (PS) after mechanical separation. Twenty-five liters were obtained and transported to the Durban University of Technology. The sludge was stored in a refrigerator at 4°C. The PS was dewatered using a filter cloth to increase the total solids (TS) concentration from 1.48% to 27.06%, thereafter the filter cake was oven-dried at 100°C for 8 hours to maintain consistent feedstock moisture content which also increased the total solid (TS) concentration. The sludge was weighed using a mass balance. This process was repeated until the sludge mass was constant, then homogenized in a grinder. Initially (dry basis) sludge was characterized to determine the elemental composition and heating values.

3.2.2. **Preparation of sugarcane bagasse**

Bagasse was collected and dirt was hand removed from the sample. The bagasse was then washed thoroughly with deionized water. Thereafter, the washed bagasse was dried in an oven at 105°C for 2 hrs. The dried bagasse was preliminarily ground and sieved to particle sizes less than 425 μm . Then the prepared bagasse was characterized and stored in a desiccator at room temperature until the HTC process was carried out.

3.2.3. **Hydrothermal Carbonization**

Hydrothermal carbonization reactions were performed in a 60 ml batch stainless steel hydrothermal reactor at temperatures of 180, 210, 240, and 260°C. A ratio variation of 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 dry sludge and bagasse(SB) material were mixed with de-ionized water (H_2O) and their masses (solid-liquid mass) were varied in four steps in the

following order: 1:10, 2:10, 3:10, and 4:10 (SB: H₂O) corresponding to 9.09wt. %, 16.67wt. %, 23.08wt. % and 28.57wt. % of the solid loadings. The mass of deionized water was maintained at 10 g throughout the experiments and the mass of total dried feedstock was varied (1, 2, 3, and 4g). The mixture was then transferred into HTC reactors. The reactors were sealed and then placed in a furnace that was maintained at the desired temperature. Reactions were conducted at a reaction time of 1 hour. Thereafter, the reactors were removed from the furnace and cooled to room temperature. The solid and liquid products were separated using a filter paper of Grade 1 qualitative circles. The solid product was air-dried for 30 minutes and then oven-dried at 100°C for 4 hours to ensure dewatering of the product (Kiran et al. 2019).

Figure 3.1 demonstrates the experimental procedure that was followed for hydrothermal carbonization experiments conducted in 60 ml hydrothermal autoclave stainless steel batch reactors that were procured from Simunye Engineering in Durban. The HTC reactors were designed to endure a temperature of 400°C respectively. The analysis of gaseous content, carbon content present in the process water, chemical oxygen demand (COD), phenols, and total nitrogen (TN) was not within the scope of this research. Therefore, the gases were not collected. The reactor was opened using a spanner and the gaseous phase was released. The liquid phase was safely discarded.

3.2.4. **Densification of Biocoal Procedure**

The densification of biocoal was carried out in a cylindrical metal clay extruder with binder Ca(OH)₂ and water added at room temperature. The mixture of biocoal, binder, and water was placed inside between the compressive bar and the pedestal for compression into a single pellet. The mold is composed of a compressive bar (15 mm diameter), and a pedestal.

Initially, the binder and water were mixed and then added into the biocoal proportionally and the mixtures were thoroughly stirred. The dosage of the binder was 10g solid/20g liquid. The amount of water added was 20g. Water was reintroduced into the biocoal before compression which enhances the salutary briquette strength through capillary binding effects. Then, the mixtures were filled into the mold cylinder and placed horizontally on the pedestal of the cylindrical metal clay extruder. The sample was then compressed by moving the compressive bar down then held for 3 min. Finally, the biocoal pellet of 15 mm diameter was ejected from the mold and stored at room temperature. The pellets were then dried in the oven at 105°C for 10 h (Qiang et al., 2015).

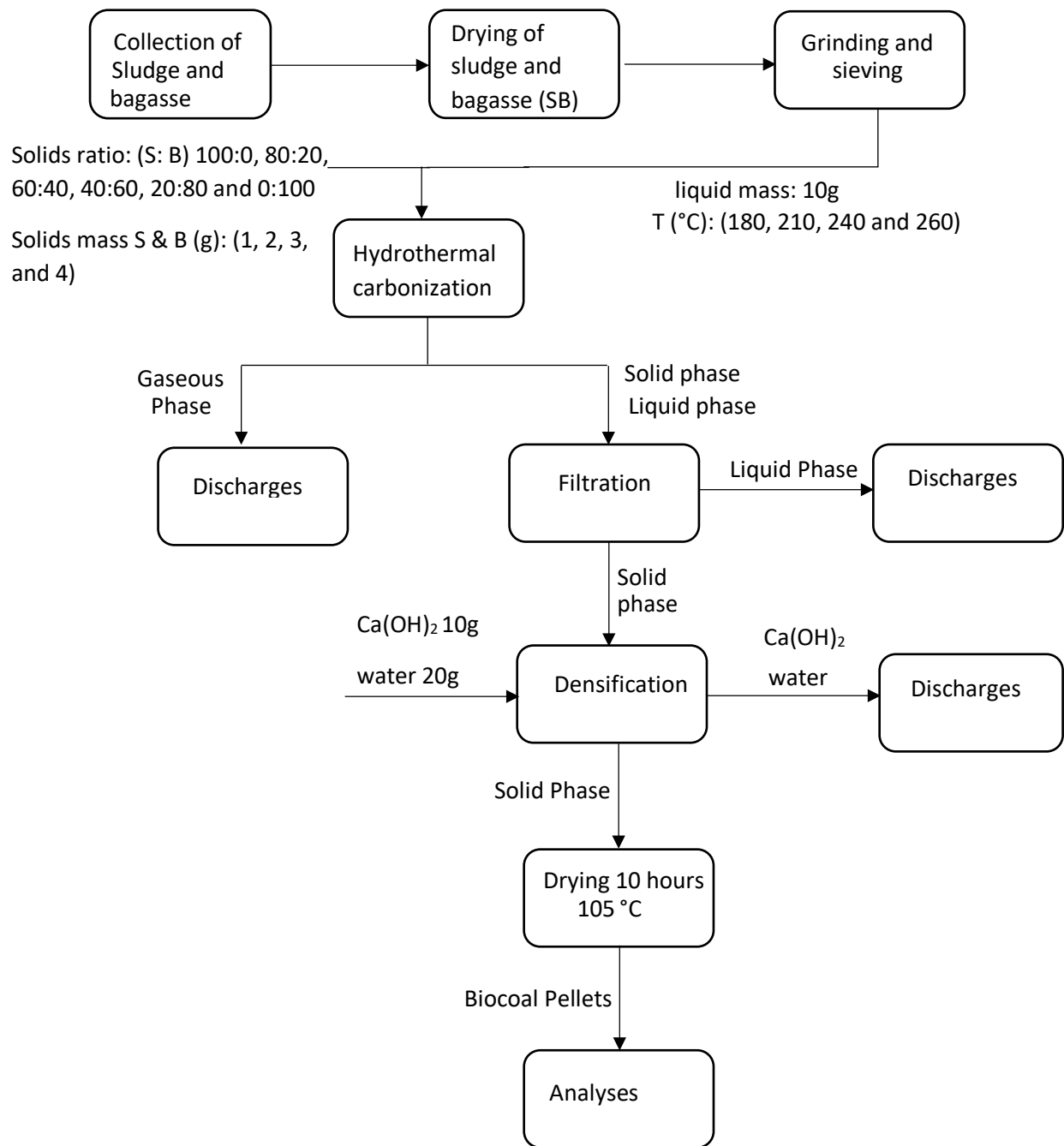


Figure 3.1 Schematic diagram of the experimental procedure that was performed for the HTC of wastewater sludge and sugarcane bagasse.

3.3. Calculation for feedstock and biocoal analysis

The characterization of feedstock and biocoal was determined based on elemental analysis, which was carried out on an Exeter Analytical CE440 Elemental Analyzer (CHNS Elemental Microanalysis) intended for the simultaneous determination of the elements C, H, N, and S in the samples. Oxygen content of the biomass and biocoal (O, wt. %) on dry basis are calculated from material balance:

$$O = 100 - (C + H + N + S) \quad \text{Equation 3.1}$$

Equation 3.1 shows that C, H, N, and S, are content of carbon, hydrogen, nitrogen, and sulfur calculated on dry basis (Khaskhachikh et al., 2019).

The high heating values were calculated from the Tillman (1978) equation based on elemental composition (ultimate analysis):

$$HHV = 0.4373[C] - 1.6701 \quad \text{Equation 3.2}$$

In equation 3.2 HHV is the high calorific value, MJ/kg; C being carbon on dry basis wt. % (Channiwala and Parikh, 2002).

The biocoal yield y_{bc} was calculated by:

$$y_{bc} = \frac{m_c}{V_s} \times 100 \quad \text{Equation 3.3}$$

In equation 3.3, m_c represents the mass of biocoal and V_s are volatile solids (Martínez, 2019).

The mass yield y_m shown in equation 3.4, describes a percentage of raw material remaining in biochar and it is calculated as the ratio of carbonized product in weight (m_c) to raw biomass weight (m_b), %:

$$y_m = \frac{m_c}{m_b} \times 100 \quad \text{Equation 3.4}$$

The energy yield y_e indicates a percentage of feedstock calorificity remains in the solid residue, %. The index is calculated by:

$$y_e = y_m \times \frac{HHV_c}{HHV_b} \quad \text{Equation 3.5}$$

Equation 3.5 shows HHV_c and HHV_b being the high heating values of product and feedstock, respectively. (Khaskhachikh et al., 2019).

The volume (V) of the biocoal pellets was calculated by:

$$V = \pi r^2 h \quad \text{Equation 3.6}$$

In equation 3.6, r^2 is the radius, and h being the height.

Bulk density (ρ) defines the density of biocoal pellets combined with a binder after hydrothermal carbonization.

$$\rho = \frac{m_c}{v} \quad \text{Equation 3.7}$$

In equation 3.7, v is the volume in m^3 , and m_c is the mass of biocoal pellets in kg.

CHAPTER 4

4. The effects of operating conditions on biocoal production

This chapter contains the results and discussion pertaining to the characterization of feedstock (sludge and bagasse) and biocoal. Furthermore, the influence of the operating variables, including temperature, solid loading, and biomass type on the biocoal yield and calorific value obtained in the batch HTC of wastewater sludge and sugarcane bagasse was also discussed.

4.1. Introduction

Hydrothermal carbonization (HTC) was firstly described by Friedrich Bergius in 1913 to describe the natural coalification process. Although the process did not gain attention until the last decades of the 20th century as a method to obtain organic compounds for the synthesis of chemicals along with the recovery of liquid and fuels (Martínez, 2019). Recently, it has been rediscovered to produce hydrochar, which has value-added applications in the industry and environment (Kambo and Dutta, 2015). Due to the growing interest in this technology, the 1st and 2nd International Symposium on Hydrothermal Carbonization was celebrated in London (2017) and Berlin (2019), respectively (Martínez, 2019). HTC has been applied to a great variety of lignocellulosic biomass, with variable composition in hemicellulose (20-40%), cellulose (40-60%), and lignin (10-25%), and non-lignocellulosic ones, such as animal manure, food, sewage sludge, and municipal solid wastes, among others, which have a significant different composition (Martínez, 2019). The findings reported in this section were obtained from HTC experiments conducted on a batch process at moderate temperatures.

4.2. Feedstock characterization

Table 7.1 in the appendices lists the ultimate and calorific value analysis of the municipal sewage sludge and sugar cane bagasse samples. The samples had a carbon content of 42.40-46.44 wt. %. Sugar cane bagasse contained the highest carbon content of 46.44 wt. %. The calorific value of the samples ranges from 16.87 to 18.64 MJ/kg, with bagasse having the highest calorific value. These results agree with those obtained by Kiran et al. (2019) in the HTC of sewage sludge and agricultural residue. Carbon content ranges from 28.6-44.1 wt. % and calorific value of 14.9-17.8 MJ/kg.

4.3. Effect of process parameters on the biocoal yield

Effects of process parameters on biocoal yield were first investigated by conducting HTC treatment on municipal sludge and sugar cane bagasse. Three phases were achieved: an aqueous phase, a gaseous phase, and a solid phase. Temperature, solid loading, and solids ratio were varied as 180, 210, 240, and 260°C, 9.09wt. %, 16.67wt. %, 23.08wt. % and 28.57wt. %, and 100:0, 80:20, 60:40, 40:60, 20:80, 0:100 dry sludge and bagasse (SB) respectively. The residence time was maintained constant at 60 min for all experiments.

4.3.1. The effect of temperature on the biocoal yield

Figure 4.1 shows the effect of temperature at various sludge content (0-100%) when (a) 9.09% solid loading, (b) 16.67% solid loading, (c) 23.08% solid loading, and (d) 28.57% solid loading were applied at a constant residence time of 60 minutes. The temperatures explored ranged from 180 °C to 260°C. For all the various solid loading and sludge contents, a similar pattern is maintained, where the yields are found to initially increase until a certain temperature, and then a notable decline is observed. Figure 4.1a, where 9.09 wt. % solid loading was used, this general trend of increasing biocoal yields followed by a sharp decline occurs when temperatures approach 210 °C, and for temperatures exceeding 210 °C, the biocoal yields are slowed down. For example, at a sludge content of 80%, the biocoal yields initially increased from 6.27wt. % at 180°C until 7.00wt. % at 210°C, thereafter, the yields started to decrease to 4.73 wt. % and further to 4.27 wt. % when temperatures increased from 240°C to 260°C. The deterioration of biocoal yield demonstrated in the experiments with an increase in temperature of HTC is explained by the chemical reactions that take place in the process (Khaskhachikh et al; 2019). The main reactions that take place during HTC: are hydrolysis, dehydration, decarboxylation, aromatization, and polymerization. Hydrolysis is one of the most significant reactions in the process and goes at the first step of HTC (Wang et al; 2018). The degree of hydrolysis of polysaccharides increases with temperature and reaction time in a direct ratio. Hence, the degree of depolarization increases, and the biocoal yield decreases accordingly (Khaskhachikh et al; 2019). It is also worth observing certain conditions in Figure 4.1b sludge contents of 20%, 60%, 80%, and 100%, and in Figure 4.1c sludge contents of 80%, and 100%. Where the yields declined after 210°C and increased at 260°C in Figure 4.1b and F4.1c the yields increased after 210°C then declined at 260 °C. It is significant to note that in Figure 4.1a, the sludge content had a negligible effect on the biocoal yields for temperatures 180°C and

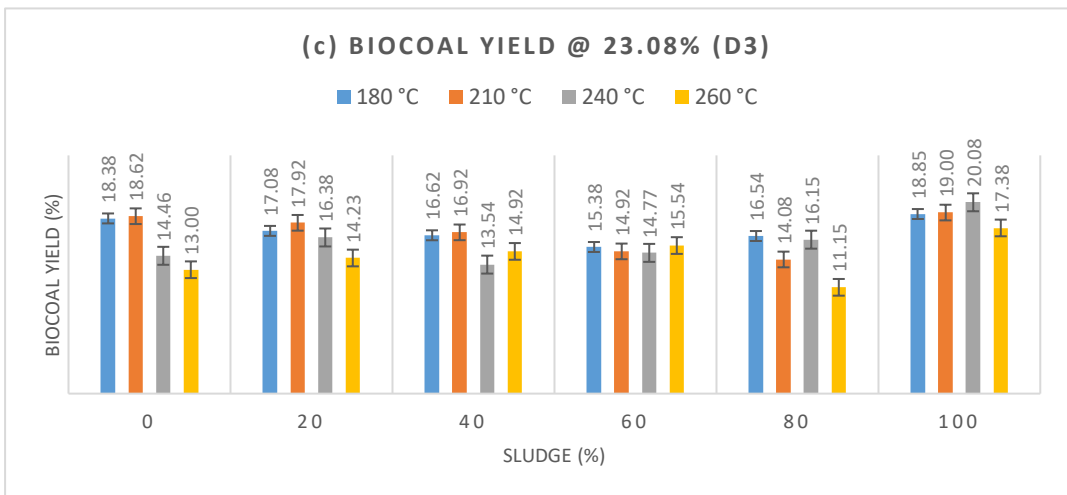
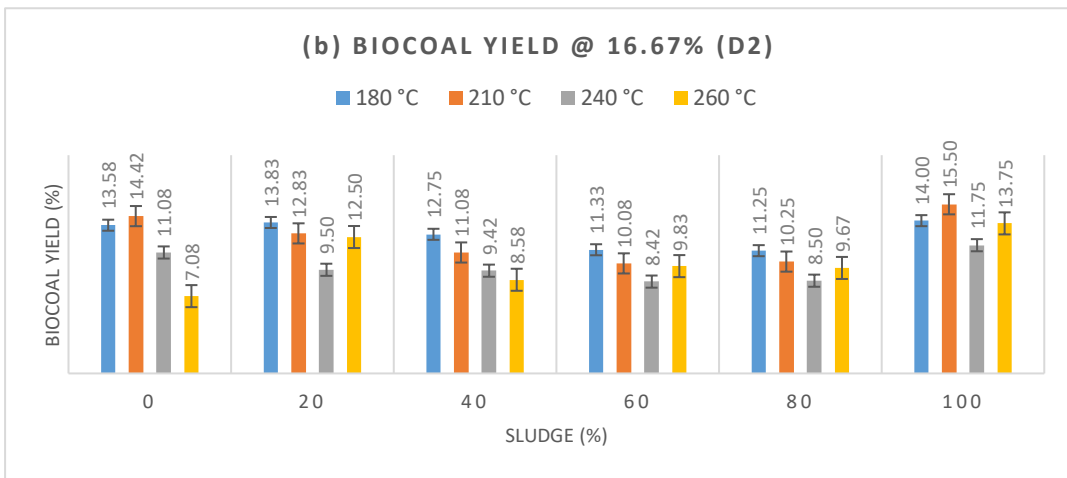
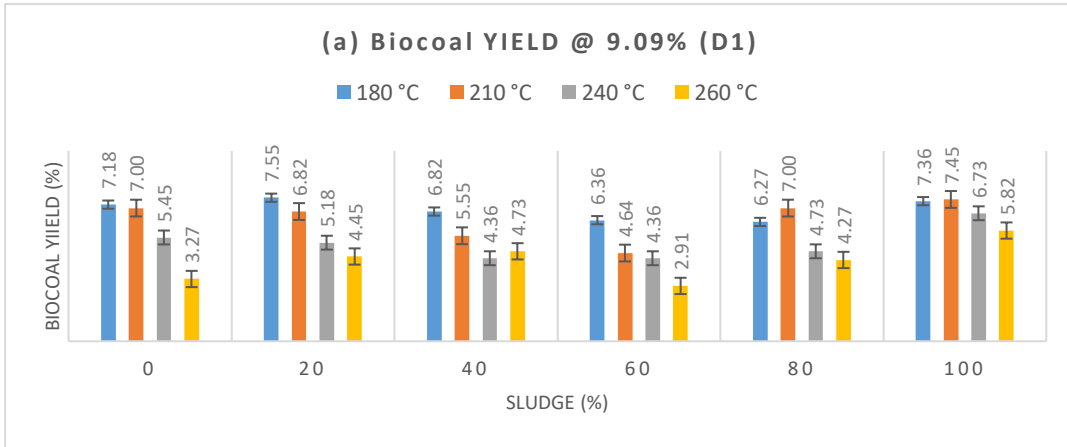
260°C. This is demonstrated by the consistent biocoal yields ranging from 7.18wt. % to 6.27 wt. % at 180°C and 0-100% sludge content followed by a major drop from 5.82wt. % to 2.91wt. % yield at 260°C and 0-100% sludge content. It is interesting to note that the biocoal yield of first increasing then decreasing pattern as temperature rises, was also depicted in Figures 4.1b, c, and d where solid loading of 16.67, 23.08, and 28.57wt. % were employed.

4.3.2. Effect of sludge and bagasse content on the biocoal yield

Figure 4.1 depicts the effect of solid ratio compositions investigated (which are pure bagasse, 20:80, 40:60, 60:40, 80:20 (S: B), and pure sludge) on the biocoal yield at various temperatures (180-260°C) and various sludge contents (0-100%). From the experiments conducted it can be seen in Figures 4.1a, and d that biocoal yields derived using pure bagasse (S0) declined gradually from 7.18-3.27 and 22.71-16.79 wt. % at 180 and 260°C. In Figures 4.1b, and c it is important to note a different trend is obtained, the biocoal yield increases to 14.42 and 18.62 wt. % at 210°C then after decreases.

Evaluating the sludge contents (S20-S80%) and temperatures (180, 210, 240, and 260°C) at different ratio variations of combined S/B gave rise to the biocoal yield. On all occasions where different ratios of S/B were employed, the yields were generally enhanced compared to that of pure bagasse biocoal yields, demonstrating that the mixture of sludge to bagasse at 20:80 (S: B) favors carbonization. It is safe to state without any uncertainties that S/B was predominantly the solid content that yielded better biocoals. This was evident in all the experiments. According to Funke & Ziegler (2010), the conversion of biomass into carbon materials by HTC is quite complex, different types of biomasses comprise of several peculiar compositions, and follows several parallel pathways, only some of which are fully understood in terms of when and how they occur. Making biomass reactions in HTC remarkably unique, enhancing carbonization which yields better biocoals.

Assessing all experiments as shown in Figure 4.1 sludge to bagasse mixture was the best performing biomass that maintained yielding high biocoals. The top highest biocoal yields were 23.36 wt. % derived from 20:80 (S: B) at 210°C with sludge content of 20% and 23.07 wt. % from pure sludge at 180°C.



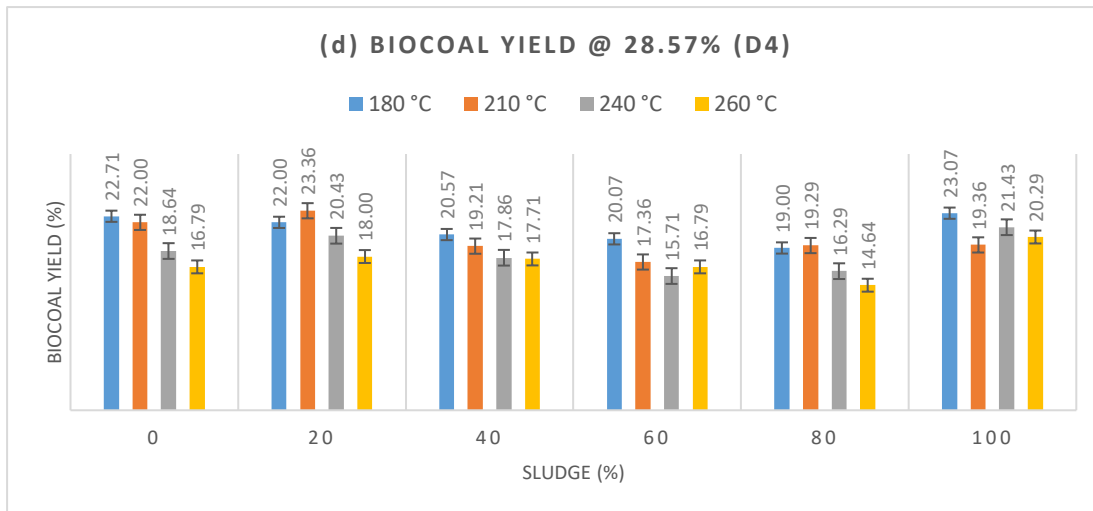
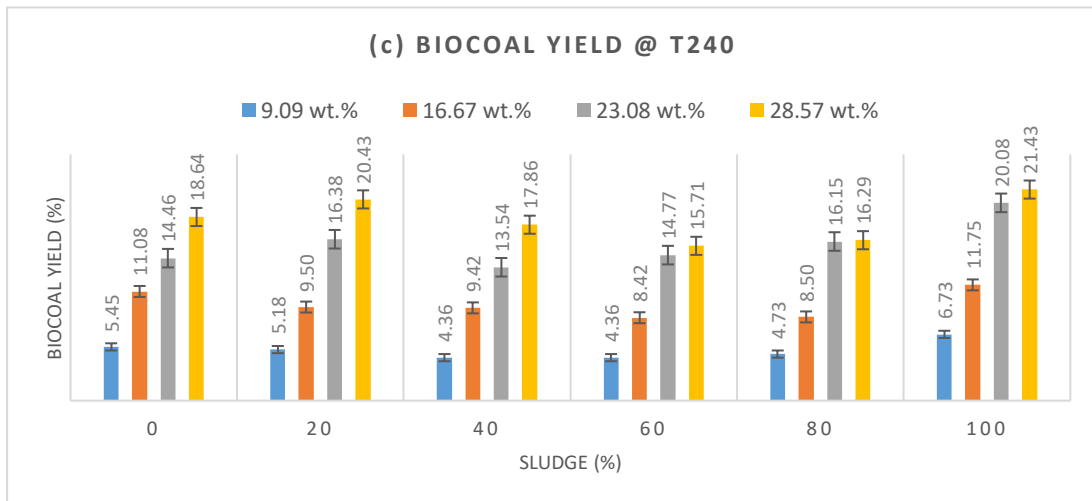
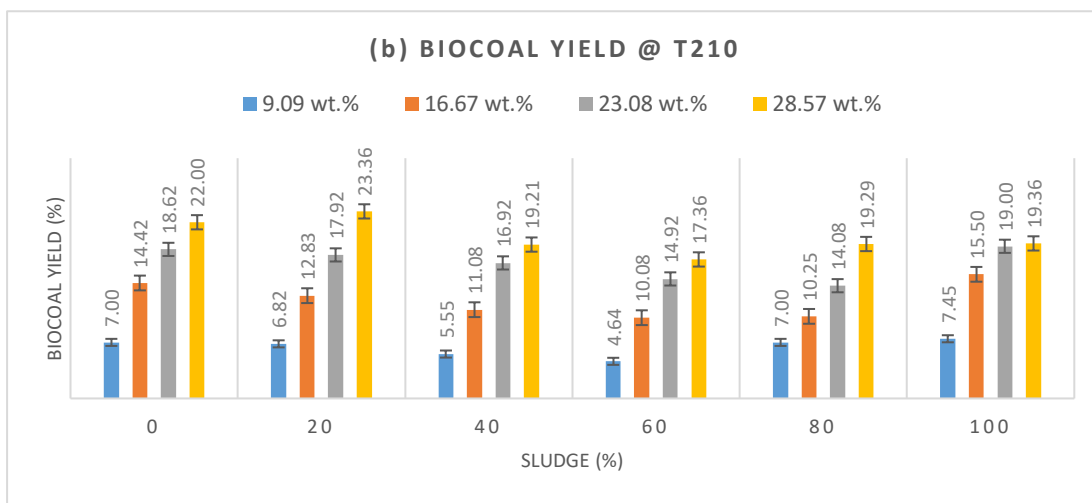
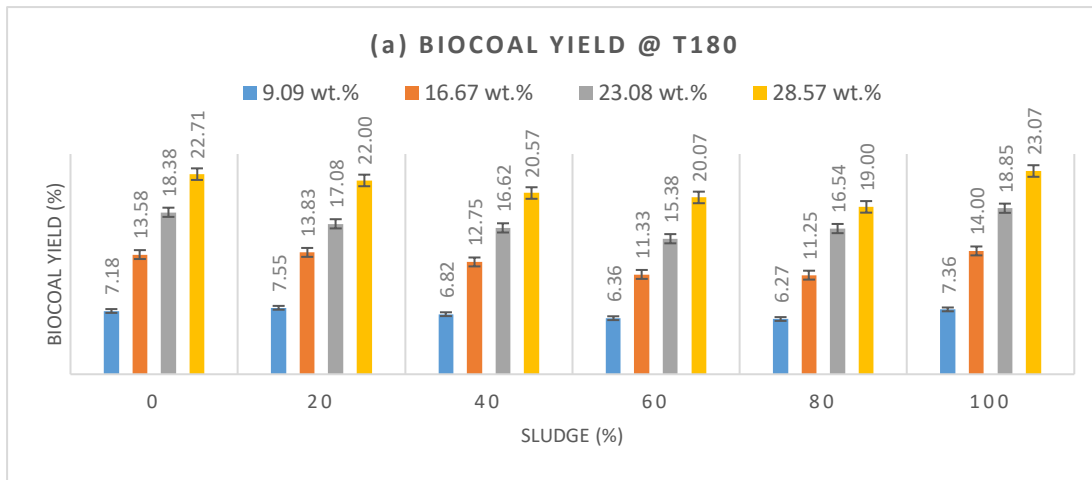


Figure 4.1 The effect of temperature on the biocoal yield at various sludge content (0-100%) when (a) 9.09% solid loading, (b) 16.67% solid loading, (c) 23.08% solid loading and (d) 28.57% solid loading were applied at a constant residence time of 60 minutes

4.3.3. Effect of solid loading on the biocoal yield

Figure 4.2 shows the effect of the solid loading on the biocoal yield. The dried feedstock was varied at 1, 2, 3, and 4 g, and the solvent deionized water (H₂O) was maintained at 10 g to achieve the desired solid loading between 9.09wt. % and 28.57wt. %. The solid loading had a meaningful impact on the yield of biocoals to a certain extent. In Figure 4.2 a-d there is a similar trend of yields observed with respect to the solid loading pattern for all four graphs. A comparable trend was observed where the yields gradually increase as solid loading wt. % increased, and this is predominant in all the graphs. This tendency reoccurred in all graphs at different temperatures, even when the solid ratio was either pure bagasse, sludge/bagasse, or pure sludge. It has become evident from the results illustrated in Figure 4.2 that low solid loading wt. % at any temperatures naturally yields low biocoal and larger solid loading such as 28.57wt. % are likewise conducive to producing greater yields. According to Fackaew et al (2015) HTC fed with higher moisture contents of faecal sludge (FS) could generate lower hydrocoals because the high amount of water (acting as a solvent) increased solubility of the FS and intermediate products, resulting in less hydrocoals formation.

As already mentioned, low solid loading facilitates the generation of less biocoal yield, therefore, a combination of low solid content and high solvent content would not favor carbonization and this occurrence is demonstrated in all the graphs in Figure 4.2. In the interest of comparing the effect of low solid loading 9.09wt. % and high solid loading 28.57wt. % at constant temperatures. Figure 4.2 demonstrates less biocoal yield was generated at low solid loading and higher yields were achieved at high solid loading. Unquestionably, higher solid loading yielded greater biocoal yields as compared to lower solid loadings. For example, in Figure 4.2a at sludge content of 20%, and 180°C, when comparing the two solid loadings (9.09wt. % and 28.57wt. %), the biocoal yields were 7.55 wt. % and 22.00 wt. % respectively. The best yield, which was the highest in all experiments, was 23.36% biocoal yield. As shown in Figure 4.2b when a combination of 20S/80B at 20% sludge content and 210°C, which amounted to 23.36 wt. %. The lowest biocoal yield obtained was 2.91 wt. %, as seen from Figure 4.2d, at 60S/40B, temperature 260°C and 60% sludge content.



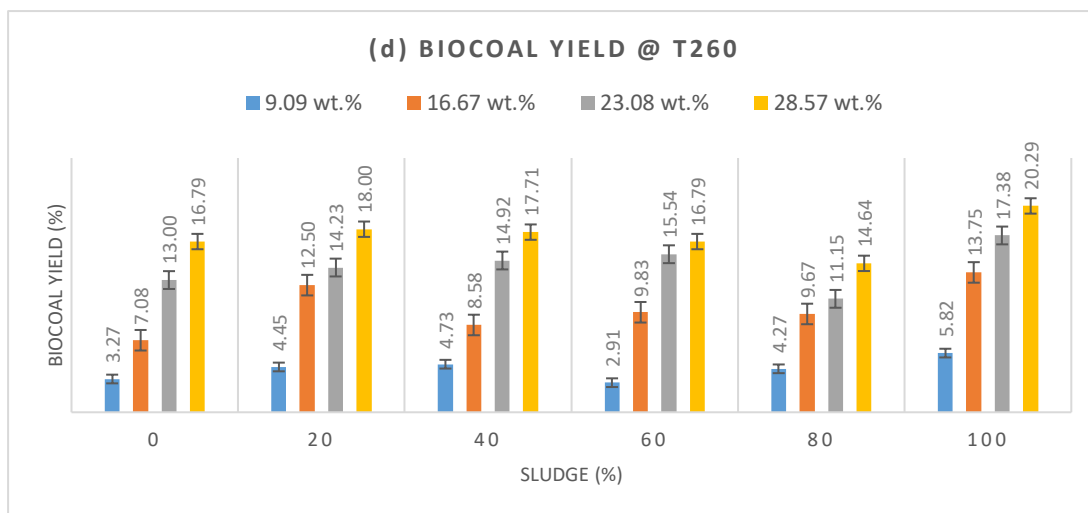


Figure 4.2 The effect of solid loading on the biocoal yield at various sludge content (0-100%) when (a) Temperature 180 °C, (b) Temperature 210 °C, (c) Temperature 240 °C, and (d) Temperature 260 °C applied at a constant residence time of 60 minutes

4.4. Effect of process parameters on the biocoal calorific value

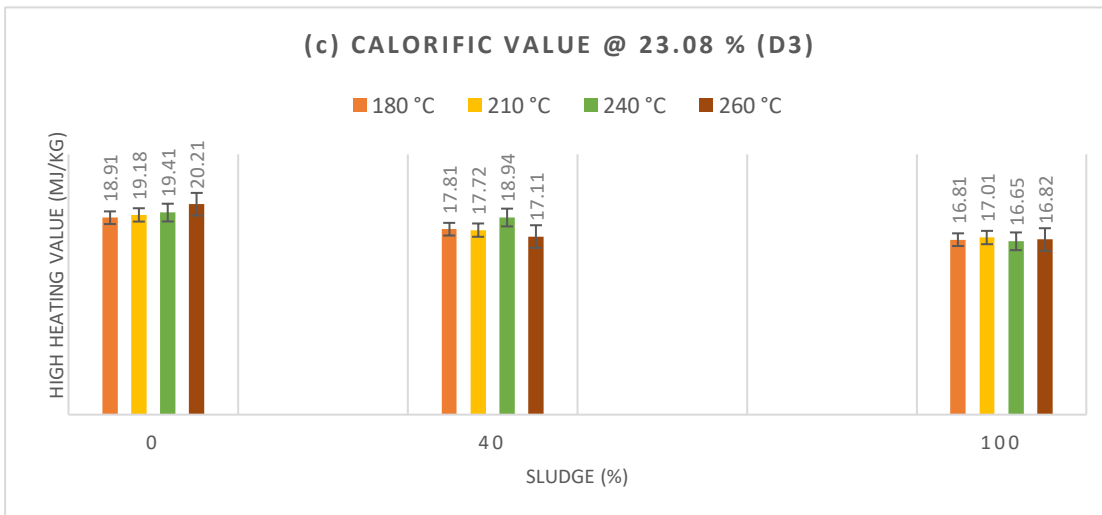
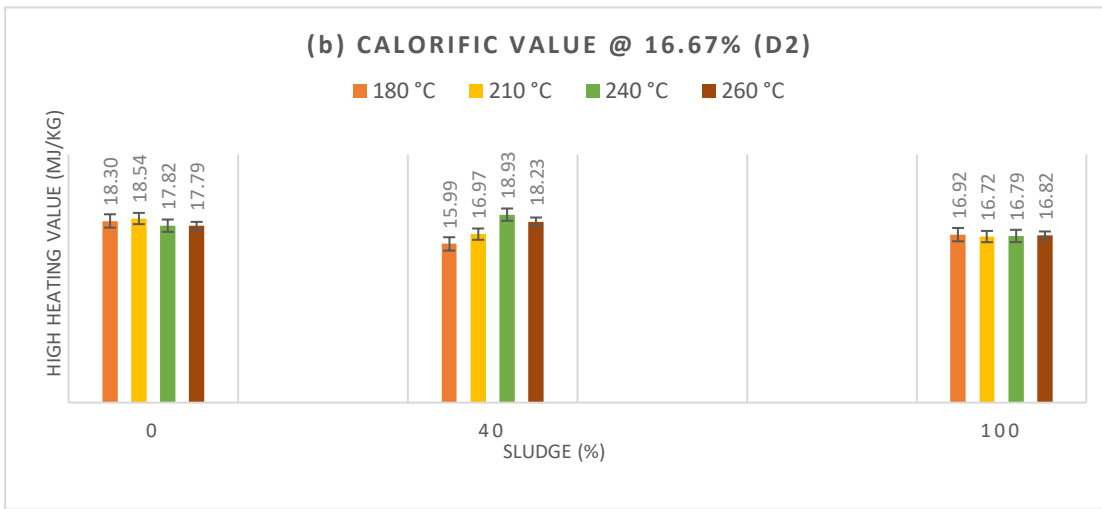
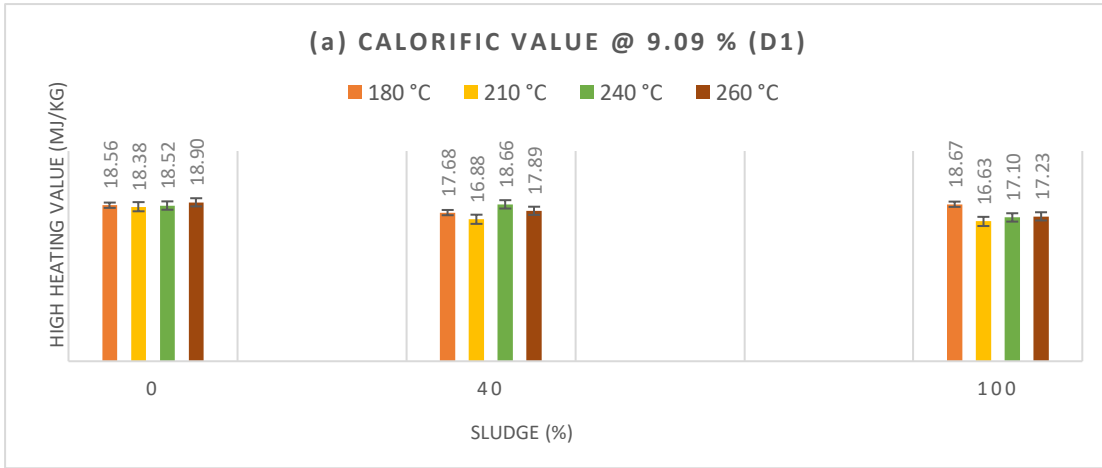
4.4.1. Effect of temperature on the biocoal calorific value

The results shown in Figure 4.3c for pure bagasse (S0) at a temperature of 260°C firmly demonstrate that temperature plays a significant role in the calorific value of biocoal. In general, increasing the temperature in the HTC reactor would result in more dehydration and decarboxylation of the biomass feedstock samples, resulting in increased energy content of the produced biocoal (Fakkaew et al; 2015). This is evident from Figure 4.3c with sludge content of 0% (which is pure bagasse), and temperatures 180-260°C. The calorific value slowly increases from 18.91 MJ/kg to 20.21 MJ/kg with the increase in temperature. Furthermore, a different trend was observed in Figures 4.3c and d, where a decline and negligible results of the calorific values are obtained at sludge content of 100% at 180-260°C. This tendency is demonstrated in almost all the graphs, this transpired under hydrothermal conditions due to the presence of hot compressed water, the reaction mechanism is initiated by hydrolysis, which results in the cleavage of ether and ester bonds between monomeric sugars by the addition of one molecule of water (Bobleter; 1994) and thereby reducing the activation energy levels of biomass polymers (Libra et al; 2011). Therefore, the degradation of hemicellulose in the HTC process occurs at an increased rate.

Among the four temperatures investigated, 260°C as shown in Figure 4.3 c, produced biocoal with the highest calorific value of 20.21MJ/kg at 0% sludge content (being pure bagasse).

4.4.2. Effect of sludge and bagasse content on the biocoal calorific value

The highest calorific value was achieved when pure bagasse was employed. This is apprehensible in Figure 4.3c, which illustrates the influence of solid content and type on the calorific value. The highest calorific value across all the runs was 20.21 MJ/kg at 260°C, with 0% sludge content. Figure 4.3c further shows that a calorific value of 18.94 MJ/kg was obtained at 40% sludge content and a temperature of 240 °C. Furthermore, at a temperature of 210 °C, a calorific value of 17.01 MJ/kg was obtained at 100% sludge content. It was discovered that pure bagasse produced better results when compared to the mixture of sludge and bagasse composition and pure sludge. This concurs with the study of Kiran et al. (2019) who performed HTC on sewage sludge and agricultural residue. Results show that biocoal produced from sludge and agricultural residue had a calorific value of 15.4 MJ/kg and 24.2 MJ/kg at 250 °C.



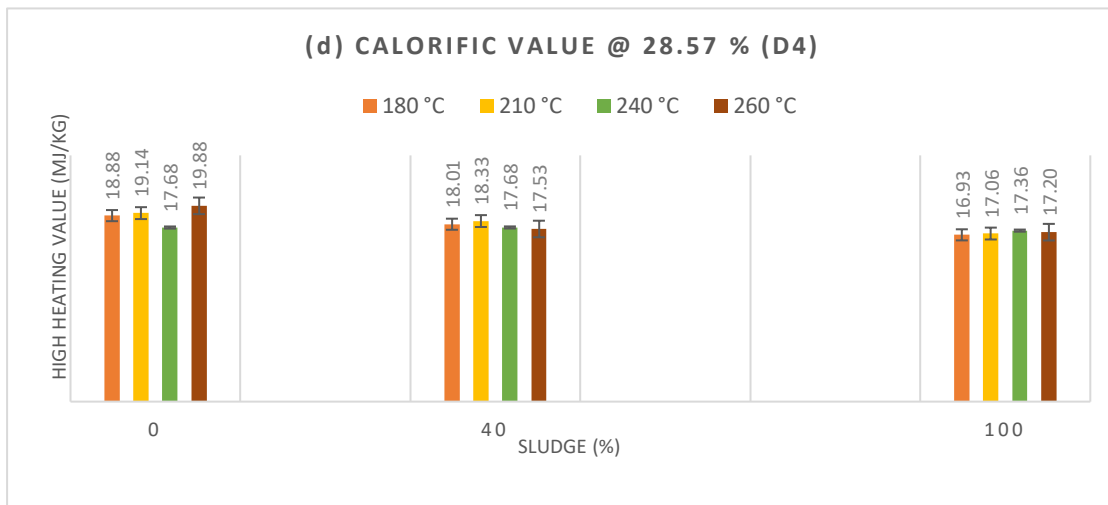


Figure 4.3 The effect of temperature on the calorific value at various sludge content (0-100%) when (a) 9.09% solid loading, (b) 16.67% solid loading, (c) 23.08% solid loading and (d) 28.57% solid loading were applied at a constant residence time of 60 minutes

4.4.3. Effect of solid loading on the biocoal calorific value

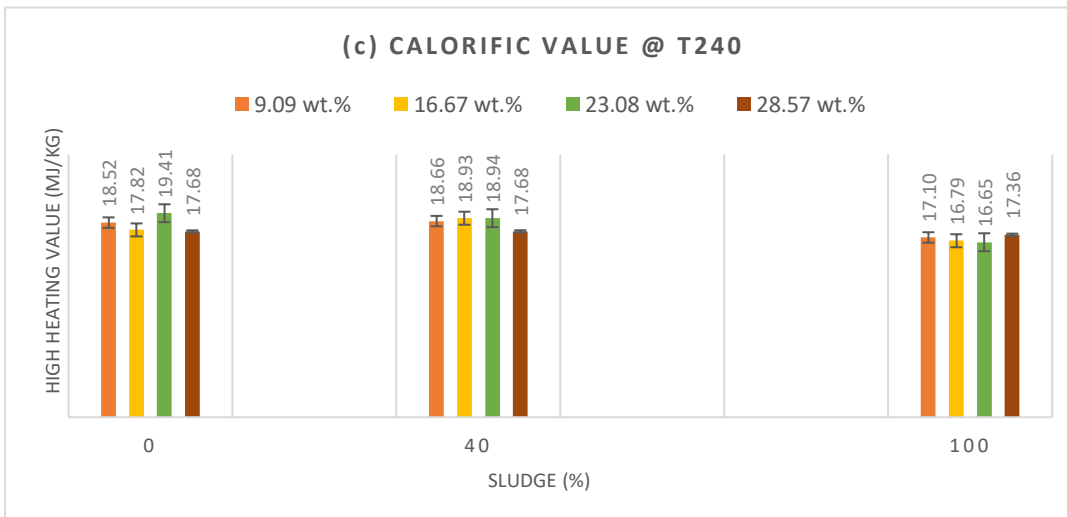
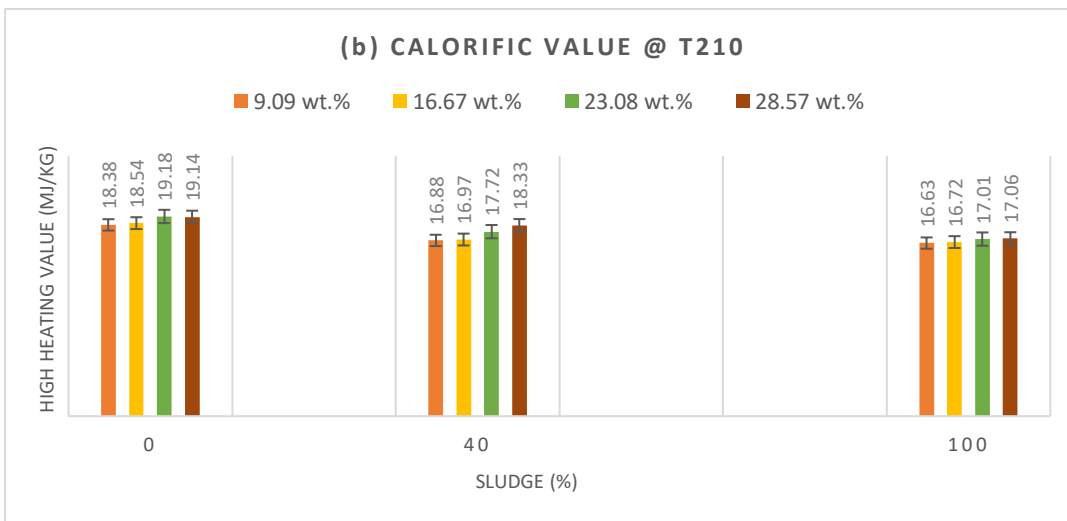
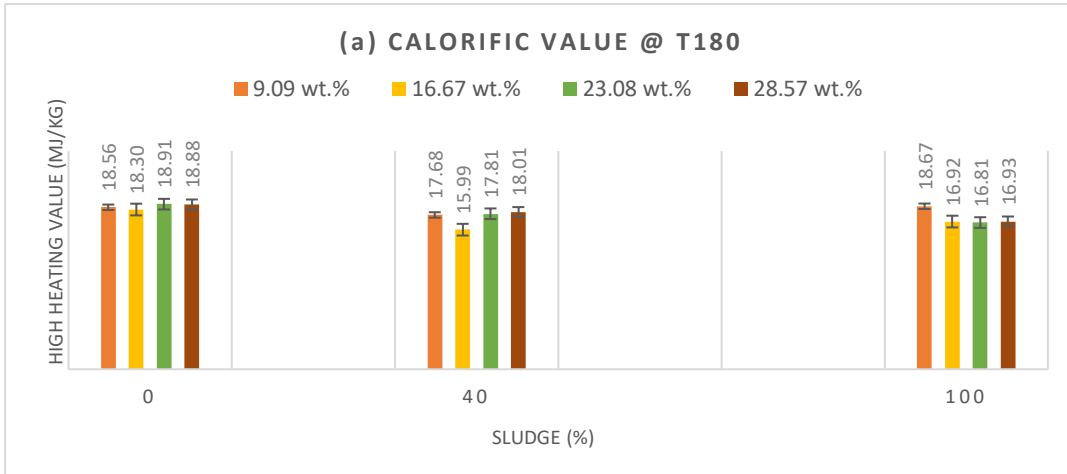
A similar pattern is sustained when the solid loading is considered. For example, in Figure 4.4d, at 0% sludge content, the calorific value decreased from 18.90 to 17.79 MJ/kg from 9.09wt. % to 16.67wt. %. Thereafter the calorific value experienced an increase to 20.21MJ/kg at 23.08wt. % then declined again to 19.88 MJ/kg at 28.57wt. %. This fluctuation trend is observed in Figures 4.4a and c. The coals having the top three calorific values 19.18, 19.41, and 20,21MJ/kg were achieved at temperatures 210, 240, and 260°C, Figures 4.4b, c, and d, at 23.08wt. % solid loading and 0% sludge content. This implies that at 23.08wt. % the best calorific values were obtained and an increase in solid loading does favor an increase in energy content. This agrees with the study of Kiran et al. (2019) who performed HTC on four dissimilar digestates from anaerobic digestion and observed that increasing solid loading lowers the solubility across all feedstocks treated resulting in an increase in energy content.

4.5. Bulk density

The bulk density analyses of selected biocoal pellets are presented in the appendices Table 4.1. Bulk density of the pellets is related to their transportation costs and energy density. Biocoal pellets exhibited the highest densities ranging from 1035.77 to 1318.77 kg/m³ when compared to all other pellets. In agreement with Qiang et al; (2015), this is linked to the reaction of Ca(OH)₂ with the inorganic constituents in biocoal and the subsequent strong binding with biocoal particles; this may have also contributed to the high mechanical strength. Other pellets showed the lowest bulk density ranging from 509.40 to 984.83 kg/m³. Through densification, the increase of bulk density indicates an increase in energy content in the biocoal pellets. This implies that densification is effective in promoting the properties of biocoal (Qiang et al; 2015).

4.6. Results summary

The best yield, which was the overall highest, was shown in F4.2b when a combination of S/B deployed at 20% sludge content and 210°C, which amounted to 23.36 wt. %. Biocoals derived using pure bagasse were overall the least effective in yielding high biocoal quantities. The lowest biocoal yield obtained was 3.27 wt. % pure bagasse at conditions of 260 °C and 0% sludge content. The highest calorific value achieved across all the runs was 20.21MJ/kg at 260°C, and 0% sludge content.



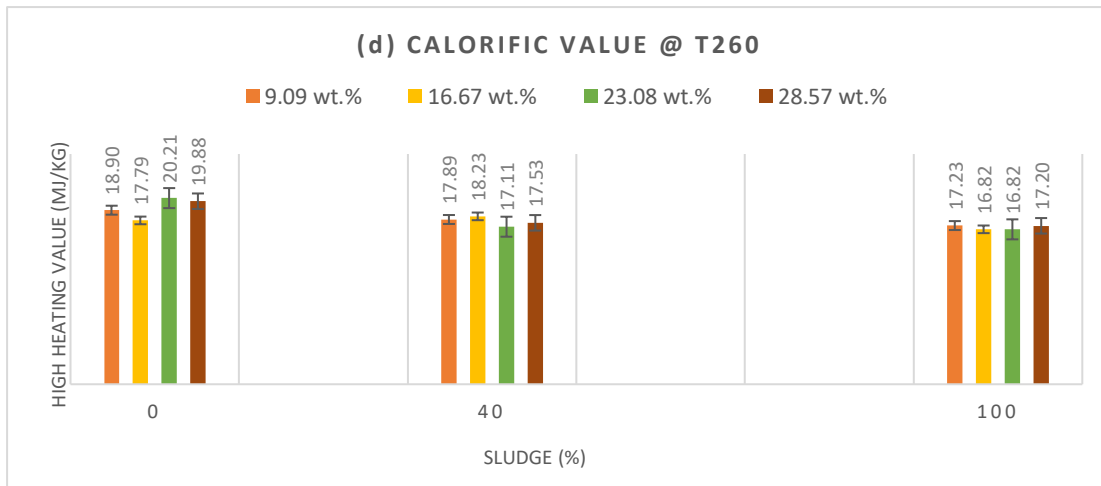


Figure 4.4 The effect of solid loading on the calorific value at various sludge content (0-100%) when (a) Temperature 180 °C, (b) Temperature 210 °C, (c) Temperature 240 °C, and (d) Temperature 260 °C applied at a constant residence time of 60 minutes

Table 4.1 Bulk density

Bulb density of biocoal		
Material	Volume-V (m ³)	Bulk density-P (kg m ⁻³)
S0 (Pure Bagasse)		
260°C @ 23.08wt. %		509.40
260°C @ 28.57wt. %	1.77E-06	764.09
S20 (Sludge & Bagasse)		
260°C @ 23.08wt. %		792.39
260°C @ 28.57wt. %	1.77E-06	1284.81
S40 (Sludge & Bagasse)		
260°C @ 23.08wt. %		1035.77
260°C @ 28.57wt. %	1.77E-06	1318.77
S60 (Sludge & Bagasse)		
260°C @ 23.08wt. %		984.83
260°C @ 28.57wt. %	1.77E-06	1075.39
S80 (Sludge & Bagasse)		
260°C @ 23.08wt. %		899.93
260°C @ 28.57wt. %	1.77E-06	758.43
S100 (Pure Sludge)		
260°C @ 23.08wt. %		690.51
260°C @ 28.57wt. %	1.77E-06	832.01

CHAPTER 5

5. Conclusion and recommendations

5.1. General conclusions

This research focused on the production of biocoal from wastewater sludge and sugarcane bagasse. In the instigation of this study, to achieve the aforementioned aim, the questions below were expected to be answered in the course of the study.

1. How effective will the hydrothermal carbonization process be in the production of biocoal from sludge and bagasse?
2. What is the effect of the operating parameters including, temperature, biomass type, and solid loading wt. % on the production of biocoal?
3. What process conditions are most likely to achieve valorization of sludge and bagasse?

The objectives of this study as stated in the introduction were to:

- Characterize wastewater sludge and sugarcane bagasse.
- Investigate the effects of temperature and solid loading on the heating value and yield of the biocoal.
- Characterize biocoal using relevant analytical techniques.

Wastewater sludge was dried at 100°C for 8 hours to maintain consistent feedstock moisture content. The dried sludge was then ground into a homogenous mass using a grinder. Sugarcane bagasse was prepared under the following conditions: washed thoroughly with deionized water, dried in an oven at 105°C for 2 hrs, ground, and sieved to particle sizes less than 425 µm. The high heating values of materials were determined based on ultimate analysis, which was carried out on an element analyzer intended for the simultaneous determination of the elements C, H, N, and S in the samples. The high heating values of the feed sludge, bagasse, and composition of sludge and bagasse were reported to be 17.07, 18.64, 16.87 MJ/kg, and carbon content of 42.85, 46.44, and 42.40 wt. % respectively.

The study presented in this research confirms that there were three process parameters investigated, which were solid loading, temperature, biomass type, and content. Out of the three process parameters, biomass type and content resulted in achieving the best biocoal yield, and the temperature was found to have the greatest effect on calorific value. The sludge and bagasse composition were determined to have a good effect, however, when pure sludge was used, the yields obtained were not high. The lowest yields were achieved when pure bagasse was used.

The most favorable process conditions were obtained at process conditions, namely: temperature of 210°C, and sludge content of 20% (which is a mixture of sludge and bagasse at a ratio of 1:4). The highest biocoal yield obtained was 23.36 wt. %. The lowest biocoal yield obtained was 3.27 wt. % where pure bagasse was used at 260°C and 0% sludge content. Among the four temperatures investigated, 260°C, gave the highest calorific value. Higher calorific values were obtained when pure bagasse was used. The highest calorific value across all the runs was 20.21MJ/kg at 260°C, with 0% sludge content.

The valorization of sludge and bagasse to biocoal from literature presented high heating values of 17.00-19.00MJ/kg and 28.2MJ/kg. The carbon content of biocoal from sludge and bagasse at 37.2-39.2 wt. % and 74.6 wt. % respectively. Consequently, results obtained were within the context of the literature with the highest biocoal calorific value of 20.21MJ/kg, carbon content of biocoal from sludge at 46.51 wt. % and bagasse 50.04 wt. % respectively.

The highest bulk densities obtained ranged from 1035.77 to 1318.77 kg/m³ and the lowest bulk density ranged from 509.40 to 984.83 kg/m³. The increase in bulk density indicates an increase in energy content in the biocoal pellets. The densification of biocoal was achieved by using Ca(OH)₂ as a binder with water added at room temperature.

5.2. Recommendations for future work

This study was conducted with the aim to produce biocoal from wastewater sludge and sugarcane bagasse. Based on the results obtained and the fact that the scope did not include the investigation of some process parameters. Therefore, it is for this reason, that the following recommendations are proposed for future investigation.

- Further work needs to be done on studying the effect of production technique on the biocoal elemental ratios H/C & O/C.
- More studies need to be conducted on the co-carbonization of different biomasses (for example, different biomasses mixed at different ratios) and the use of suitable catalysts that will influence yield and calorific value.
- Conduct analysis of the gaseous and aqueous by-products.
- Investigate the amount of energy used during the hydrothermal carbonization process.
- Study the effect of reaction time on the yield and calorific value.

In the future, investigate biocoal as an adsorbent for impurities present in the wastewater.

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Appendices

7.1. Sample of Calculations

7.1.1. Moisture Content of Pure Sludge

Before drying

Mass of 500ml empty plastic beaker = 61.96g

Mass of beaker + pure sludge = 349.63g

Mass of pure sludge = 349.63 - 61.96

$$= 287.66\text{g}$$

After drying

Mass of 500ml empty plastic beaker = 61.96g

Mass of beaker + dry pure sludge = 66.23g

Mass of dry pure sludge = 66.23 - 61.96

$$= 4.27\text{g}$$

$$\text{Moisture content}_{(wet\ basis)} = \frac{W_w - W_d}{W_w} \times 100 \quad \text{Equation 3.8}$$

Where W_w stands for wet weight and W_d is the dry weight.

$$\begin{aligned} \text{Moisture content}_{(wet\ basis)} &= \frac{287.66 - 4.27}{287.66} \times 100 \\ &= 98.52\% \end{aligned}$$

7.1.2. Total Solids of Pure Sludge

$$TS = \frac{W_d}{W_w} \times 100 \quad \text{Equation 3.9}$$

$$\begin{aligned} TS &= \frac{4.27}{287.66} \times 100 \\ &= 1.48\% \end{aligned}$$

7.2. Moisture Content of Filtered Cake after Filtration

Before drying

Mass of 500ml empty plastic beaker = 61.96g

Mass of beaker + wet filter cake = 213.02g

Mass of wet filter cake = 213.02 - 61.96
= 151.06g

After drying

Mass of 500ml empty plastic beaker = 61.96g

Mass of beaker + dry filter cake = 102.84g

Mass of dry filter cake = 102.84 - 61.96
= 40.88g

$$\text{Moisture content}_{(\text{wet basis})} = \frac{151.06 - 40.88}{151.06} \times 100$$
$$= 72.94\%$$

7.2.1. Total Solids of Filtered Cake after Filtration

$$TS = \frac{40.88}{151.06} \times 100$$
$$= 27.06\%$$

7.3. Solid Loading wt. % (SL) of solid to liquid sample of calculation

Total mass of solids (sludge and bagasse): 1g

Mass of deionized water: 10g

$$\text{Solid Loading (SL) \%} = \frac{\text{mass of total solids}}{\text{mass of solvent} + \text{total solids}} \times 100 \quad \text{Equation 3.10}$$

$$SL = \frac{1}{(1+10)} \times 100$$
$$= 9.09\%$$

7.4. High heating value

$$\text{HHV}=0.4373[\text{C}] -1.6701 \quad \text{Equation 3.11}$$

7.5. Biocoal yield

$$y_{bc} = \frac{m_c}{V_S} \times 100 \quad \text{Equation 3.12}$$

7.6. Mass yield

$$y_m = \frac{m_c}{m_b} \times 100 \quad \text{Equation 3.13}$$

7.7. Energy yield

$$y_e = y_m \times \frac{\text{HHV}_c}{\text{HHV}_b} \quad \text{Equation 3.14}$$

Run 1 (180S0D1): T=180 °C, biomass: pure bagasse (0% sludge content) and solid loading 9.09wt. % (D1).

$$\text{HHV}=0.4373[\text{C}] -1.6701 =0.4373[46.25] -1.6701 =18.56\text{MJ/kg}$$

$$y_{bc} = \frac{m_c}{V_S} \times 100 = \frac{0.79}{1+10} \times 100 =7.18\%$$

$$y_m = \frac{m_c}{m_b} \times 100 = \frac{0.79}{1} \times 100 =79\%$$

$$y_e = y_m \times \frac{\text{HHV}_c}{\text{HHV}_b} = 79 \times \frac{18.56}{18.64} =78.66\%$$

7.8. Volume

$$V = \pi r^2 h \quad \text{Equation 3.15}$$

7.9. Bulk density

$$\rho = \frac{m_c}{v} \quad \text{Equation 3.16}$$

Run 1 (260S0D3): T=260 °C, biomass: pure bagasse (0% sludge content) and solid loading 23.08wt. % (D3).

$$V = \pi 0.0075^2 (0.01) = 1.77E - 06 \text{ m}^3$$

$$\rho = \frac{0.0009}{1.76681E-06} = 509.40 \text{ kg/m}^3$$

Table 7.1 Raw data of ultimate and heating value analysis of feedstock and biocoal

Ultimate, and heating value analysis of feedstock and corresponding biocoal									
Material	Elemental Composition (wt% db)					High Heating Value (MJ/kg db)	Biocoal yield (%)	Mass Yield (%)	Energy Yield (%)
	C	H	N	S	O	HHV	Ybc	Ym	Ye
FS (Feed Sludge)	42.85	6.47	2.79	0.00	47.89	17.07	0.00	-	-
FB (Feed Bagasse)	46.44	5.96	0.64	0.00	46.95	18.64	0.00	-	-
FSB (Feed Sludge & Bagasse)	42.40	6.33	2.63	0.00	48.64	16.87	0.00	-	-
PS (Pure Sludge)									
180°C @ D1	41.94	6.37	2.88	0.00	48.81	16.67	0.00	-	-
210°C @ D1	41.46	6.25	2.35	0.00	49.93	16.46	0.00	-	-
210°C @ D2	41.46	6.418	3.23	0.00	48.90	16.46	0.00	-	-
240°C @ D1	37.61	5.73	2.10	0.00	54.56	14.78	0.00	-	-
240°C @ D2	41.54	6.37	2.93	0.00	49.16	16.49	0.00	-	-
260°C @ D1	41.85	6.31	1.75	0.00	50.09	16.63	0.00	-	-
260°C @ D2	40.72	6.08	1.84	0.00	51.36	16.14	0.00	-	-
S0 (Bagasse)									
180°C @ D1	46.25	6.10	0.00	0.00	47.65	18.56	7.18	79.00	78.64
210°C @ D1	45.84	5.99	0.00	0.00	48.17	18.38	7.00	77.00	75.91
240°C @ D1	46.16	5.85	0.00	0.00	47.99	18.52	5.45	60.00	59.60
260°C @ D1	47.04	5.88	0.00	0.00	47.08	18.90	3.27	36.00	36.50
180°C @ D2	45.66	5.99	0.00	0.00	48.35	18.30	13.58	81.50	80.00
210°C @ D2	46.22	6.04	0.00	0.00	47.74	18.54	14.42	86.50	86.04
240°C @ D2	44.57	5.89	0.00	0.00	49.55	17.82	11.08	66.50	63.58
260°C @ D2	44.50	5.88	0.00	0.00	49.62	17.79	7.08	42.50	40.56
180°C @ D3	47.07	6.55	0.00	0.00	46.38	18.91	18.38	79.67	80.84
210°C @ D3	47.69	6.29	0.00	0.00	46.02	19.18	18.62	80.67	83.02
240°C @ D3	48.20	6.20	0.00	0.00	45.60	19.41	14.46	62.67	65.25
260°C @ D3	50.04	5.90	0.00	0.00	44.06	20.21	13.00	56.33	61.09
180°C @ D4	47.00	6.11	0.00	0.00	46.89	18.88	22.71	79.50	80.54
210°C @ D4	47.58	6.11	0.00	0.00	46.32	19.14	22.00	77.00	79.05
240°C @ D4	44.24	5.39	0.00	0.00	50.37	17.68	18.64	65.25	61.88
260°C @ D4	49.27	5.86	0.00	0.00	44.87	19.88	16.79	58.75	62.64
S40 (Sludge & Bagasse)									
180°C @ D1	44.24	6.108	1.47	0.00	48.18	17.68	6.82	75.00	78.59
210°C @ D1	42.43	6.25	1.79	0.00	49.53	16.88	5.55	61.00	61.05
240°C @ D1	46.49	6.21	0.92	0.00	46.39	18.66	4.36	48.00	53.09
260°C @ D1	44.73	6.16	1.14	0.00	47.97	17.89	4.73	52.00	55.15
180°C @ D2	40.38	5.64	1.68	0.00	52.30	15.99	12.75	76.50	72.49
210°C @ D2	42.62	6.25	2.10	0.00	49.04	16.97	11.08	66.50	66.89

240°C @ D2	47.12	6.18	1.33	0.00	45.38	18.93	9.42	56.50	63.41
260°C @ D2	45.51	6.26	1.40	0.00	46.84	18.23	8.58	51.50	55.65
180°C @ D3	44.55	6.34	1.86	0.00	47.25	17.81	16.62	72.00	76.02
210°C @ D3	44.35	6.16	1.58	0.00	47.91	17.72	16.92	73.33	77.04
240°C @ D3	47.12	6.10	1.28	0.00	45.49	18.94	13.54	58.67	65.85
260°C @ D3	42.94	6.07	1.55	0.00	49.44	17.11	14.92	64.67	65.57
180°C @ D4	43.40	6.30	1.35	0.00	48.95	18.01	20.57	72.00	76.87
210°C @ D4	45.74	6.28	1.38	0.00	46.60	18.33	19.21	67.25	73.08
240°C @ D4	44.26	6.23	1.53	0.00	47.99	17.68	17.86	62.50	65.51
260°C @ D4	43.90	6.08	1.45	0.00	48.57	17.53	17.71	62.00	64.41
S100 (Sludge)									
180°C @ D1	46.51	6.92	1.98	0.00	44.59	18.67	7.36	81.00	88.60
210°C @ D1	41.84	6.21	2.10	0.00	49.85	16.63	7.45	82.00	79.88
240°C @ D1	42.93	6.23	1.29	0.00	49.55	17.10	6.73	74.00	74.16
260°C @ D1	43.22	6.20	0.00	0.00	50.58	17.23	5.82	64.00	64.61
180°C @ D2	42.51	6.47	2.43	0.00	48.59	16.92	14.00	84.00	83.27
210°C @ D2	42.06	6.37	2.49	0.00	49.08	16.72	15.50	93.00	91.12
240°C @ D2	42.26	6.36	2.42	0.00	48.96	16.79	11.75	70.50	69.34
260°C @ D2	42.29	6.38	2.45	0.00	48.88	16.82	13.75	82.50	81.32
180°C @ D3	42.25	6.54	2.88	0.00	48.33	16.81	18.85	81.67	80.42
210°C @ D3	42.72	6.53	2.47	0.00	48.29	17.01	19.00	82.33	82.06
240°C @ D3	41.89	6.39	2.41	0.00	49.31	16.65	20.08	87.00	84.86
260°C @ D3	42.28	6.30	3.20	0.00	48.22	16.82	17.38	75.33	74.24
180°C @ D4	42.54	6.51	2.44	0.00	48.51	16.93	23.07	80.75	80.11
210°C @ D4	42.84	6.38	1.41	0.00	49.37	17.06	19.36	67.75	67.74
240°C @ D4	43.52	6.32	2.36	0.00	47.80	17.36	21.43	75.00	76.29
260°C @ D4	43.16	6.49	1.50	0.00	48.85	17.20	20.29	71.00	71.57