PROCESS OPTIMISATION AND TECHNO-ECONOMIC ANALYSIS OF BRIQUETTE PRODUCTION FROM CORN-STOVER

by

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DECLARATION

I, Nqobile Felicia Ngubane, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date**

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ABSTRACT

The world is currently challenged with an energy crisis associated with global warming, and environmental pollution caused by the increase of global population and industrial activities. Renewable energy sources such as biomass is an alternative source of fuel to traditional fossil fuel sources and their use could be an important contributor in satisfying South Africa's growing energy demand. Biomass usually consists of an animal, forest, and agricultural residues. South Africa being the largest producer of maize (corn) in Africa generates approximately 5.1 million metric tonnes of corn residues per annum as agricultural wastes remain untapped. This is a potential renewable feedstock that is sustainably available with no competition for resources with no food/feed production. This study aimed to add value to corn-stover (CS) by converting it into an eco-friendly solid fuel (briquettes) with high carbon content and high calorific value (HHV) to meet the increasing energy demand in South Africa through slow pyrolysis and densification process. This work investigated biochar and char briquettes in terms of its ultimate and proximate analyses. Moreover, a statistical optimisation tool, central composite design (CCD) was used to maximise the production of high-quality briquettes, in terms of HHV, compaction pressure, durability, and density. Furthermore, the optimised conditions were used to develop a process design and economic evaluation of a briquette production scale-up plant. The results indicate that the HHV (25.5-28.81 MJ/kg) of the briquettes was only influenced by binder concentration. Whereas the compressive strength (3.45-6.11 N/mm^2) and density (420-788 kg/m^3) of the briquettes were both influenced by compaction pressure and binder concentration. Finally, the results show that all 3 factors influenced the durability (97-100%) of the briquettes. Therefore, under these optimised conditions compression pressure (40MPa), binder concentration (8.74%) and drying temperature (21.6 ºC), HHV, compressive strength, density and durability as predicted by the respective developed models are 27.32 MJ/kg, 5.48 N/mm^2, 770.40 m^3/kg and 98.87% respectively. These briquettes were comparable to that of domestic char bio-briquettes made from wood, and South African bituminous A grade coal used for domestic and industrial purposes. Techno-economic analysis of 550 kg/h of CS briquetting plant showed that it was able to generate 300 kg/h of dry briquettes. The economic evaluation of this study showed that with a total capital investment (TCI) of $518 790.68 the plant was found to be economically feasible with a DBPB <4 years and DCFROR >30%. Although this study is seen to be technically and economically profitable, the goals and environmental surroundings of the project should be decided based on the location and availability of feedstock.

DEDICATION

My humble efforts I dedicate to my loving, caring and sweet:

Mother

“A strong and God-fearing woman who allowed me to be my own person and taught me to believe in myself, believe in God and trust the process”

Father

“For being the man of his own words and for supporting and believing in me for as long as I remember. My hero”

Grandmother

“For being my first teacher and all the prayers every day”

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GLOSSARY

Abbreviation	**Definition**
AD	Anaerobic digestion
ASTM	American Society for Testing and Materials
BBD	Box Behnken Design
CCD	Central Composite Design
CCS	Carbonised corn-stover
CECPI	chemical engineering cost price index
CS	Corn-stover
DCFROR	Discounted Cash Flow Rate of Return
DPBP	Discounted Payback Period
EU	European Union
FCC	Fixed Capital Costs
HCV	High calorific value
HHV	Higher Heating Value
IEP	International Energy plan
IRR	Internal Rate of Return
kg	kilogram
MJ	Mega Joule
NPV	Net Present Value
PBP	Payback Period
RSM	Response Surface Methodology
TBA	To be assessed
TCI	Total Capital Investment
TGA	Thermogravimetric Analyser
TMC	Total Manufacturing costs
WCC	Working Capital Costs

CHAPTER ONE

1. INTRODUCTION

1.1. Introduction

With the increasing global population and industrial activities, the world is currently challenged with energy crisis and waste management issues owing to the exhaustion of conventional fuel reserves and excessive waste generation. Fossil fuels consumption is increasingly becoming a major concern globally and locally due to their high greenhouse gases emissions, pollution to the environment and global warming contribution (Helwani et al., 2018). Consequently, these continuously increase the gap between environmental sustainability and economic growth thus leading to sustainable energy sources and waste management methods being implemented (Nizami et al., 2017). Mostly, waste management approaches are for pollution reduction and public health protection. However, it is essential to have an integrated approach that not only focuses on waste management but also energy recovery from these residues.

Bioenergy is derived from biological sources, and it has recently gained interest due to it being renewable unlike, conventional fossil fuel. Renewable energy particularly lignocellulosic biomass is inexpensive and abundant, and it is derived from organic matter such as forest residue, agricultural residue, and municipal waste (Hiremath et al., 2009; Qiao et al., 2018). Furthermore, the properties of biomass such as low sulphur, and nitrogen content in addition to being CO_2 neutral makes it a promising renewable energy source (Balasubramani et al., 2016). South Africa is very active in crop production and its major driver is the agricultural sector. This indicates the potential of abundant agricultural residues/wastes attributed to the increase in food demand from population growth and rural-urban migration (Mohlala et al., 2016).

South Africa the largest producer of maize in Africa, is estimated to generate approximately 16 million metric tonnes of corn-stover (CS) per annum. The untapped CS is around 5.1 million metric tonnes of total CS and is available in excess yearly (Batidzirai *et al.*, 2016). Corn stover consist of the leaves, stalks and stems of a maize plant that remains after harvest (Schon, 2012). In most cases, CS is used as a soil amendment and animal feed and the remaining gets disposed of or destroyed by burning for preparation of the next harvest (Anukam et al., 2017). Therefore, the disposal of these biomass wastes constitutes inefficiently can pose a threat to the environment by causing pollution and contributing to climate change during decomposition (Mohlala et al., 2016).

Nevertheless, the significant amount of the biomass waste generated yearly can be converted to useful products. This essentially shifts the dependency on fossil fuels to using energy conceived from the sunlight of which is renewable (Dhyani & Bhaskar, 2018). In addition to South Africa’s major energy challenges such as unplanned outages, high energy tariffs, and poor power infrastructure development, a significant energy shortage in low-income households is a serious issue (Pollet et al., 2015). To eradicate this, incorporating and harnessing the potential benefits of biomass residue will assist to secure a reliable energy supply to meet the basic living needs of the middle class and urban poor (Essex & Groot, 2019).

However, due to biomass’ unstable material and low energy and bulk density, it becomes very difficult to store and transport loose biomass. This is associated with high operational cost (Laird et al., 2010). Additionally, directly burning biomass leads to inefficient use of energy due to its hygroscopic nature (Si et al., 2016). Therefore, it is essential to use low cost, and environmentally friendly technologies to utilise these biomass residues efficiently. Conversion process such as biological, thermochemical, and physical processes are commonly used or integrated to treat different residue feedstocks to produce value-added products for chemicals, fuel, power, and heat (Nizami et al., 2017).

These biomass types can be utilised using one of the thermochemical processes known as pyrolysis (Russell et al. 2017). The pyrolysis process leaves a carbon-rich solid residue (char) from the thermal decomposition of organic polymers that release vapours of various molecular weight compounds (Park et al., 2014). These pyrolytic vapours can be separated into condensable and non-condensable volatiles (oil and gases). This technology can be integrated with the densification process to produce charcoal briquettes from the derived biochar in the pyrolysis process. Densification is also known as briquetting/pelletising is one of the most common ways to convert biomass into solid fuels by densifying the material into a uniform shape and increase its energy and bulk density (Si et al., 2018). Densification not only increases the bulk density of the biomass from approximately 40-200 kg/m^3 up to 600-800 kg/m^3, but it also helps with handling, storage, and transportation-related problems (Brand et al., 2017). Pressure agglomeration which involves mechanical compression and tumble agglomeration where binding agents are used are the two key approaches in the briquetting process (Bajwa et al., 2018).

Briquettes are blocks of combustible energy carrier made from typically compressed biomass residue for heating and cooking purposes (Onchieku et al, 2012). They are sustainable and eco-friendly, and their properties can be comparable to that of firewood and coal. Thermal and physical properties such as heating value, ash content, volatile matter content, moisture content, fixed carbon content and density amongst others are used to determine the quality of briquettes (Wilson, 2016). These properties are influenced by factors such as compaction pressure, particle size, moisture content, drying temperature, binder ratio/concentration and others (Kaliyan & More, 2009b). There is a wide range of studies that have shown the utilisation of corn-stover in South Africa particularly for bioethanol, biochar, bio-oil, and gases (Mohlala et al., 2016). However, there is a dearth of literature that covers the production of biochar briquettes from corn-stover (CS). Pyrolysis and densification are intricate and challenging processes and with each biomass material having unique process variables for briquettes to be produced with desirable thermal and physical properties, optimum process variables need to be determined.

Therefore, the main aim of this study is to encourage sustainable growth through the creation of value addition to the CS into an eco-friendly solid fuel with high carbon content and high calorific value to meet the increasing energy demand in South Africa. This will be achieved by determining the influence of the densification parameters on the quality of the product employing experiments with a factorial design. The physical and densification characteristics of briquettes will be accessed via ultimate and proximate analyses. Statistical software package Design-Expert® will be used to optimise targeted variables due to their major advantages that they do use rough estimation and allows a larger number of factors to be assessed. The targeted variables compaction pressure, binder concentration and drying temperature. Also, the economic analysis of the briquetting process be will then be assessed in terms of the major costs and SuperPro Designer® will be employed.

1.2. Research problem

The depletion of energy resources and the environmental impacts related to the use of conventional fossil fuels are major global concerns. Hence, there is a strong interest worldwide in the development of technologies that exploit renewable energy sources. Corn stover can be a major pollutant as solid waste and its disposal can be challenging which can pose a harmful threat to the environment. Corn-stover is a naturally abundant, potential energy source, that is promising to relieve energy scarcity. It can be treated via thermochemical and compaction technologies. Thus, integrating a strategy aimed at both reduction of pollution and energy generation by producing clean high-density fuels.

1.3. Hypothesis and research questions

It is hypothesised that energy can be harnessed from CS waste as solid fuel in the form of briquette. To validate the hypothesis, the following questions were formulated:

- Can the biomass briquetting of biochar from corn residues be improved through process optimisation?
- Is the process technically and economically feasible in the South African context?

1.4. Research aim & objectives

This study explored the potential of CS as a feedstock for eco-friendly solid fuel production to meet the increasing energy demand in South Africa and to answer the research questions and achieve the aim, the following objectives were developed:

- To produce biochar using slow pyrolysis at optimum conditions
- To investigate carbonised corn-stover (CCS) /Briquette as an alternative fuel source to coal by characterisation
- To optimise the densification of CS into briquettes
- To investigate the techno-economic feasibility of the briquetting process

1.5. Significance of research

The search for renewable resources to replace the traditional fossil fuels and environmental issues motivates the need to explore other alternatives for producing green and clean energy. This research will be of significant benefits to relieve the energy crisis especially in small communities, the need for raw material and environmental issues. Hence the following rationale and significance could be an outcome based on the research scopes and objectives mentioned above:

- Minimisation of handling, transport, and storage of corn-residues
- Production of a valuable product (bio-briquette) from CS biomass waste
- Production of alternative portable renewable energy source
- Relief of environmental issues (waste management)

1.6. Delineation/ limitations

In this study, slow pyrolysis technology was used to produce biochar at optimum conditions obtained from the literature. While three products were produced via pyrolysis only char was utilised to produce briquettes. This study is only limited to the technical feasibility aspects of producing carbonised briquettes from CS.

1.7. Thesis outline

Chapter 1: This chapter provides a brief introduction to the thesis. It covers the problem statement, hypothesis, objectives, significance, and delineation of the study.

Chapter 2: This chapter contains an overview of the literature that regarding lignocellulose biomass resource, agricultural residues and their micro-components, thermochemical and densification processes. It describes the desirable briquette qualities, factors affecting briquetting, process optimisation as well as economic theory and analysis.

Chapter 3: This chapter covers the research design and methodology. It describes the materials and methods used in this study to determine the objectives. The sampling procedures, production processes, analytical and optimisation techniques are described.

Chapter 4: This chapter entails the results and discussion of the characterisation of the raw CS, biochar, and briquettes as well as the process optimisation of briquetting.

Chapter 5: This chapter covers results and discussion of the techno-economic analysis which entails the process development and economic analysis of briquette.

Chapter 6: This chapter entails the general conclusions and recommendations of the current study.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Biomass resource

The organic polymers originally produced by sunlight is called biomass. It is a dry matter which is an abundant and very cheap source of renewable energy and can be referred to as lignocellulosic biomass (Dhyani & Bhaskar, 2018; Park et al., 2014). The categories of typical lignocellulose biomass sources are shown in **Figure 2.1**.

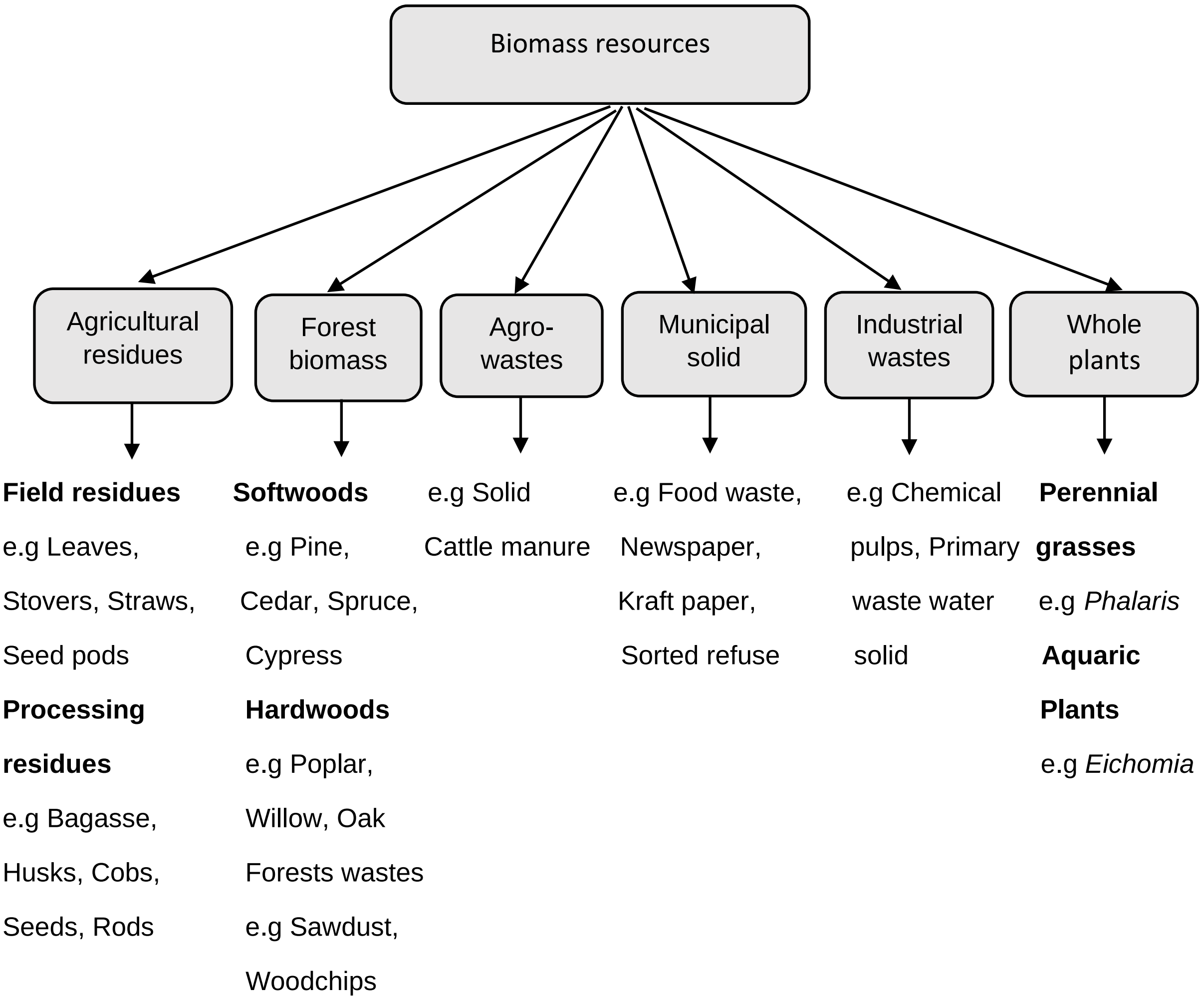


Figure 2.1: Available resource of biomass waste (Adapted from Zabed et al., 2016).

Lignocellulose biomass can be divided into mainly forest biomass and residues, municipal wastes, animal wastes and agricultural residues as demonstrated in **Figure 2.1** (Biswas et al., 2017; Akubo et al., 2019). Biomass resources are cheap and easy to access as wastes than conventional fuel on an energy basis (Dhyani & Bhaskar, 2018). They contribute 10% globally as primary energy supply and have the potential to supplement fossil fuels in the rural economy as a source of energy (Naqvi et al., 2018).

2.1.1. Agricultural residues

The world's total biomass is made up of agricultural residues obtained from crops which are wheat, rice, sugarcane, and corn (Zabed et al., 2016; Biswas et al., 2017). Apart from being environmentally friendly, agricultural residues are considered as short-harvest ration which makes them more readily available than forest residues and reduces the reliance on woody biomass which causes deforestation (Limayem and Rickle, 2012). Therefore, different high-value products such as biofuels and added fine chemicals can be produced from the hugely available amount of agricultural residues. Agricultural residues possess high energy content in the form of cellulose, hemicellulose, and lignin (Biswas et al., 2017). According to Limayem and Rickle (2012), they are 25-35% more hemicellulosic than forest biomass. Potential agricultural lignocellulosic feedstocks and their composition are described in **Table 2.1**.

Table 2.1: Potential agricultural lignocellulosic feedstocks and their composition.

Biomass	**Component composition (wt.%)**			**Reference**
	Lignin	**Hemicellulose**	**Cellulose**	
Sugarcane bagasse	20	25	42-48	(Anwar et al., 2014)
Rice straw	18	24	32.1	(Moneim et al., 2018)
Corn stover	14.4	30.7	51.2	
Wheat straw	15-16.4	27.3-50	42-45	(Dhyani & Bhaskar, 2018)
Corn cobs	14-15	35-39	42-45	
Barley straw	14-19	27-38	31-45	(Zabed et al., 2016)

Agricultural residue's high levels of hemicellulose (24-32%) and low levels of lignin (3-13%) makes them advantageous over woody biomass because they do not require as much energy during pre-treatment such as size reduction of their a less resistant texture (Limayem and Rickle, 2012).

2.1.2. Lignocellulose biomass physicochemical characteristics

Approximately 70% of the total biomass is made up of cellulose and hemicellulose. Due to covalent and hydrogen bonds, they are directly linked to the lignin component which makes the structure highly robust and resistant to any treatment (Limayem and Rickle, 2012; Viikari et al., 2012). According to Zabed et al. (2016), the recalcitrance is attributable to the crystallinity of cellulose, accessible surface area, and protection by lignin, and heterogeneous character of the biomass particle. As shown in **Table 2.1** cellulose, hemicellulose and lignin proportions of lignocellulosic biomass components differ according to biomass types which gives variation in the digestibility.

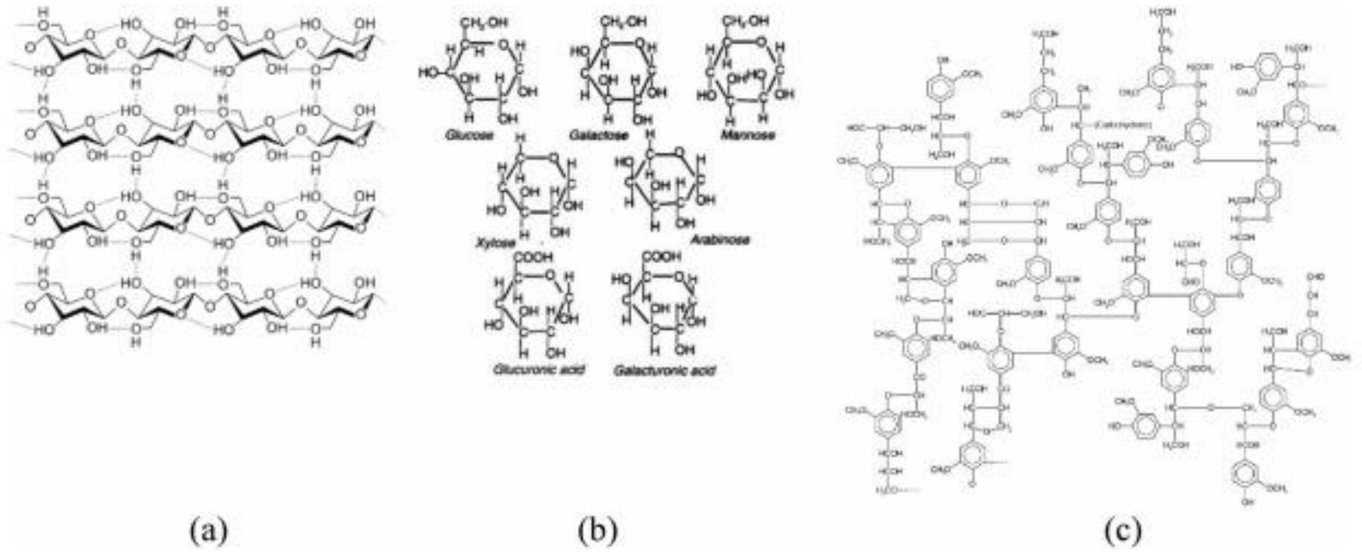


Figure 2.2: Components of lignocellulosic biomass: (a) cellulose, (b) structure monomers of hemicellulose, and (c) lignin (Dhyani & Bhaskar, 2018).

2.1.2.1. Cellulose

Cellulose (**Figure 2. 2. a)**) is an organic polymer that contributes approximately 30% of the plant composition (Limayem and Rickle, 2012). The polymer is joined with linear chains up to 12 000 residues containing glucose and it is largely composed of (1,4)-D-glucopyranose units with an average molecular weight of around 100 000 which are connected by β-1,4 linkages (Anwar et al., 2014). This cross-link between numerous hydroxyl groups creates extensive hydrogen bonds among the cellulose molecules forming microfibrils that result in a crystalline matrix structure which makes molecules more rigid and water-insoluble and resistant to de-polymerisation (Zabed et al., 2016).

2.1.2.2. Hemicellulose

Hemicellulose (**Figure 2.2. b)**) is a heterogeneous group of branched polysaccharides surrounding the cellulose fibres which is a connecting link to cellulose and lignin and its structure element contains various monomers such as glucose, galactose, mannose, xylose, arabinose, and glucuronic acid (Dhyani and Bhaskar, 2018). The β-1, 4 linkages that include approximately 90% D–xylose and 10% L–arabinose are made up of xylan which is the backbone chain of the polymer (Zabed et al., 2016). Comparing hemicellulose to cellulose, the degree of polymerisation is much lower by 50-200 monomers. Also, hemicellulose is amorphous and has lower physical strength which makes it susceptible to hydrolysis by dilute acids, alkalis, and enzymes (Dhyani and Bhaskar, 2018).

2.1.2.3. Lignin

Lignin (**Figure 4.2. c)**) is a heterogeneous polymer that contributes approximately 10-25% of the biomass by weight and is largely composed of long-chain phenyl-propane units that are commonly linked by ether bonds (Anwar et al., 2014). It is present in all lignocellulosic biomass, and it binds cell walls component together by filling the gab around and between the cellulose and hemicellulose polymers (Dhyani and Bhaskar, 2018; Anwar et al., 2014). There is approximately 3-15% of lignin in agricultural residues (Zabed et al., 2016).

2.1.3. Corn residues

As mentioned earlier, agricultural residues make up a huge amount of the total biomass and its utilisation for bioenergy production is common for many countries but there is little experience in energy conversion for other agricultural residues (corn residues) for solid fuels production (Batidzarai et al., 2016). Thus, this study focuses on the use of South Africa’s staple food maize, where the interest is the corn-stover (CS) for bio-briquettes production.

2.1.3.1. Description of corn-stover

Corn-stover is usually left in the field after the harvest of maize (**Figure2.3**). Its structural components comprise the leaves, stalks, husks and stem without the grain, accounting for 80% of the corn residue in agricultural crop production (Barten, 2013). According to Danje (2011), CS contains 32.4% cellulose, 40.8% hemicellulose and 25% lignin. This composition illustrates that CS has a great potential as renewable raw material just like corn cobs. Due to the abundance of CS, it attracts interest in the energy sector to be used as a raw material to produce solid composite fuel known as briquettes for industrial and domestic uses (Klingenfeld et al., 2008).

Figure 2.3: Corn stover biomass (Thoreson et al., 2010).

2.1.3.2. Characterisation

Agricultural Biomass feedstocks have a variety of characteristics that are essential when considering their potential use (Milhollin et al., 2011). The key chemical characteristics in terms of HHV, ultimate and proximate analyses of various agricultural feedstocks are detailed in **Table 2.2**.

Table 2.2: Chemical characteristics in terms of HHV, ultimate and proximate analysis of various feedstocks.

Reference	**(Capunitan & Capareda, 2012)**	**(Park et al., 2014)**	**(Dhyani & Bhaskar, 2018)**		**(Biswas et al., 2017)**	
Biomass	Corn-stover	Rice straw	Barley straw	Flax straw	Wheat straw	Corn cob
Ultimate analysis (wt%, dry basis)						
C	44.30	48.75	41.40	43.10	38.34	42.10
H	6.28	5.98	6.20	6.20	5.47	5.90
N	0.80	1.99	0.63	0.68	0.60	0.50
S	0.23	-	0.01	0.09	0.37	0.48
O	41.80	43.20	51.70	49.93	55.22	51.02
Proximate analysis (wt. %, dry basis)						
Ash content	6.62	22.55	9.80	3.00	6.63	2.30
Volatile matter	78.70	60.84	78.50	80.20	83.08	91.60
Fixed content	14.70	16.61	4.80	8.80	10.29	6.54
Moisture	6.18	7.30	6.90	7.90	12.81	12.77
HHV (MJ/kg)	17.00	13.45	15.70	17.00	14.68	16.00

According to Capunitan and Capareda, (2012) for biomass to render as suitable biofuel, the oxygen content must be reduced to improve its heating value. The authors further mentioned that it is desirable to have biomass with relatively low ash content and high volatile matter as a feedstock during any conversion process, because it readily releases a lot of volatile compounds while leaving the solid product with less ash and high fixed carbon content. Hence, improving its heating value and rendering it a valuable solid fuel. As shown in **Table 2.2**, CS is desirable as a potential feedstock for biofuel production as not only does it have lower ash contents and high volatile matter and it also has lower sulphur contents as well as being carbon neutral. Also, although materials burn better than others, the easy access and availability of biomass is usually the determining factor for raw material selection (Sani, 2008).

2.2. Corn-stover availability and its current use

The agricultural sector generates corn residues every year particularly corn-stover (Salema et al., 2017). Power plants, cellulosic ethanol plants, and biomass densification businesses would be interested in potentially using this feedstock (Milhollin et al., 2011). It is estimated that a total amount of 16 million tonnes of CS biomass is generated per year in South Africa. This total includes the below and above ground biomass at 6.3 million and 9.7 million tonnes, respectively. CS is potentially available in different provinces across South Africa, with significant amounts in Mpumalanga (31%), Free State (32%) and Northern Cape (26%) (Batidzirai et al., 2016). Conventionally, CS is used for animal bedding and feed and as well as a soil amendment. (Klingenfeld, 2008; Salema et al., 2017). However, excess biomass remains, and the need to safely dispose of it is still a challenge (Huang et al., 2013). It is important to note that the below-ground biomass is not available for removal and can only be used for soil organic control maintenance. Therefore, the required CS for soil erosion control is about 4.2 million tonnes and about 9.3 million tonnes for soil organic carbon (SOC) maintenance. For districts that have excess residue, it is estimated that about 260 thousand tonnes of CS account for animal feed. This results in about 5.1 million tonnes of total CS that remains and is available in excess per year after the combined estimated required 9.5 million tonnes for soil amendment and animal feed (Batidzirai et al., 2016). This motivates the use of the most abundant agricultural biomass CS as the feedstock in this study.

2.3. Limitations

Despite CS being a potential renewable energy source, it has a very low bulk density, irregular shapes, and sizes, has high moisture content making it to be difficult to handle, transport and store (Wang et al., 2011). CS has a potential challenge such as high alkaline content in the stover ash when directly combusted. This usually causes slagging and fouling during burning in boilers etc (Milhollin et al., 2011). Also, CS as loose biomass tends to retain the moisture content of about 33% and high moisture content affects its higher heating value. The heating values of CS and various other solid fuels are shown in **Table 2.3** where CS has the lowest HHV value in comparison to conventional fuels due to the characteristics it possesses.

Table 2.3: The heating values of corn-stover and various other solid fuels (NCPC-SA, 2019; Capunitan & Capareda, 2012).

Fuel	HCV (MJ/kg)
Light fuel oil	44
Heavy fuel oil	41.8
Diesel	45.6
Petrol	46.4
Coal (Bituminous)	30.2
Coal (Sub-bituminous)	24.4
Wood fuel (dry)	16.2
Natural gas (LNG)	55.2
Liquid petroleum gas (LPG)	49.3
Corn-stover	17

2.4. Biomass conversion technologies

To manage waste sustainably and meet the increasing energy demand, using cost-effective conversion technologies seems to be a solution. To convert biomass waste into fuels biochemical, thermochemical, and physical processes are often used (Nizami et al., 2017). An appropriate conversion method is selected based on the type and amount of biomass, desired products, environmental and economic standards, and conditions (Chen, 2012).

2.4.1. Biochemical processes

Biochemical conversion is when biomass is converted into reducing sugars by breaking down molecules into smaller molecules through pre-treatment (Shen et al., 2015). Digestion (anaerobic and aerobic), fermentation and hydrolysis (enzymatic or acid) are the three major routes for biochemical conversion.

- **Digestion (anaerobic and aerobic)**: the process whereby biomass access oxygen from itself instead of ambient air is known as anaerobic. A solid residue, methane and carbon dioxide are the main products (Naqvi et al., 2018). On the other hand, aerobic digestion uses air to break down the biomass through composting by using different types of microorganisms that access oxygen from the air which results in the production of carbon dioxide, heat, and a solid digestate (Basu, 2010). The typical feedstocks for anaerobic digestion (AD) reactors are usually animal slurries, energy crops, and other agricultural, retail, and industrial wastes (Roddy, 2012).
- **Fermentation** is a process where the mixed hexose and pentose sugars present in biomass are converted to produce fuel sugars using acid or enzymes

(Stephanopoulos, 2007). The main products are usually ethanol and other chemicals often from corn or sugarcane as feedstocks.

- **Hydrolysis** is the process of breaking down cellulose and hemicellulose into fermentable sugars by enzymatic or acidic decomposition. Lignocellulose biomass like wood is appropriate feedstocks for hydrolysis (Chen et al., 2012).

The complexity of the biochemical process and technical issues associated with low- bulk density feedstock, high viscosity substrate and low fermentability of some substrates makes end products from the process more costly than fossil fuels and the technology uncompetitive (Lin and Tanaka, 2006; Chen, 2012).

2.4.2. Thermochemical processes

Thermochemical conversion is the use of chemical and heat to convert biomass into solid, liquid, and gaseous high-value products for biofuels and energy purposes (Ubando, et al., 2019). Thermochemical processes can be categorised into namely, combustion, gasification, and pyrolysis. According to Kunkes et al. (2008), the limited number of steps and process steps involved in thermochemical processes make it favourable over biochemical processes. The compatibility of thermochemical processes end products to the current fossil fuels makes it is easy to introduce them to the same distribution system. Besides, numerous sub-processes on a large scale have good economics as there are commercially proven technologies. Even though there are still issues surrounding the thermochemical process, they still have a good chance of being commercialised than the biochemical processes (Goyal et al., 2008).

2.4.3. Combustion

Combustion is a traditional conversion method that has been used for centuries since the discovery of fire (Quispe et al., 2017). The process involves the production of flame and smoke when a solid feedstock is reacted in the presence of oxygen at high temperatures. During the process, inorganic compounds burn completely (Quispe et al., 2017). Due to its commercial availability, it has been commonly used in biomass power generation methods over a wide range of scales (1-100 MW). One of the drawbacks of this method is the emission of by-products, such as CO, CO_2, NO_x, dust, and soot (van de Kaa et al., 2017).

2.4.4. Gasification

Gasification is an endothermic process that involves a solid feedstock heated at high temperatures (>700 °C) to produce bio syngas in an absence of oxygen to prevent combustion (van de Kaa et al., 2017). The syngas product is a mixture of H_2, CO, CO_2, CH_4 and N_2 and steam, air, oxygen, and carbon dioxide are commonly used as gasification agents (Chan et al., 2019). The gas product is normally used to provide heat for steam production or electricity generation (van de Kaa et al., 2017). Lower quality of syngas, tar and CO_2 removal, char impurities, heating value and gas cleaning process are some of the challenges associated with this process (Khan et al., 2010; Pratama et al., 2016).

2.4.5. Pyrolysis

2.4.5.1. Introduction to pyrolysis

Pyrolysis reaction is carried out under controlled conditions to convert lignocellulosic biomass with the aid of heat to produce brittle solid residue and volatiles under an inert atmosphere (Collard and Blin, 2014: Park et al., 2014). The volatiles undergo condensation, then in the end, non-condensable gases remain. The targeted products depend on the operating conditions of the pyrolysis process. The pyrolysis process has been of interest due to its flexibility to adapt to a wide range of designs to process lignocellulosic biomass distribution (Collard et al., 2016). The thermal degradation of lignocellulosic biomass occurs to provide the main reaction products char, bio-oil, and non-condensable gas (Park et al., 2014).

Pyrolysis involves a complex chemical process of primary, secondary, and tertiary reactions between reactive intermediates and the various components that are involved in the multiple reactions during the process can significantly influence the overall product distribution (Carrier, et al., 2011; Collard et al., 2016). Pyrolysis is affected by different parameters and conditions which are monitored according to the targeted products (**Table 2.4**). Thus, it is vital to study the process variables and conditions that influence the process (Park et al., 2014). There are different types of pyrolysis namely, torrefaction, slow pyrolysis, and fast pyrolysis.

Table 2.4: Types of pyrolysis (Mohan et al., 2006; Bridgewater, 2012; Sharma et al, 2015; Chen et al., 2018; Zaker et al., 2019).

Mode	Operating conditions	Liquid	Solid	Gas
Slow	Low-moderate temperature (~300-450°C), long solid residence time (>15 min)	30% (70% water)	35%	35%
Intermediate	Low-moderate temperature (~500-650°C), hot vapour residence time (~10-20s)	50% (50% water)	25%	25%
Vacuum	Medium temperature (~400-600°C), hot vapour residence time (~2-30)	35-50%	-	-
Fast	Moderate temperature (~500°C), short hot vapour residence time (<1s)	75% (25% water)	12%	13%
Gasification	High temperature (>800°C), long vapor residence time (10-20s)	5% tar (55 water)	10%	85%

2.4.5.2. Fast pyrolysis

This process is operated under an oxygen-free environment in a short vapour residence time of <2s. Fast pyrolysis product yields are typically 50-75 wt. % of liquids, 12-25 wt. % of solid residue and 10-20 wt. % of non-condensable gas (**Table 2.4**) (Yang et al., 2019; Hu and Gholizadeh, 2019). The primary product of interest is bio-oil, and it can be characterised by its process parameters of high heating rates of approximately 10-200°C/s and high temperatures of 450-650°C (Bridgewater, 2012; Kan et al., 2016). Therefore, the reacting biomass needs to be operated at optimum conditions by avoiding lower temperatures which favour the production of solid residue. The typical biomass particle size required for fast pyrolysis is <2mm (Brown et al., 2011). Bio-oil can be used as high-value biochemicals such as food additives, phenols for resin production, pharmaceutical industries, etc (Al Arni, 2018; Nsamba et al., 2015).

2.4.5.3. Intermediate pyrolysis

The pyrolysis process that is utilised to make a balance between liquids and solid products is known as intermediate pyrolysis and its operation conditions are between slow and fast pyrolysis. Generally, the vapour pressure remains 0.1 MPa and the heating rate is between 0.1-10°C/min (**Table 2.4**). This process typically operates in a temperature range of 500-650°C and vapour residence times of 2-4s (Kebelmann et al., 2013; Tripathi et al., 2016). Hornung et al. (2011) reported that the product yield is typically distributed into 40-60 wt. % liquids, 15-25 wt. % solid residue and 20-30 wt. % non-condensable gases. Dhyani and Bhaskar (2018) stated that intermediate pyrolysis entails, more controlled chemical reactions which makes it flexible for production optimisation. Moreover, compared to fast pyrolysis it can accommodate large biomass particles sizes without milling and this offers the opportunity for a gasifier to be operated with low ash, independent of the ash content of the material before pyrolysis. According to Mahmood (2013), the bio-oil produced does not contain a high quantity of reactive and thus, it can be used directly for boilers and engines.

2.4.5.4. Vacuum pyrolysis

One of the processes that are considered as a promising technology for resource and energy recovery is vacuum pyrolysis. Unlike slow pyrolysis, the process is done under vacuum, instead of inert gas to replace the air (Chan et al., 2019). It is conducted under low pressures between 0.05 and 0.20 MPa and the vacuum helps in the removal of pyrolysis vapours from the reaction which prevents further re-condensation and secondary reactions (Tripathi et al., 2016; Chan et al., 2019). The reaction temperature is kept between 450 and 600°C and its short residence time (0.001-1s) and high heating rates (0.1-1°C/s) result in high liquid yields of 35-50 wt. % (Ma et al., 2017; Zaker et al., 2019). According to Chan et al. (2019), vacuum pyrolysis can reduce energy consumption by lowering the reaction temperature of organic materials and can prompt internal diffusion to produce relatively pure products.

2.4.5.5. Slow pyrolysis

Slow pyrolysis is the conventional type of pyrolysis known to produce biochar. It is performed at low heating rates and long residence time (**Table 2.4**) (Singh and Shadagi, 2011). Biomass is typically pyrolysed at a temperature range of 400–500 °C with a heating rate are between 0.1 and 1°C/s for a vapour time of 300-550s (Park et al., 2014; Elkhalifa et al., 2019). Having low heating rates allows lower levels of volatile compounds such as gas and tar to be released while forming high char yields as this promotes the completion of secondary reactions (Tripathi et al., 2016; Machado et al., 2018). It has been reported that increasing the biomass particle size to at least <1 mm increases the char yield by more than 50% (Collard et al., 2016). Notably, larger amounts of biochar can be achieved at relatively lower temperatures. However, crucial biochar properties, such as pore structures and surface area are well developed around temperatures of 400-500°C (Lee et al., 2013). Slow pyrolysis product yields are typical, 35 wt. % biochar, 30 wt. % bio-oil and 35 wt. % combustible gasses (Song & Guo et al., 2012).

The current study proposed to convert biomass into biochar to produce bio-briquettes with properties relative to low or medium solid fuels to help supplement conventional solid for heating and cooking purposes particularly in small communities. Slow pyrolysis is considered a simple, robust, and low-cost process as it applies to small scale setup for biochar production (Song & Guo et al., 2012). According to Tripathi et al. (2016), this process releases lesser amounts of harmful gases like SO_X and NO_X. This makes slow pyrolysis to be superior to other biochar production pathways. Also, the flexibility in handling various types of biomass and different operating conditions makes the process attractive (Elkhalifa et al., 2019).

Accordingly, it has been reported that fluidised bed reactors and rotatory kiln reactors are the most suitable for slow pyrolysis (Czajaczyiska, 2017; Dhyani & Bhaskar, 2018). The influence of process variables has a significant impact on the quality and formation of various products. Therefore, critical factors influencing pyrolysis will be briefly discussed in the following sections.

2.4.5.6. Influence of operating conditions on the yields of char

The purpose of pyrolysing biomass is to maximise the product char yield as previously mentioned. It has been reported that temperature, heating rate, particle size, pressure, etc (Tripathi et al., 2016) influence the production of biochar. Also, not only do these parameters control the char yield but also affect the quality of the final product.

Temperature

Collard et al. (2016) indicated that the most critical factor responsible for influencing the extent of reaction is temperature. The biochar yield is negatively affected when the temperature is increased as this promotes thermal cracking of heavy hydrocarbon materials and this leads to the decrease of biochar yield caused by the increase of liquid and gases etc (Tripathi et al., 2016; Abbas, 2014). Hence, lower temperatures of 400–500°C are appropriate for high biochar yields as high temperatures may exceed the bond termination that supports the release of the volatile components of biomass when energy is given (Tripathi et al., 2016).

Collard et al. (2016) also mentioned that this temperature range puts the HHV of the biochar at approximately 25 MJ/kg or higher which is comparable to South Africa's sub-bituminous coals.

Heating rate

According to Pourkarimi et al. (2019), another significant factor is a heating rate which controls the nature and composition of the final products to a certain limit. The possibility of secondary pyrolysis reactions being reduced can be achieved by having lower heating rates. This prevents thermal cracking from taking place, hence, increasing biochar yield. Moreover, taking care of the particle size during pyrolysis is important as it is responsible for controlling the rate at which the heat is transferred to the biomass (Tripathi et al., 2016). The yields and properties can be influenced by the size of particles (Pourkarimi et al., 2019). A study on corn cob indicated that increasing the particle size from 0.5 to 2.2 mm increased the biochar yield from 5.7 to 16.6% (Tripathi et al., 2016). This is due to the delay of rapid heat flow from the cold to hot end and this temperature slope that aids an increased in char yield.

Vapour residence time

The vapour residence time directly affects the number of re-condensation and cracking reactions (Collard et al., 2016). Thus, for higher char yields vapour residence time needs to be increased as this allows enough time for the biomass constituents to respond to polymerisations to increase the latter and not only does it affect the biochar yield it promotes micro and macropore development on the biochar (Pourkarimi et al., 2019; Tripathi et al., 2016). However, it should be noted that vapour residence will be affected by temperature and heating rate mostly which makes it difficult to understand its role in the production of biomass (Tripathi et al., 2016).

2.4.5.7. Composition and use of char

In this study, CS feedstock was pyrolysed to produce biochar. Biochar is a solid residue from pyrolysis which consists of unconverted organic solids and carbonaceous residues that remains from the complete or partial decomposition of biomass feedstock (Kan et al., 2016). For biochar produced at temperature >400°C, the proportion of benzene rings increases from converted pyran and furan rings which result in a significant increase in carbon content (Collard & Blin, 2014; Collard et al., 2016). Moreover, around this temperature, the carbon content is expected to be up to 70% and an HHV usually higher than 25 MJ/kg. Biochar can be characterised in terms of proximate and ultimate analyses as well as HHV analysis and **Table 2.5** shows biochar characterisation from various biomass feedstock.

Table 2.5: Summary of corn stover biochar properties at different temperatures (Capunitan & Capareda, 2012)

Pyrolysis temperature (°C)		**300**	**500**	**600**
Proximate analysis (%dry)	Volatile matter	26.50	18.80	12.00
	Fixed carbon	56.50	62.90	67
	Ash	16.90	18.30	20.10
Ultimate analysis (%dry)	C	71.20	74.40	74.90
	H	3.80	2.50	1.70
	N	2.10	2.10	1.70
	S	0.20	0.10	0.15
	O	5.70	2.50	1.50
HHV (MJ/kg)		27.90	22.90	23.10

Biochar can be used for different applications depending on its characteristics and without any physical and chemical improvements it can be used in composting, building sectors, textile, and energy applications (Abbas, 2014). According to (Chen et al., 2018) due to similar properties, biochar is a renewable substitute for coal. Hence, the high HHV makes it attractive in some fuel applications as a source of heat for domestic and industrial uses. Biochar produced from pyrolysis can further be converted into briquettes. Section 2.4.6 discusses the densification of biochar into bio-briquettes suitable for heating and cooking purposes.

2.4.6. Physical processes

2.4.6.1. Densification

The current study aims to explore the potential of CS biomass as a feedstock for eco-friendly solid fuel production to meet the increasing energy demand in South Africa. An alternative way to conventional energy use is to beneficiate waste biomass through densification, which improves the physical properties and the combustion behaviour of the biomass (Mamvura et al., 2018). Densification promises to be a solution to handling, transporting, storage and waste management issue of CS biomass (Bajwa et al., 2018). Also, densifying biomass increases the energy density, low moisture, and better fuel homogenisation (Gendek et al., 2018; Okot, et al., 2019). These densified solid fuels are called pellets or briquettes and they are blocks/shapes of compressed combustible energy carriers used for heating and cooking purposes (Kongprasert et al, 2019). Notably, pellets and briquettes are commonly classified based on their sizes where pellets diameter range is 5-25 mm and length of 10-75 mm and briquettes diameter range is 50-100 mm and length of 50-250 mm (Tabakaev et al., 2017). However, for this study, only briquettes will be a focus. They are eco-friendly alternatives as fuel instead of charcoal, firewood, or coal because they are smokeless and characterised by low ash content and low sulphur content (Wang et al., 2019; Okot, et al., 2019).

2.4.6.2. Briquetting

Briquetting technology can be classified into two which can be by directly densifying the biomass and by densifying carbonised biomass to produce solid fuels. In the following section, a detailed review of each class will be discussed.

2.4.6.3. Briquetting from direct biomass

Direct biomass briquetting is often a high-pressure compaction process where raw biomass is compacted to produce briquettes (Kakooza, 2017). Even though this can be achieved with a binder present it is usually without a binder and the briquetting machine is often with a heating device which activates the lignin in the raw biomass to act as a binder (Oladeji, 2015; Shuma & Madyira, 2017). Notably, biomass under high pressure creates mechanical interlocking that forms intermolecular bonds from increased adhesion between particles (Grover and Mishra, 1996). Hence, the lignin will glue cellulose together from the high pressure and temperature, solidifying the biomass to form a briquette (Oladeji, 2015). However, according to Belay (2014), additional binding agents is necessary if high temperatures and pressure > 5MPa cannot be achieved. Ultimately, briquetting process reduces the bulk density of the biomass which reduces handling, storage, and transportation costs (Goh et al., 2013). The typical briquetting process of biomass is illustrated in **Figure 2.4.**

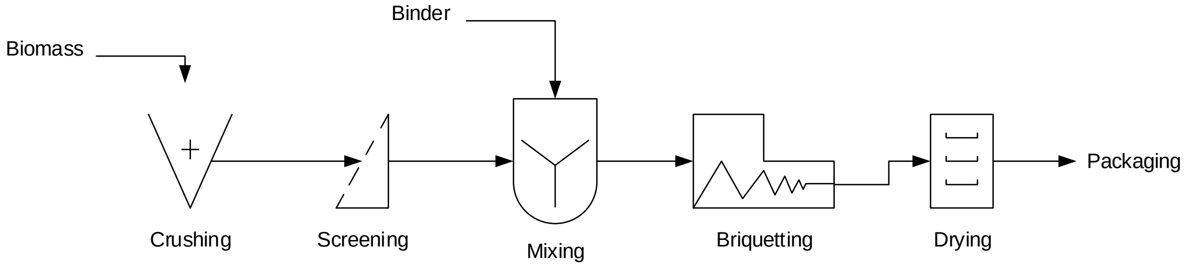


Figure 2.4: Briquetting process for uncarbonized biomass (Adapted from Zubairu & Gana, 2014).

The raw biomass briquetting process consists of sorting also known as sieving where unwanted materials and larger materials are removed (Chaney, 2010). Lignocellulose biomass is then shredded into the desired size to enhance its workability and compactness usually by chopping, crushing or by hand-cracked devices such as a pestle and mortar

(Oladeji, 2015). The next step is binder application which depends on the technology employed. This is where the biomass and an appropriate binder is thoroughly mixed usually under medium to low pressures to prevent the biomass from disintegrating apart. Lastly, a briquette is formed through either low (1-5 MPa) or high pressure (~60-150 MPa) at room/low temperatures sometimes at high temperatures (200-300°C) for pressure lower than 5 MPa (Chaney, 2010; Oladeji, 2015; Aransiola et al., 2019). The briquettes produced can be in different shapes and sizes as shown in **Figure 2.5.**

Figure 2.5: Common biomass shapes and sizes of briquettes; (a) Pellet (b) Briquette (c) Solid rod (d) Hollow rod (Xu et al., 2015).

Direct biomass briquetting is a popular technology due to its simplicity, convenience, and low cost. However, it is characterised by low calorific values, high oxygen contents and limited fixed carbon fractions and smoky during combustion (Gan et al., 2019: Ifa et al, 2020) This remains a technical and economic issue in creating a sustainable energy source that competes with conventional fossil fuel (Kongprasert et al., 2019; Gan et al., 2019). Hence, Trubetskaya et al. (2019) mentioned that to increase the efficiency of biomass fuel, it can be converted into biochar via a thermochemical process before briquetting.

2.4.6.4. Briquetting from carbonised biomass

Properties such as better water resistivity, higher heating values and better-fixed carbon and durability are characteristics of biochar briquette. Hence, it has significant potential for domestic use and industrial processes, supplementing or replacing conventional fossil fuels such as coal (Wang et al., 2017). Also, pre-treatment methods to the biomass can be employed before densification to enhance better combustion quality and reduce biomass pollutant emissions. Thus, the implementation of pyrolysis is highly recommended to achieve a high-quality biofuel, particularly biochar.

2.4.7. Carbonised briquettes

In addition to densification, pre-treating the biomass before densification can improve the product significantly (Alanya-Rosenbaum and Bergman, 2019). This helps in decreasing the volatile matter, which increases the fixed carbon and HHV due to the decomposition of cellulose and hemicellulose (Wang et al., 2017). The biochar product from pyrolysis which was discussed in section 2.4.5.7 is used as a densification feedstock instead of using raw biomass. The **Figure 2.6** illustrated a typical biochar briquettes production.

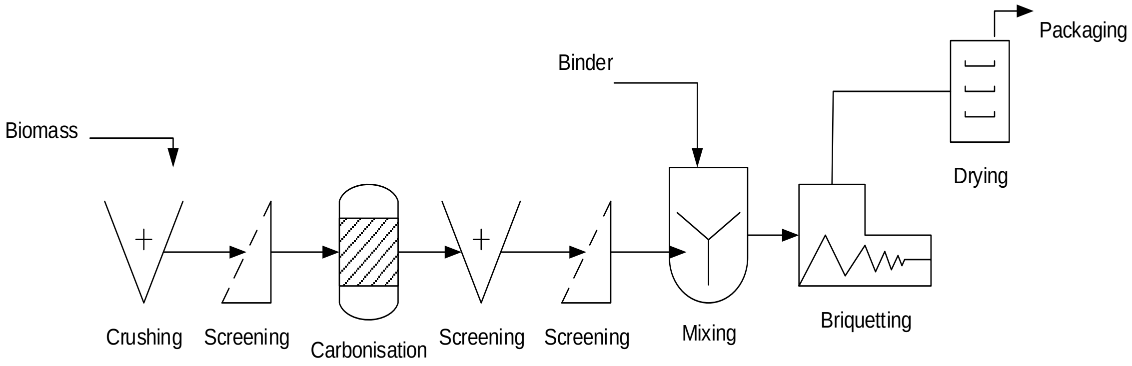
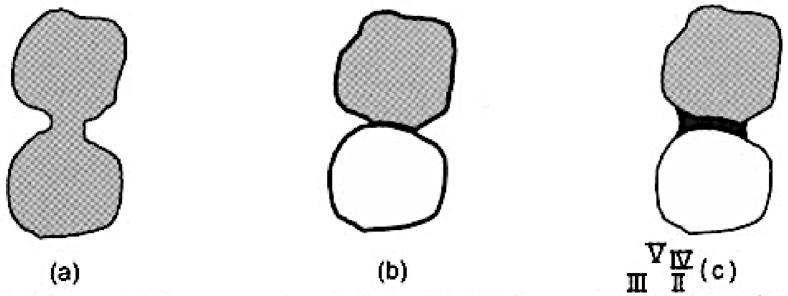


Figure 2.6: Briquetting process for uncarbonized biomass (Adapted from Zabairu & Gana, 2014).

Densification of carbonised biomass is commonly a medium to low compaction process and due to biochar not having good cohesive property between particles, the process requires the addition of an external binder (Zanella et al., 2017). Similarly, like densifying raw biomass the biomass for carbonised densification needs to be prepared before undergoing the pre-treatment process and during this step, it is reported that biomass is reduced to a particle size of < 6 mm and a moisture content of at least 15% (Belay, 2014). Then, the biomass undergoes carbonisation via pyrolysis which is detailed in section 2.4.1.3. Furthermore, biochar is crushed and sieved into a particle size < 2 mm and the prepared binder is then mixed with the powdered biochar. As seen in **Figure 2.6** the following step is briquetting where compaction will occur by the desired pressure (Zubairu & Gana, 2014). **Figure 2.7** illustrates the binding mechanisms during densification also known as agglomeration.



(a)
Sinter Bridges (I.1)
Partial Melting (I.2)
Crystallization of Soluble Substances (I.5, I.6a)
(Solube Particles)

(b)
Chemical Reaction(I.3)
Hardening Binders (I.4)
Highly Viscous Binders (II.1)
Adsorption Layers (<3 nm Thickness)(II.2)

(c)
Liquid Bridges (III.1)
Hardening Binders (I.4)
Crystallization of Dissolved Substances (Dissolved in Liquid)(I.5, I.6a)
Deposition of Suspended Particles (I.6b)

Figure 2.7: Pictorial representation of binding mechanisms of agglomeration (Pietsch, 2002).

Pietsch (2002) mentioned that interaction forces on briquetted materials are classified into solid bridges, adhesion and cohesion forces, surface tension and capillary pressure, attraction forces between solids and lastly, mechanical interlocking bonds (**Figure 2.7**). Due to chemical reactions, increased pressure or the addition of hardening binders that fill the voids within particles, solid bridges can form from particles fritting when they closely reach their melting point through partial melting at roughness points (Ward, 2014). Also, the evaporation of liquids can form crystal bridges between particles due to the crystallisation of dissolved colloidal particles (Pietsch, 2002).

According to Zhang et al. (2018) and Ward (2014) using a highly viscous binder such as molasses or tar pitch will govern adhesion and cohesion forces between carbonised particle and binder as these forces act to bind particle together. This causes thin adsorptive layers at particle contact points to rise by adding deformed and rough surfaces, which increases adhesive and cohesive force strength (Grover & Mishra, 1996). Moreover, using water when adding adhesives to the carbonised particle and an external force will result in an increased attraction narrows the distance between particles (Zhang et al., 2018). Hence, there is a significant crushing strength on the briquettes when repulsive force is less than attractive force. All in all, it should be noted that the binding mechanisms shown in **Figure 2.7** only illustrates a two-dimensional situation at one coordination point between two solid surfaces and due to varying microscopic surface structures and distances in each interaction point, the effect of each binding force is different at every coordination point (Ward 2014; Pietsch, 2002). **Figure 2-8** shows a typical carbonised briquette.

Figure 2.8: Carbonised briquettes (Pilusa et al., 2013).

Correspondingly, densifying carbonised biomass not only reduces transportation, handling, and storage cost, it also, results in biochar briquettes that have significantly improved properties such as reduced volatile matter, increased bulk density, HHV and grindability (Alanya-Rosenbaum and Bergman, 2019). For briquettes to be suitable to supplement or replace traditional charcoal or coal they need to possess certain qualities. Section 2.4.8 will briefly review the desirable qualities of briquettes.

2.4.8. Desirable briquette quality

During the production of briquettes, the two critical concerns are quality and energy efficiency. A standard briquette should possess good qualities such as being able to produce enough heat, burn without smoke, have reduced emissions, and mused be convenient for the user (Wilson, 2016; Borowski et al., 2017). It is reported that the quality of briquettes is measured based on their durability, strength and density and energy efficiency (Si et al., 2016; Gendek et al., 2018). The quality is dependent on operating conditions. The different types of carbonised biomass and their desirable qualities are shown in **Table 2.6**.

Table 2.6: Different briquettes with their qualities.

Type of charcoal	**Particle size (mm)**	**Pressure (MPa)**	**Binder type**	**Binder %**	**Briquette size (mm)**	**Drying Temp (°C)**	**Density (kg/m^3)**	**Strength (MPa)**	**Durability (%)**	**HHV (MJ/kg)**	**Reference**
Wood	0.05-02	-	Wheat starch	-	60×50×30	-	700	24.5	98.8	26.5	Borowski et al., 2017
Rice husk	2	5	Molasses	10	40×100	In door dried	628-700	-	-	26.8-25.2	Chirchir et al., 2013
			Clay				537-586			14.6-11.3	
			Cow dung				576-645			18.5-16.1	
Eucalyptus	-	50	Molasses	10	24.8×100	30	1107	-	80.36	29.51	Tanui et al., 2018
EFB	0.15	12	Crude glycerol	40	-	Sun-dried	932	0.67	-	28	Helwani et al., 2018
Palm kernel	0.3	60	Starch cassava	-	25×25	-	701-680	0.821	-	28.18-27.51	Bazargan et al. 2014
Orange bagasse	2-4	-	Corn starch	5	-	80	594	1.41	85.75	26.857	Zanella et al., 2016
Peat	2	-	Dextrin starch	5	50×50	20-40	-	0.20-0.46	100	20.1	Tabakaev et al., 2017
Corn cob	4	8	Cassava	5	52.2×20×120	Sun dried	409.88	-	-	25.25	Wilson et al., 2016

2.4.8.1. Higher heating value

Manyuchi et al. (2016) and Zanella et al. (2016) mentioned that HHV is the intensity and amount of heat released from a fuel. Thus, harnessing as much as possible energy from briquettes high HHV is mandatory. According to Ward (2014), 22 MJ/kg is the desirable HHV for commercial charcoal briquettes with a binder added and for briquettes without binder should be 25 MJ/kg (**Table 2.6**).

2.4.8.2. Density

Galvari et al. (2019) described bulk density as the mass ratio per volume of bulk material to its volume and cavities between atoms. The type of biomass and its characteristics affects the physical and mechanical properties of the final product (Cavallo & Pampuro, 2017). Higher bulks promote compactness which is desirable in terms of handling, storage, and transportation costs (Tarasov et al., 2013; Galvari et al., 2019). Therefore, for efficient transportation and safe storage, it is recommended that the value for densified materials is approximately 600 kg/m^3 (Davies and Davies, 2013). Other authors mentioned that densified biomass can increase their bulk density to approximately 450-800 kg/m^3 (Tumuluru et al., 2011b; Malatji et al., 2011; Okot et al., 2018) (**Table 2.6**).

2.4.8.3. Compressive strength

Katimbo et al. (2014) defined compressive strength also known as tensile strength, as the diametric compression and maximum load a briquette can withstand mechanical impacts before breaking or crushing. Mendoza Martinez et al. (2019) stated that briquettes with low compressive strength tend to crumble very quickly which cause problems during their combustion, storage, and transportation. For good resistance to mechanical fragmentation, the tensile strength should be >1-2.56 MPa (Faizal et al., 2010; Okot et al., 2019; Borowski et al., 2017) (**Table 2.6**).

2.4.8.4. Durability

The durability or impact resistance is the measure of mechanical strength that defines the abrasion resistance of a briquette to yield dust or break when exposed to disruptive force (Okot et al. (2019). Therefore, for better transportation, storage, and handling efficiency, it is necessary to minimise rupture and dust by producing briquettes with a durability > 80% (Tarasov et al., 2013; Okot et al., 2019). In some cases, other standards such as the European standards require the impact-resistant not to be less than 97.5% (Tarasov et al., 2013; Bazargan et al., 2014). The desirable briquette quality variable described above are affected by certain factors discussed in section 2.4.8.

2.4.9. Effects of operating parameters

To produce reproducible briquettes from a certain material it is essential to understand the influence of these factors on their final properties (Chaney, 2010). Therefore, the common factors affecting the densification process are namely, moisture content, compressive pressure, binder, and cooling and drying temperature. Below is a detailed explanation of each effect of these parameters.

2.4.9.1. Moisture content

Chaney (2010) mentioned that for many biomass materials the moisture content plays an important role in the production of densified material. Thus, the limit for the formation of a briquette is dependent on the feedstock material. Bazargan et al. (2014) reported that without the presence of moisture it is not possible to make strong pellets. According to Krizan et al. (2016), the moisture content is one of the essential variables which act as a facilitator of natural binding agents. Bazargan et al. (2014) and Gilvari et al. (2019) investigated the effect of moisture content on the strength and durability of briquettes, and they found that increasing the moisture initially increases the strength. However, if the moisture content is too high (>25-30 %) it starts to decrease (Chaney, 2010). In the study by Jackson et al. (2016) on corn stover pellets, the highest durability was observed at 20% moisture content. Bazargan et al. (2014) observed that briquettes made with moisture content above 40% were semi-solid solid and during handling, they broke easily. Furthemore, Kaliyan & Morey (2009) and Gilvari et al. (2019) mentioned that increasing the moisture content can negatively affect the bulk density. Moreover, the authors mentioned that moisture content sometimes is dependent on factors such as temperature and pressure. Hence, it should not be investigated independently. In conclusion, to understand their influence on the product quality the effect of the factors simultaneously needs to be studied.

2.4.9.2. Compressive pressure

According to Bazargan et al. (2014), compressive pressure is known to influence volume density, compressive or durability, and energy consumption. Frequently, briquetting pressure is essential when the biomass feedstock used contains protein, lignin, or starch and under a certain pressure, it will firmly press around particles and will enable inter-particle bonding (Ward, 2009). Firstly, when applying pressure during briquetting will create some non-permanent elastic deformation of the material that will last for as long as pressure is applied. However, as the pressure rises permanent plastic deformation starts to occur. Moreover, increasing the pressure will raise the bonding diffusions of molecules which will lead to the formation of solid bridges that are more probable under high pressure (Bazargan et al., 2014). Also, Gilvari et al. (2019) indicated that several studies investigated the effect of compressive pressure on the density and compressive strength of briquettes and the results showed that increasing the pressure will increase the density and the compressive strength when 1-50 MPa is used. Grover & Mishra (1996) and FAO (2019) stated that there are three types of compaction mechanisms which are high compaction pressure (>100 MPa), medium compaction pressure (~5-100 MPa) with a heating device and low compaction pressure (<5 MPa) with a binder. The briquetting of raw biomass as mentioned earlier on is usually with high pressures and some of the reported pressure ranges are up to 130 MPa (Gilvari et al., 2019). Nevertheless, for carbonised/ pyrolysed biomass with a binder present, it was reported that pressures as low as 5 MPa can form a solid fuel depending on the type of material being used (Zanella, et al., 2017). It is reported that although briquettes can be formed at lower pressures, it is essential to produce them at optimum conditions. A study conducted by Tanui et al. (2018) on charcoal dust briquettes, reported that the briquette's optimum conditions were obtained at a compressive pressure of 50 MPa. All in all, increasing the pressure for a certain limit of a material is known to decrease its porosity causing a better connection at the points of contacts which results in more dense and durable briquettes (Bazargan et al., 2014).

2.4.9.3. Cooling and drying temperature

According to Galvari et al. (2019) drying and cooling temperature, and time of densified material is an important factor because if not dried or cooled correctly, it may lose its quality which can result in caking during transportation. It is important to understand the dynamics of moisture output during the drying process of the briquettes produced as it may affect their density and mechanical strength (Lela et al., 2016). Mechanical strength tests from different drying temperatures of biochar briquettes are shown in **Table 2.7**.

Table 2.7: Mechanical strength tests from different drying temperatures of biochar briquettes (Tabakaev et al., 2017).

Drying temperature (˚C)	Drying time (h)	Mechanical strength	
		Durability (%)	Compression (MPa)
20	12	100	0.46
40	18	100	0.46
80	5.3	100	0.46
100	3.3	100	0.26
120	3.0	100	0.26
140	2.0	100	0.26

Tabakaev et al. (2017) investigated drying temperatures of briquettes in the range 20-140°C. As seen in **Table 2.7** all briquettes showed high resistance to fracture when dropped. However, briquettes dried at a temperature range of 20-40°C were stronger in terms of compressive strength when compared to briquettes dried at higher temperatures. Higher temperatures dry the briquettes in a short amount of time approximately 2 hours whereas lower temperatures take about 12-18 hours. Galvari et al. (2019) showed that when briquettes are dried too quickly, the inner layer tends to remain warmer when the outer layer gets dried, and that stresses the material which decreases the mechanical strength caused by the crack formation in the outer. **Figure 2.9** shows briquettes dried at lower and higher temperatures.

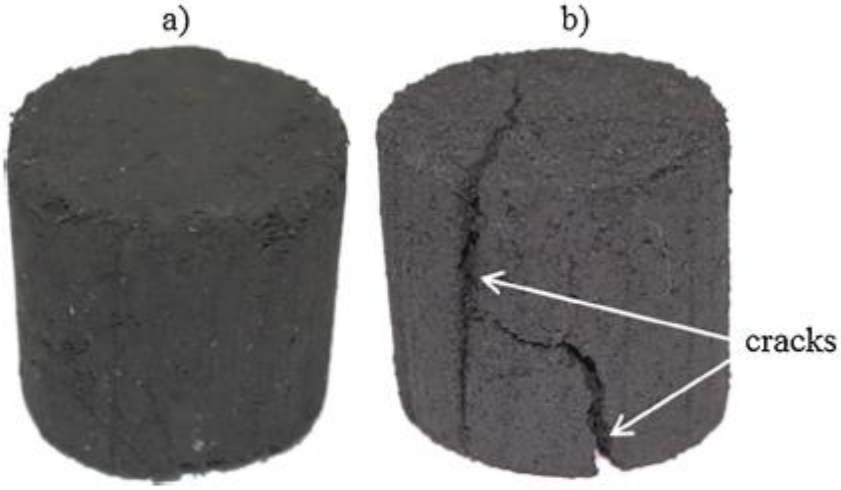


Figure 2.9: Briquettes (d = 50, h = 50 mm) after drying: a) temperature 20°C; b) temperature 80°C (Tabakaev et al., 2017).

The crack shown in **Figure 2.9. b)** is a result of high drying temperatures which causes rapid evaporating moisture. On the other hand, a long drying period can result in a material that is too dry which increases brittleness and reduced quality. Therefore, it is important to find the optimum drying temperature conditions to have a good quality final product (Lela et al., 2016 and Tanui et al., 2019).

2.4.9.4. Binder

Binders play an important role in the process of briquette production as it enhances the compactness of the material to prevent it from falling apart (Oladeji, 2015; Gageanu et al., 2018). As mentioned earlier, that binders are needed for most medium and low-pressure briquetting process and incorporated binders such as protein and lignin in biomass can help create strong bonding between particles. However, it is reported that having a high content of lignin can cause densified biomass to become brittle (Galvari et al., 2019). Biochar lacks plasticity and does not have good cohesive properties like raw biomass. Hence a binding material is required to assist in forming firm briquettes (Zabairu & Gana, 2014; Zanella et al., 2017).

Quality attributes of briquettes such as thermal behaviour and combustion characteristics as well as density, impact resistance and compressive strength are influenced by the type and amount of binder (Ugwu & Agbo, 2013; Borowski et al., 2017). Briquette binders are required to possess certain properties to be considered for briquetting namely, a strong bond, be pollutant-free, have no effect on the heat release, be environmentally friendly as well as economically available (Zhang et al. 2018). Moreover, binders can be classified as inorganic which includes clay, lime, plaster, cement etc., and organic binders such as biomass, coal tar pitch, petroleum bitumen, tar residue and polymer binder (Galvari et al., 2019).

Notably, the most used binders in the densification process that have great advantages are polymer binders (starch) such as potato, cassava, corn starch etc. (Tarasov et al., 2013; Ugwu & Agbo, 2013; Zubairu & Gana, 2014; Zanella et al., 2016; Gageanu et al., 2018). Moisture functions as both lubricant and binding agent, but beyond the optimum level of moisture content, the briquetted material would not be compacted, irrespective of the pressure level. The ideal moisture level is dependent on the binder type and densification process (Davies, & Davies, 2013). It was reported that adding 10% starch and 20% water as a binder increased the hardness of the briquettes more than 100 times. This was observed in a study of charcoal briquette production from orange bagasse using corn starch as a binder, it was reported that briquettes made with 10% of corn starch resulted in great mechanical strength of 1.41 MPa which is great for domestic and commercial use (Zanella et al., 2017). However, the total cost of the process may increase due to binder being added and, in some cases, it can affect the combustion and density of the briquettes hence, it of vital importance that the right binder type and dose are properly selected to have a solid composite fuel with optimum strength and durability as well as combustion properties (Antwi-Boasiako & Acheampong, 2016; Galvari et al., 2019).

2.5. Briquetting technologies

In recent years, different briquetting machines and techniques have been fabricated to accommodate various feedstock for small scale briquetting technology for developing countries (Gebresas et al., 2015). Their operation mode is different from one principle to another. Grover and Mishra (1996) and Ahmed et al. (2014) made a comparison between the piston and the screw press, which are considered typical briquetting machines. The authors mentioned that piston presses can accept raw material with a moisture content of up to 22% whereas for screw presses the moisture content needs to be less than 12%. Hence, the type of briquetting machine will not only depend on the costs but also the type of raw material used.

The capacity of this equipment can range as low as 25-50 kg/h to up to 700-1800 kg/h, depending on the availability of feedstock and size of the equipment (Grover and Mishra, 1996). There are different types of densification technologies, and they are dependent on the type of equipment used.

2.5.1. Roll press densification

This equipment uses two adjacently counterrotating rollers with indentations to produce pillow-shaped briquettes. The material usually charcoal, gets through the hopper and falls into the indentation while turning the roller to compress it (Gebresas et al., 2015). The roller press is more suited for wet powders with a binding material and is currently reported to be widely used to produce carbonised briquettes in many developing countries owing to its simplicity and low cost (Kaliyan et al., 2009).

2.5.2. Piston press densification

2.5.2.1. Hydraulic press

The hydraulic press uses a high-pressure system where the piston is transmitted via an electric motor to compact the material through a vertical direction. The feedstock is fed in front of the press cylinder by a press-dog and the piston speed is low during operation to help reduce the wear of the parts (approximately 7 cycles/ minute) (Oladeji et al., 2015; Sharma et al., 2015).

2.5.3. Pelletising

Pelletising follows a similar concept as briquetting, the difference is the diameter of the dies used (approximately 30 mm). Pelletisers usually produce briquettes in a cylindrical shape, and they tend to have good mechanical strength (Kaliyan et al., 2009). However, they require high energy input and investment. They are commonly employed in industrial applications where automatic feeding is required (Sapariya et al., 2010).

2.5.4. Screw press densification

Screw extrusion is another type of mechanical press, and it is one of the popular equipment for small scale application (Sharma et al., 2015). There are three types of screw press namely, conical crew, screw press with heated dies and screw press without heated dies and they are known to produce briquettes that are denser and stronger (Grover and Mishra, 1996). In this equipment, the material is continuously fed into a screw, which forces the material to go through a cylindrical die that is often heated to increase the temperature to activate the lignin for binding (Oladeji et al., 2015).

2.6. Process optimisation

The most important goal in densification processes is to develop the best production conditions and this can be achieved via process optimisation (Tanui et al., 2018). The assessment of product development and optimisation of process parameters leads to the higher efficiency of the process. Optimisation targets are usually process quality, time, and budgetary requirements (Clarkson and Eckert, 2005). Generally, sequential steps are applied to maximise the potential of the optimisation process. Therefore, it is essential to implement developed approaches that have been used to optimise densification processes to achieve better and cost-effective optimum process parameters. One of the most common statistical design approaches is fractional factorial such as the Taguchi method which has been widely used in single-response applications to reduce response variation (Sibalija and Majstorovic, 2015). However, this method approach is proven not to effectively deal with multi-response problems. Recent interest is in multi-response optimisation. In this study, the compaction pressure, binder concentration and drying temperatures were studied to evaluate the effect they have on the HHV, compressive strength, density, and durability. These multiple responses are better evaluated using suitable approaches such as the response surface method (RSM) with the CCD technique tool. This technique design was used in this study because of its flexibility and compatibility to give multiple responses and use factorial levels more than three to optimise process variables (Sibalija and Majstorovic, 2015).

2.6.1. Response Surface Method (RSM)

Response surface methodology (RSM) employs both mathematical and statistical tools to assess individual and interactive effects of process variables on the targeted output, usually through non-linear regression equation to model the process (Kumar and Lakshmishr, 2017). This approach is coupled with modelling and optimisation to evaluate and quantify process parameters by multivariate analysis techniques such as partial least square regressions. To employ RSM for optimisation of experiments, it is essential to select a suitable experimental design that will accurately fit a mathematical function and evaluate the quality of the fitted model (Bezerra et al., 2008).

There has been a recent development in the use of mathematical modelling coupled with the adoption of RSM for briquetting process optimisation. Tanui et al. (2018) studied the effects of binder mass fraction, drying temperature and compaction pressure using the Box–Behnken Design (BBD) methodology. Applying the RSM enabled the physical and thermal properties of briquettes to be investigated. The results showed that compaction pressure (50 MPa), drying temperature (29.51°C) and binder mass ratio (10%) gave the optimised values of HHV (29.03 MJ/kg) and shatter index (80.36%). Helwani et al. (2018) used the RSM to investigate the effects of applied pressure, particle size and binder composition on the density, compressive strength of briquettes. When the process variables were optimised, the density increased from 623 to 923 kg/m^3, the HHV reached up to 28.99 MJ/kg and the compressive strength was found to be 6.99 N/mm^2. Both studies indicated that compaction pressure and binder concentration/ ratio play an important role in the physical and chemical properties of briquettes. Even though RSM has been widely used to optimise processes and process variables for briquetting processes, there is a dearth of literature when using the CCD method to predict optimum process conditions.

2.7. Economic analysis theory and methods

To perform an economic analysis the first step required is to estimate the total capital investment (TCI) and the total manufacturing costs (TMC). These costs are associated with the day-to-day operation as well as the construction of the plant. The theory required to access the economic feasibility of briquetting process is described in the following sections.

2.7.1. Estimation of capital cost

The capital costs are once-off expenses that are associated with the construction of a new plant or modification of existing plants and these costs are made at the beginning of a project, to begin with, plant operation. According to Turton et al (2013), there are five general classifications for capital cost estimations that are acceptable and are likely to be used in the Chemical Industries and these are the detailed estimate, definitive estimate, preliminary estimate, study estimate and the order of magnitude estimate. The cost estimation considered mostly is the ''study estimate'' at an expected accuracy of -20% to +30% (Turton et al, 2013). This cost estimation is based on limited cost data and rough sizing of major equipment. Nevertheless, this technique is still enough for a comparison between different process alternatives. The sum of the fixed capital cost (FCC) and working capital cost (WCC) is the TCI of a plant. According to Sinnot (2005), the total costs of the plant ready for a start-up are represented by the FCC which takes account of the total installed costs of equipment, contingencies and fees, and auxiliary facility costs. Then WCC represents the additional investment required over the FCC until income is earned when starting and operating the plant.

2.7.2. Estimation of operating cost

To assess the feasibility of the project, an estimate of the operating cost needs to be determined to make alternative processing schemes. The operating cost is also known as the total manufacturing cost (TMC) are namely the fixed cost, variable cost, and general expenses (Sinnott et al, 2005). Furthermore, Sinnott et al (2005) defined the fixed cost as costs that are associated with depreciation, plant overhead, local taxes, and insurance. These costs do not vary with production rate, and they must be paid irrespective of quantity produced.

On the other hand, Turton et al (2013) described the variable cost as the cost that varies with the production rate, and they depend on the product produced. These include the raw materials, utilities, patent and royalties, maintenance and repairs and labour (operation, charges, direct supervisory and operating supply). Moreover, general expenses are costs that are not directly related to the manufacturing cost but associated with the administrative work and management level activities and they include administration, selling and research and development costs. The raw materials, utilities, operating labour, and the fixed capital need to be known to determine the TMC.

2.7.3. Profitability analysis

The profitability of an investment is assessed based on assumptions and profitability criteria after the TCI and TMC of a project. When the estimation of capital investment and manufacturing cost have been conducted the profit generated is used to predict the profitability of the project (Mbadinga, 2015). The non-discounted and discounted technique are the criteria used to access profitability. Turton et al (2013) reported that the non-discounted does not consider the time value of money and are not suggested for assessing new and big projects but have been used for process improvement schemes. Whereas the discounted technique takes into consideration the time value of money and can estimate the cash flow of the entire project (Ji et al., 2018). Various quantitative measures can be used to estimate the profitability of a process using the discounted technique such as the discounted payback period (DPBP), discounted cash flow rate of return (DCFROR), and the net present value (NPV) (Turton et al, 2013).

2.7.3.1. Discounted payback period (DPBP)

The DPBP is the period required to recover the fixed capital cost needed for a project after start-up. This is the point at which the sum of all the cash flow discounted back to time 0 (Hakizimana et al., 2016). For comparison purposes, the project is considered profitable and attractive when the DPBP does not exceed 4 years. However, in some cases projects less than 2 years are considered as high risks projects. Therefore, to make a sound decision supplementary information is required (Turton et al., 2013).

2.7.3.2. Discounted cash flow rate of return (DCFROR)

The DCFRR is defined as a measure of the maximum rate that the project could pay and still break even by the end of the project life (NPV=0) (Sinnott, 2005). Therefore, for a project to be regarded as profitable, its DCFROR needs to be greater than the lending rate which means it needs a positive NPV, and the higher the DCFROR, the more attractive the project.

2.7.3.3. Net present value (NPV)

The NPV is the worth of all the cash flow of the project at the end of the project life. To determine the NPV all the inflows and outflow cash flows are summed up at the desired discount rate and brought back to the first period (Sengar et al., 2013). Therefore, accounting for the time value of money while indicating profitability when the NPV is greater than zero (Sinnot, 2005).

2.7.4. Economic analysis literature review

For briquetting technology to be commercialised, it is essential to assess if the technology is viable economically. The economic evaluation outcome differs for each method used, type of equipment, location, and availability of raw materials involved. Therefore, each briquetting technology route needs to be evaluated to check its feasibility. The type of briquetting technology and profitability criteria assessment on bio-briquettes is shown. Literature emphasises that the type of raw material has a major impact on the profitability of the briquetting process which can be attributed to the availability and process conditions used (**Table 2.8**).

Islam et al. (2003) produced briquettes from a mixture of un-carbonised rice husks and sawdust using a screw press briquetting machine. Although rice husk was more suitable raw material because of its high production rate, briquettes from sawdust showed better properties. Hence, blending 70% of risk husk and 30% of sawdust was appropriate and it gave the best blend product which was within the limit of the experiment. The briquette production cost was found to be comparatively less than that of fuelwood and the process was found to be economically feasible with a payback period of 1.73 years.

Table 2.8: summary of the techno-economic analysis of briquetting production.

Raw material	Type of technology	Profitability criteria		Comments	Reference
		PBP (months)	Net present value ($)		
Un-carbonised Rice husk + sawdust	Screw press	20.76	-	Economically feasible	(Islam et al., 2003)
Carbonised	Screw press				(Sengar et al., 2013)
a. Cashew nutshell		8.1	26952.59	Economically feasible	

b. Grass husk		7.56	31423.83		
c. Rice husk		29.35	437.62		
Carbonised corn cobs	Hydraulic press	43.2	20 532.20	Economically feasible with IRR of 36%	(Wilson et al., 2016)
Carbonised wood chips	Hydraulic press	-	-	Economically feasible with MSP $145	(Sahoo et al., 2019)

Sengar et al. (2013) estimated the economics of briquettes produced from carbonised cashew nutshell, grass, and rice husk using a screw press extruder machine. Better results were observed in the cashew nutshell briquettes as they burnt with good flame and 15% thermal efficiency. Compared to grass and rice husk briquettes, cashew nutshell had better calorific value, shattering indices test, tumbling test, and degree of densification. The payback periods for cashew shell, grass, rice husk briquettes were 8.1, 7.56, and 29.35 months respectively and with a net present value of $26952.59, $31423.83, and $437.62, respectively. The positive NPV and PBP of less <4 years makes the production cost analysis economically feasible.

Wilson et al. (2016) studied the effects of cassava binder ratio, compaction pressure, and particle size on thermo-physical properties of carbonised corn cobs briquettes. These independent variables showed a significant effect on briquette quality. The briquettes burnt without smoke, implying there will be reduced air pollution during burning. A cost-benefit analysis of the corn-cob briquettes production had an NPV of $20 532.2, an internal rate of return (IRR) of 36%, and a payback of 3.603 years. These results show that the production of carbonised corn cobs is economically viable due to its positive NPV, higher IRR and a PBP of less than 4 years.

Sahoo et al. (2019) conducted a techno-economic study on the production of woodchips briquettes (WCB), torrefied-woodchips briquettes (TWCB) and biochar from forest residue using three portable systems. These portable systems were expected to eliminate a transportation distance of about 200 km which sets the mean selling price (MSP) of an oven-dry metric ton (ODMT) of WCB, TWCB, and biochar to be $162, $274, and $1044, respectively. However, using the logically improved portable system could reduce the MSP of WCB, TWCB, and biochar to $65, $145, and $470/ODMT, respectively. This means that portable systems have the potential to produce useful products at current prices using forest residues while concurrently reducing potential wildfires and greenhouse gas emissions. Hence, making it to be economically feasible.

The techno-economic analysis of solid fuels from biomass especially carbonised biomass is still in its infancy stage. To produce and commercialise briquettes with comparable compositions as fossil fuels such as coal, more critical information is required, and it differs from biomass to biomass. Successful briquette production from biomass can allow industries to utilise these solid fuels for heating purposes (Bazargan et al., 2014). Techno-economic analyses of carbonised biomass briquettes have been critiqued but there is a dearth in literature for other biomass such as CS to conclude its economic and environmental viability. Thus, conducting technical and economic research on briquette production from CS is essential.

CHAPTER THREE

3. MATERIALS AND METHODS

Waste biomass can be converted into a solid composite fuel through thermochemical and densification processes as these methods improve biomass properties. The influence of the densification parameters such as pressure, binder, density, and particle size are vital to the quality of the product. This chapter covers detailed materials and methods used in the production of briquettes from pyrolysed corn-stover (CS) and the optimisation techniques. CS waste biomass was analysed via thermogravimetric analysis (TGA). A rotating retort reactor was used to produce biochar at optimum conditions. Briquettes of dimensions 50 mm by 50 mm were produced using a piston press. The physical and chemical characteristics of CS, biochar, and briquettes were accessed via both ultimate and proximate analyses. Briquettes were also assessed via HHV, strength tests, density, and burning time. Statistical software package Design-Expert® was used to optimise targeted variables of briquetting process, the process was developed using software SuperPro Designer® and economic indicators were used to conduct an economic analysis on the briquetting process.

3.1. Biomass selection and preparation for pyrolysis

Corn stover was collected from a maize farm in Western Cape, South Africa soon after harvesting. Approximately, 50 kg of the collected sample was sun-dried to 10% moisture content. A hammer mill was used to grind the dried sample to a size of 4 mm. Thereafter pilot shaker apparatus coupled with series of sieves of different sizes were then used to sieve the milled sample particle size of <2 mm required by the rotating retort reactor. Particle sizes that are greater than 2 mm were re-milled until the particle size was within the desired particle size of <2 mm. The sample was stored in sample polypropylene bags at room temperature.

3.2. Production of biochar

Biochar production was carried out in duplicate for reproducibility purposes. A rotating retort reactor with a 2-zone heating chamber shown in **Figure 3.1** was purged with nitrogen for 15 minutes at a rate of 10 L/min. The reactor was set to pyrolysis temperature of 400°C for each set of experiments. CS sample was fed into the rotating retort reactor after it has maintained an oxygen level of 3% concentration at the rate of 1kg/hour while constantly purging nitrogen at 1.5 L/min for each set of temperatures. The reactor was followed by a residue collection container which was maintained at 300°C to limit the condensation of tars where the solid product (char) was collected. A condensation system with 4 containers (C1-C4) housed in separate water tanks (~ 8°C), was used to collect the volatiles from the char pot. The gas exiting the last condenser was then passed through an open-flame pilot burner system to the atmosphere. The sample was held at the set temperature to cool for 24 hours. The charred mass and the oil were collected separately, weighed, and recorded.

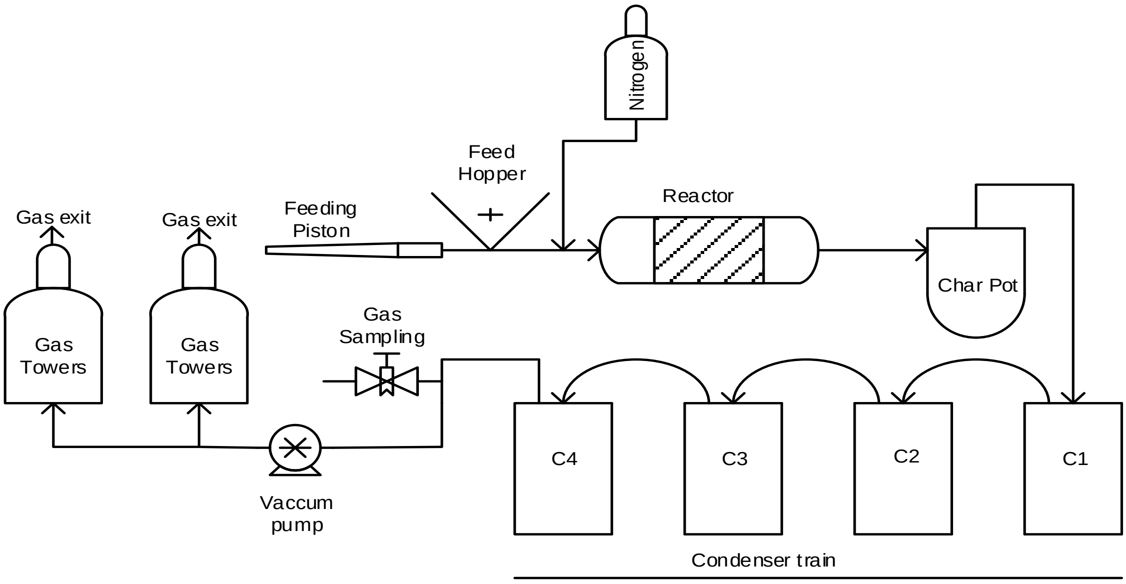


Figure 3.1: Pyrolysis pilot scale set-up.

3.3. Biomass and biochar characterisation methods

Biomass and biochar were characterised based on ultimate analysis at the University of KwaZulu Natal, KwaZulu Natal, South Africa. Proximate analysis and energy content were assessed by HHV analysis at the Department of Process Engineering, Stellenbosch University, Western Cape, South Africa. For reproducibility, the samples were assessed in duplicate.

3.3.1. Proximate analysis

Proximate analysis was conducted on the biomass and biochar samples to determine ash content, volatile matter, and fixed carbon content in accordance with the ASTM E1131 standards, using STARe TGA analyser (Mettler Toledo, Ohio, USA). A mass of 10 mg of each sample was separately heated from ambient temperature to 110°C at a heating rate of 50°C /min in a nitrogen atmosphere for 5 minutes. Thereafter, the temperature was increased from 110 to 900°C at a heating rate of 100°C/min for 5 minutes. In the last step, the sample was held at 900°C for a further 5 minutes with oxygen replacing nitrogen to allow for complete combustion of the sample. To determine the moisture content, volatile matter, fixed carbon, and ash content the TGA curve drawn were used.

3.3.2. Ultimate analysis

Ultimate analysis was conducted on the biomass and biochar samples to determine its elemental composition of carbon (C), hydrogen (H), nitrogen (N), and sulphur (S), using a

Vario EL Cube elemental analyser (Elementar, Langenselbold, Germany). To determine the total of the elemental composition (wt. %) a TruSpec Software program was used. Finally, the oxygen content was then calculated by difference.

3.3.3. Higher heating value (HHV)

The energy content of biomass can be analysed by conducting a higher heating value analysis. The HHV's of biomass, biochar, bio-oil, and briquette samples were analysed using an Eco Cal2K (DDS, Instruments, Rheinlands, Germany) bomb calorimeter in accordance with ASTM D5865 standard procedure. A mass of 0.2 g of each sample was placed in a crucible and installing a fuse. Oxygen at a pressure of 1500 kPa was charged to the bomb calorimeter and firing cotton sparked which ignited the combustion reaction. After 20 minutes the analysis was complete, and the results were displayed on the screen of the Eco Cal2K bomb calorimeter.

3.4. Design of experiments

A total of 20 experimental runs were generated using Design-Expert® software version 10.0.0 (Stat-Ease Inc., Minneapolis, USA) via central composite design (CCD). This approach statistically designed experiments then estimated the mathematical model coefficients and lastly it predicted the responses (HHV, compression strength, mechanical strength, and density). Drying temperature, densifying pressure, and binder percentage were evaluated as independent variables. They were coded as A, B, and C respectively (**Table 3.1**). They were chosen based on the reported ranges for maximum results (Tabakaev et al., 2017; Hamid et al., 2016).

Table 3.1: Process variable used in the CCD for optimisation of briquette production using temperature, pressure, and binder as controllable experimental factors.

Variables	Code	Low level (-1)	Medium level (0)	High level (+1)
Temperature	A	20	45	70
Pressure	B	20	30	40
Binder	C	5	7.5	10

The system's behaviour is described by the quadratic equation below **Equation 3.1**, where optimum values were selected by analysing the response surface contour plots and solving the regression equation (Silva et al.,2011).

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \qquad \text{Equation 3.1}$$

Where Y is a response variable and β_0, $\beta_{i,}$ β_{ii}, and β_{ij} are intercept of the response variable, coefficients corresponding to the factor are $X_i, X_j (i, j = 1, 2, \ldots. n)$. The input variables that influence the response Y are X_i and X_j; the random error was represented by ε. A regression equation demonstrates the significance of individual coefficients, overall model significance, multicollinearity, heteroscedasticity, and autocorrelation (Stillwell and Webber 2016). A confidence level of 95% ($p< 0.05$) was evaluated by ANOVA as the statistical significance of the model. The multiple correlation coefficients (R^2) were expressed to fit the quality of the model. The statistical significance of each parameter was determined via P-values (Silva et al., 2011). Design-Expert® software version (10.0.0 Stat-Ease Inc, Minneapolis, USA) was used to carry out the experimental runs shown in **Table 3.2**.

Table 3.2: Design of experiments for process variables optimisation.

Run	Compression pressure (MPa)	Binder concentration (%)	Drying temperature (°C)
1	13.82	7.5	45
2	20	5	20
3	20	10	20
4	20	10	70
5	20	5	70
6	30	11.70	45
7	30	7.5	45
8	30	3.30	45
9	30	7.5	3.0
10	30	7.5	45
11	30	7.5	87.04
12	30	7.5	45
13	30	7.5	45
14	30	7.5	45
15	30	7.5	45
16	40	5	70
17	40	10	70
18	40	5	20
19	40	10	20
20	46.82	7.5	45

3.5. Production of briquettes

3.5.1. Sample selection and preparation for briquette production

Biochar produced via slow pyrolysis at a temperature of 400°C was used as the starting material for briquette production. Corn-starch was selected as a binding material due to its ready availability as waste and its superior pasting properties. The corn-starch was collected from Tongaat Hullet, an agriculture and agri-processing company (Western Cape, South Africa). In preparation for densification, biochar was pounded using a mortar and pestle and then sieved using a mesh size of 2 mm. Both biochar and corn starch were exposed to room temperature conditions for 24 hours before briquetting.

3.5.2. Binder and biochar mixture preparation

The binder concentrations of 5, 7.5, and 10% at (3:1, biochar; corn-starch) was prepared to mix water (80:20, biochar; water) and heating at 80°C to activate the binder, until gum point. Thereafter the binder and biochar were mixed to form the mixture to be densified. This methodology was adapted from methods by Tamilvanan (2013), Zanella et al. (2016) and Tabakaev et al. (2017) with modifications.

3.5.3. Densification production

A piston press (briquetting machine) operated manually was designed by Pride Lab Equipment (Pty) Ltd (Cape Town, South Africa) using a mild steel material with a capacity of one briquette per turn. The press (**Figure 3.3**) has a 10 Ton jack connected to the pressure gauge. The press is connected to a load-cell logger which is coupled with software that receives data from the piston press. A hardened stainless-steel cylindrical mould (ID= 50 mm; H= 50 mm) aided with a funnel to load the starting material at the top and a collector to receive the product at the bottom. A release valve handle with a piston, connected to the pressure jack was used to compact the feed material manually (Biochar and binder mixture).

To prepare a briquette sample, the material was fed on top of the mould using a funnel at the required compaction pressure and it was held for 30 seconds before releasing the handle. Thereafter, a steel mould designed to push out the sample was then used to eject the briquette sample by pressing it out and collecting it at the bottom of the mould. All briquette samples were placed in a drying tray and dried at desired temperatures. The dried briquettes were then taken for laboratory analyses. The experiments were done in duplicate for reproducibility purposes.

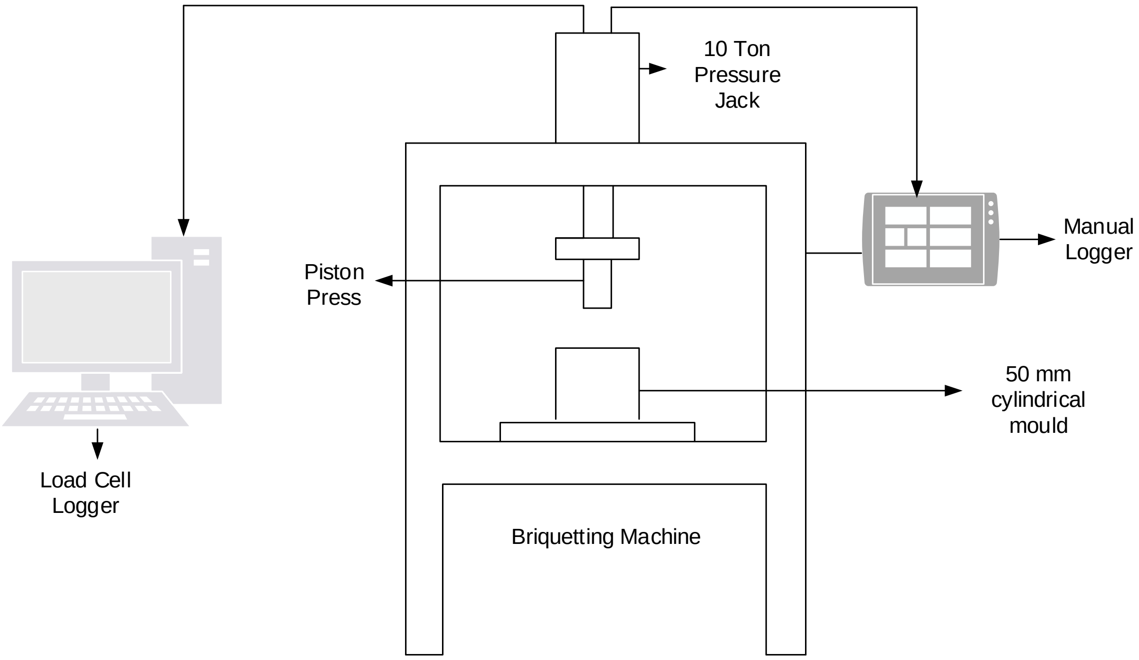


Figure 3.2: Briquette machine set-up.

3.6. Briquettes Characterisation

Briquettes samples were characterised based on energy content by HHV analysis and proximate analysis as outlined in sections 3.3.2 and 3.3.1. Strength test and density were conducted on the briquettes to determine their quality at the Department of Civil Engineering, Cape Peninsula University of Technology, Western Cape, South Africa. For repeatability, the samples were done in duplicate.

3.6.1. Strength tests

3.6.1.1. Mechanical strength (Durability)

Mechanical strength was conducted on the briquette samples in accordance with GOST 21289-75 standard procedure (Tabakaev et al., 2017). A briquette sample was weighed and dropped three times on a metal surface at a height of 1.5 m. The dropped sample was collected, sieved, and weighed again. **Equation 3.2** was used to calculate the ratio between the masses of the briquette before and after.

$$X = \frac{m - m_1}{m} \qquad \textbf{Equation 3.2}$$

Where:
m is the mass of briquette before the test (g)
m1 is the mass of briquette after the test (g)
X is the ratio between the masses

3.6.1.2. Compression strength

Compression strength was conducted to determine the maximum load the briquette can sustain without failing. Each briquette sample was placed in a cube crusher and the pressure was uniformly increased at a rate of 100 kN/min compressing the sample to failure. The test was done in accordance with the study (Tabakaev et al., 2017). A data logger connected to the cube crusher recorded the force (F) applied to the briquette. **Equation 3.3** below was used to calculate the maximum compression strength.

$P = \frac{F}{d}$ **Equation 3.3**

Where:
P is maximum compression strength (MPa)
F is the force applied on the briquette (kN)
A is the area of the briquette (mm^2)

3.6.2. Density

The density of briquettes indicates desirability in terms of transportation, storage, handling, and burning time (Kaur et al. 2017). To determine the density of the briquettes, **Equation 3.4** (Wilson, 2016) was used. The area of each briquette was calculated, and the mass and height were measured to determine the briquette density.

$\rho = \frac{m}{A \times h}$ **Equation 3.4**

Where:

ρ presence the density of the briquette (kg/m^3)
m is the mass of the briquette (kg)
A is the area of the briquette (m^2)
h is the height of the briquette (m)

3.6.3. Burning time

The optimised briquettes were tested for their burning characteristics based on burning time which is the average time that the briquettes take to burn into ash after ignition. The sample weight of briquettes was used to heat 1L of water using an improved cookstove to which the time for the briquettes to burn into ash and the water to boil was recorded. The test was done with modifications in accordance with studies by Kabok et al., 2018 and Ndingeng et at., 2015.

3.7. Process development and economic evaluation

To determine the probability of developing an efficient method for briquette production, process evaluation for pilot plant and commercial scale methods was conducted. The material and process conditions were based on the lab-scale experiments detailed in section 3.2. A process flow diagram (PFD) for briquetting plant that comprises the pyrolysis section and the briquetting section was developed highlighting the preliminary plant plot and major equipment for briquetting process. Intelligen (Scotch Plains, NJ, USA) software SuperPro Designer® was used as a simulation software to give detailed methods for process model and design parameters for briquette production. To simulate on SuperPro Designer®, corn starch, biochar, and briquettes were manually defined and were regarded as non-conventional components in this study as they are not originally defined in the software. Briquetting machine was also regarded as non-conventional equipment which was selected as a generic box and recipe operation conditions were used. A unit procedure, analogous to SuperPro Designer® was used to describe each operational step that takes place in the production of briquettes.

The mass and energy balances generated in the process simulation was useful to estimate the capital and operational costs of the large-scale briquetting plant. An Excel spreadsheet was used to estimate costs associated with equipment purchase and installation, civil construction, utility installation, land, and engineering as well as the raw materials and products. These costs were estimated from reported historical data from literature and individual suppliers (Wang & Jan, 2018; Alibaba, 2019; Brigagao et al., 2019; City of Cape, 2019), using Lang factors when necessary. Economic analyses were then conducted and reported in terms of the discounted cash flow rate of return (DCFROR), discounted payback period (DPBP), and net present value (NPV) (Sinnot, 2005).

CHAPTER FOUR

4. CHARACTERISATION AND PROCESS OPTIMISATION

4.1. Introduction

In the biomass densification process, it critical to ensure that the densified product is of high quality and meets the set standards, to sustain quality control at both national and international markets (Pradhan et al., 2018). Biochar briquette quality properties are affected by the type of biomass, physicochemical composition of biomass and biochar as well as process conditions (Kaliyan & Morey, 2009). Hence, it is of importance to assess these properties in the production of briquettes that will serve as a good source of fuel compared to coal and support environmentally benign combustion (Kers et al., 2010; Emerhi, 2011). Characteristics of raw corn-stover (CS) and biochar from pyrolysis as assessed via HHV, proximate and ultimate analysis are reported herein. Thus, to improve the cost-effectiveness of densification the effects of compaction pressure, binder concentration, and the drying temperature were investigated. CCD was used as a statistical optimisation tool to evaluate the effect the factors have on the HHV, compaction pressure, durability, and the density of the briquettes. The process of optimisation is important as its main goal is to maximise the quality of CCS briquettes in terms of energy contents while obtaining high strength and density. Further, a mathematical model that links the influential parameters and ANOVA and regression analysis was used to achieve the appropriate mathematical models.

4.2. Characterisation of biomass

4.2.1. Ultimate analysis

The carbon content of the raw biomass was found to be 40.97 wt.% dry basis, and this is comparable to previous studies by Azuara et al, 2016; Cong et al, 2018; He et al., 2018 on raw CS (**Table 4.1**). The oxygen content of the biomass was found to be 53.23. wt. % This reveals that raw CS has low carbon content and relatively high oxygen hence, obtaining H/C and O/C ratios of 0.12 and 1.30, respectively. It is believed that the H/C molar ratio should increase while oxygen content (or O/C molar ratio) should decrease for biomass feedstock to produce potential biofuels (Capunitan and Capareda, 2012). The results are consistent with values obtained by other researchers (Cong et al, 2018; Al-Wabel, 2013). Higher O/C ratios are expected in biomass due to structurally well-defined compounds (Danje, 2011). Therefore, these demonstrate the need for further processing of CS to remove oxygen as much as possible to increase its energy content and make it a valuable biofuel (Capunitan and Capareda, 2012). It is evident from the results in **Table 4.1** that CS is an environmentally friendly source of feedstock for fuel production given that it has low concentrations of nitrogen

(0.71 wt.%) and no sulphur content. Low nitrogen and sulphur contents indicate the capability of the biomass to be suitable for thermochemical conversion (Chen et al., 2015). Sulphur and nitrogen oxides are major pollutants produced from burning fossil fuels like coal. Hence, if the raw CS and pyrolysis products from raw CS are combusted, they would give off lower concentrations of these pollutants. Consequently, contributing to the reduction of global warming and climate change.

Table 4.1: Ultimate analysis of corn-stover biomass.

	This Study	**He et al. (2018)**	**Cong et al. (2018)**	**Azura et al. (2016)**
Feedstock	CS	CS	CS	CS
Ultimate analysis (wt. %, dry basis)				
C	40.97	43.28	44.92	44.40
H	5.10	5.92	5.77	5.60
O* by difference	53.23	39.32	41.00	49.12
N	0.71	1.96	0.98	0.43
S	-	0.66	0.21	0.45
H/C Molar ratio	1.45	1.63	1.5	1.50
O/C Molar ratio	0.97	0.68	0.68	0.83

4.2.2. Proximate analysis

Corn-stover biomass was characterised by a high volatile matter value of 69.04 wt. % and minimal ash content of 4.96 wt. % (**Table 4.2**). High volatile matter is advantageous for thermochemical conversions because during heating it readily releases more volatile compounds that produce a solid product with low ash and high fixed carbon (Singh & Shadangi, 2011; Vassilev, 2015; Yorgun & Yaldiz, 2015). Lower amounts of ash in biomass feedstocks during degradation could reduce slagging and fouling in the furnace, which is caused by the alkali content in the high-ash feedstocks (Shariff et al., 2016). The observed high fixed carbon content implies that the heating value of the pyrolysis product will be improved, consequently making CS a desirable starting material for fuel production via pyrolysis (Yorgun & Yaldiz, 2015). In addition, the CS has undesirable qualities as compared to the typical low-grade coal (**Table 4.2**) used for domestic for heating and cooking purposes. Hence the need to upgrade CS into a competitive solid fuel is significant. These values are comparable to the characteristics of other biomass previously reported in the literature (**Table 4.2**).

Table 4.2: Proximate analysis of corn-stover biomass.

	This Study	**Capunitan & Capareda (2012)**	**Liu et al. (2015)**	**Azuara et al. (2016)**	**Chelgani et al. (2019)**
Feedstock	CS	CS	CS	Pine wood	Coal
Proximate analysis (wt.%, dry basis)					
Volatile matter	69.04	78.7	80.30	80.85	28.54
Ash content	4.96	6.62	2.25	8.05	20.21
Fixed carbon	17.43	14.7	9.93	11.1	44.16
HHV (MJ/kg)	16.8	17	-	18.83	22.18

4.2.3. Heating value

The HHV is an indicator of how much energy the biomass contains, which is the overall energy content released when the fuel is burnt (McKendry, 2002). The HHV of the raw CS in this study was determined to be 16.80 MJ/kg. To know if biomass needs to be upgraded to a better-quality solid fuel, it is essential to know its HHV to help determine the conversion efficiency of the process (Mabizela, 2014). Likewise, the HHV value in this study was close to the one found by Capunitan & Capareda (2012) on CS biomass and Azuara et al. (2016) on pinewood biomass considered for conversion processes (**Table 4.2**).

4.2.4. Product yields

The total mass distribution of CS product yields after thermochemical decomposition at an optimum temperature of 400°C was observed and is shown in **Table 4.3.** The product yields of biochar, bio-oil, and biogas were found to be 46.11, 30.40, and 23.20 % respectively. Typically, the product yields of solids and liquids tend to decrease with temperature increase while gaseous products increase. As expected, biochar had the highest yield among the products as described in chapter 2 (**Table 2.8**) for slow pyrolysis products. This can be attributed to secondary cracking reactions that occur due to pyrolytic vapour caused by lower heating rates and lower to moderate temperatures (400-450°C). This means that there will be a rise in the production of carbonaceous material and a decrease in liquids and gases (Azuara et al., 2016). In the same way, the values are consistent with those reported by other studies (**Table 4.3**) The study on slow pyrolysis of hazelnut shells at 400°C by Quispe et al. (2017) reported the biochar, bio-oil, and biochar yield to be 47.50, 20.10 and 18.90 % respectively. Similarly, Capunitan & Capareda. (2012) reported biochar, bio-oil, and biogas yield to be 37, 31, and 15 % correspondingly, from the slow pyrolysis of CS at 400°C.

Table 4.3: Product yield distribution at 400°C.

Reference	This Study	Capunitan & Capareda. (2012)	Quispe et al. (2017)
Feedstock	CS	CS	Safflower
Biochar yield (%)	46.11	37.00	47.50
Biooil (%)	30.40	31.00	20.10
Biogas (%)	23.20	15.00	18.90

4.3. Characterisation of biochar

4.3.1. Ultimate analysis

The hydrogen and oxygen contents were found to be 3.66 and 67.55 wt. % respectively. The hydrogen and oxygen content show a decrease of 28 wt. % and 26. 9 wt. % from the raw CS when it pyrolysed at 400˚C. According to He et al. (2018), the degree of aromatisation is promoted during pyrolysis which consumes a certain amount of H and O elements in lignocellulosic resides. These results are similar to the values reported in previous studies by (Angin, 2013) and Liu et al. (2018) on the pyrolysis of safflower and CS at 400˚C. The H and O contents of the safflower were 3.84 and 68.54 wt. % and of the CS were 3.67 and 58.09 wt. % respectively. Biochar results (**Table 4.3**) shows the carbon content increased from 40.97 to 71.40 wt. % compared to the raw CS. This indicates that after CS went under thermal decomposition oxygen content and other volatile were removed increasing carbon content (Poundel & Oh, 2014). The carbon content increase is consistent with fixed carbon content and the content in this study is comparable to that of South African coal which has a carbon content of 78.50 wt. % (John Thompson (Pty) Ltd., 2019).

In comparison with raw CS, the H/C and O/C ratios were found to be 0.64 and 0.30, respectively. The biochar values (**Table 4.3**) show that there was a decrease in the H/C and O/C ratios when CS went through carbonisation at 400˚C. Lower ratios are desirable after pyrolysis since they indicate that the material has high energy content and during decomposition, the carbonisation and aromaticity of biochars were fully elevated (Hu & Gholizadeh, 2019). The results show that H/C and O/C ratios were like those illustrated on a Van Krevelen diagram in the study by Capunitan and Capareda (2012) on CS biochar. The authors mentioned that their H/C and O/C ratios were 0.65 and 0.10, respectively. Similarly, the Van Krevelen plot for solid fuels in the study by McKendry (2002) shows values obtained in this study are within the coal region (H/C=0.4-0.8 and O/C=0.01-0.35). Besides, it is important to know how much nitrogen and sulphur contents are present before the combustion of biochar as they contribute to the greenhouse effects. In this study, nitrogen content was found to be 1.05 and there was no sulphur detected which makes the biochar to be favourable over convention fossils like coal.

Table 4.4: Ultimate analysis for biochar.

Reference	**This Study**	**Liu et al. (2014)**	**Angin. (2013)**	**John Thompson (Pty) Ltd. (2019)**
Feedstock	CS	CS	Safflower	C smalls coal
Ultimate analysis (wt. %, dry basis)				
C	67.55	79.65	68.54	65.03
H	3.66	3.96	3.67	3.43
O* by difference	27.91	15.72	24.16	8.26
N	0.88	0.62	3.63	1.70
S	0	0	0	0.66
H/C Molar ratio	0.64	0.79	0.64	0.66
O/C Molar ratio	0.30	0.20	0.26	0.10

4.3.2. Proximate analysis

The volatile matter content obtained in this study decreased from 69.04 to 21.19 wt.%. The decrease in the volatile matter is because the pyrolysis process removes the volatile constituent of the biomass which increases the fixed carbon content (Capunitan and Capareda, 2012). According to John Thompson (Pty) Ltd (2019), it is favourable to have a volatile matter content around 20-30 wt. % to offer a product as industrial fuel to compete with coal. After carbonisation, the fixed carbon content in this study increased from 17.43 to 65.18 wt. %. The increase in the fixed carbon can be attributed to its linear relationship with H/C ratios, where the H content gets removed during devolatilization. This leaves the fixed carbon with very low H content which gives rise to the HHV (Ronsse et al., 2013). The ash content in this study increased from 4.96 to 13.86 wt.% after pyrolysis. The rise in ash content can be explained by the progressive concentration of minerals and obstructive volatilisation of biomass when pyrolysed (Raqid et al, 2016; Dooley, 2015). These results are consistent with the values obtained from other studies indicating pyrolysing biomass decreases the volatile matter while it increases the fixed carbon and ash content (**Table 4.4**) (Angin, 2013; Liu et al., 2014; John Thompson, 2019). The presence of high ash content in fuels is not desirable as it may reduce its energy content. The biochar produced in this study has a relatively low ash content than that of a typical industrial C grade coal which has an ash content of 18.22 wt. % (John Thompson (Pty)Ltd, 2019). Therefore, with these characteristics the biochar produced has the potential to compete with coal as a source of fuel for heating and cooking

Table 4.5: Proximate and HHV analysis of biochar.

Reference	**This Study**	**Liu et al. (2014)**	**Angin. (2013)**	**John Thompson (Pty) Ltd. (2019)**
Feedstock	CS	CS	Safflower	C smalls coal
Proximate analysis (wt%, dry basis)				
Volatile matter	21.19	20.8	19.8	24.84
Ash content	13.86	5.4	8.5	18.22
Fixed carbon	65.18	71.7	71.7	54.24
Yield	43.4	36.9	34.18	-
HHV	28.89	-	28.77	26.0

4.3.3. Heating value

To determine the amount of heat released when the biochar will be combusted, the HHV was evaluated. The HHV of biochar in this study increased from 16.80 to 28.89 MJ/kg after raw CS was pyrolysed at 400°C. The rise in the HHV is attributed to the removal of oxygen and hydrogen at 400°C from the biomass feedstock which increases the carbon content (Poudel and Oh, 2014). This validates the claim made in section 4.3.1 that an increase in carbon content consistently increases the fixed carbon which contributes to the increase in HHV (Ronsse et al., 2013). Correspondingly, these values were like the results reported by Angin. (2013) after safflower biomass went under carbonisation at 400°C and he reported an HHV 28.77 MJ/kg (**Table 4.5**). Nevertheless, the HHV of the biochar in this study has more energy value than the raw CS and hence more favourable as a suitable energy source than the biomass itself. In this study, the biochar had an HHV value comparable to that of South African C grade coals (22.18-25 MJ/kg) (Chelgani et al., 2019). Also, the biochar had better qualities (low ash and no sulphur contents).

4.4. Optimisation of briquettes

4.4.1. The effect of process variables on higher heating value

The regression model (R^2) of the effect of process variables on the HHV was found to be 0.9814 (**Table 4.6**) and shows that it is in reasonable agreement with the adjusted R^2 of 0.9252. The high R^2 demonstrates that there is a good correlation between the actual values with the predicted values and the low calorific value, which was found to be 2.25, confirms that the quadratic model is precise and reliable. The Adeq precision was found to be 25.6499 and a ratio greater than 4 is desirable (Design-Expert® software version (10.0.0 Stat-Ease Inc, Minneapolis, USA)). Therefore, this indicates that the model is adequate to be used for the process design. The model shown in **Equation 4.1** describes the variation of the HHV with compaction pressure, binder concentration, and drying temperature. The model terms B, A^2 were found to be significant. Hence, the final equation for predicting the HHV was attained as follows:

$$\mathrm{HHV} = 30.89419 - 0.203006\mathrm{B} + 0.001463\mathrm{A}^2 - 0.019018\mathrm{B}$$ **Equation 4.1**

where A is compression pressure, B is binder concentration and C is drying temperature

Table 4.6: ANOVA and fit stats summary for HHV.

Factor	**P-value**	**F value**	**Effect**	**Fit stats**
Compression pressure (A)	0.2057	1.83	Insignificant	R^2=0.9765
Binder concentration (B)	0.0001	397.09	**Significant**	Adjusted R^2=0.9553
Drying temperature (C)	0.4016	0.7672	Insignificant	CV%=0.7215
AB	0.4016			Adq precison=25.6499
AC	0.8894			
BC	0.6778			

4.4.1.1. Interactions between process variables on the HHV

The 3-D surface plot shown in **Figure 4-1. a)** indicates the effects of compaction pressure from 20 to 40 MPa and binder concentration from 5 to 10% on the HHV at a constant drying temperature of 45°C. The interaction between the compaction pressure and drying temperature was insignificant (p>0.05). Figure 4-1. a) shows a linear decrease on the HHV as the binder concentration is increased and a slight decrease on the HHV when pressure is increased. However, the HHV is seen to start to slightly pick up an increase at 30 MPa. Though individually as shown in **Table 4.6** binder concentration influences the HHV, the compaction pressure does not maximise the HHV under the set conditions. **Figure 4.1. b)** shows the absolute nature of the 3-D surface plot for the interaction between binder concentration and drying temperature. The interaction is shown for binder concentration from 5 to 10% and drying temperature from 20 to 70°C, maintained at 30 MPa. A decrease of HHV is observed on the figure as the binder concentration is increased while there is a slight increase on the HHV when the drying temperature is increased. The two variables showed an insignificant interaction to the HHV, owing to the p=0.6778 indicated by ANOVA on **Table 4-6**. With respect to the interaction between compaction pressure from 20 to 40 MPa and the drying temperature 20 to 70°C, held at 7.5% binder concentration shown in **Figure 4.1. c)** there was no significant interaction as validated by ANOVA in **Table 4.6**. Their individual effects on the HHV further validates and supports the insignificance.

4.4.1.2. The influence of process variables on the HHV

The HHV obtained through the densification process ranged from 25.5 to 28.80 MJ/kg. These values are consistent with charred risk husk (Chirchir et al., 2013) and palm kernel briquettes values of 26.8 to 25.2 MJ/kg and 28.18 to 27.51 MJ/kg (Bazargan et al., 2014) The 3-D surface plots illustrated in **Figure 4.2** and the values shown in **Table 4.6** show the effects of the briquetting process variables and their interactions on the resulting HHV. The results in **Table 4.6** shows binder concentration (B) to be the most significant factor influencing the HHV of briquettes as indicated by the larger F-value of 397.09 and smaller p-value of <0.0001. The HHV significantly decreases from 28.80 to 25.59 MJ/kg as the binder concentration is increased from 5 to 10% (**Figure 4.2**). The decrease in HHV could be attributed to the type of corn-starch quality and the amount (Kaur et al., 2017). Besides, if the HHV of the binder itself is lower than the material used it decreases its fixed carbon thus decreasing the HHV of the briquettes (Haykiri-Acma and Yaman, 2010; Thabuot et al., 2015). Similar behaviour was observed when starch binder concentration was used on kernel palm briquettes, the HHV decreased from 28.18 to 27.51 MJ/kg (Bazargan et al. 2014). On the other hand, the compression pressure does not show any impact on the HHV as indicated by the p-value of 0.2057 and a small F-value of 1.83 (**Table 4.6**). This is because the pressure is responsible to enhance the volumetric value of the briquettes but not the HHV (Grover and Mishra, 1996; Lela et al., 2016). In this study, it was included to check its possibility of mechanical strength improvements. According to a study by Tanui et al. (2018), there were similar observations of no statistical influence on the HHV when the pressure was increased from 50 MPa and 150 MPa on eucalyptus briquettes. Additionally, the p-value of 0.4016 and a smaller F-value of 0.7672 (**Table 4.6**) indicates that the drying temperature does have not a statistical effect on HHV. The limited effect of the drying temperature could be attributed to the fact that this study only limited to a drying temperature of 70°C. Whilst the studies conducted by Tanui et al. (2018) observed a slight decrease in the HHV as the drying temperature was increased at temperatures above 80°C on eucalyptus briquettes.

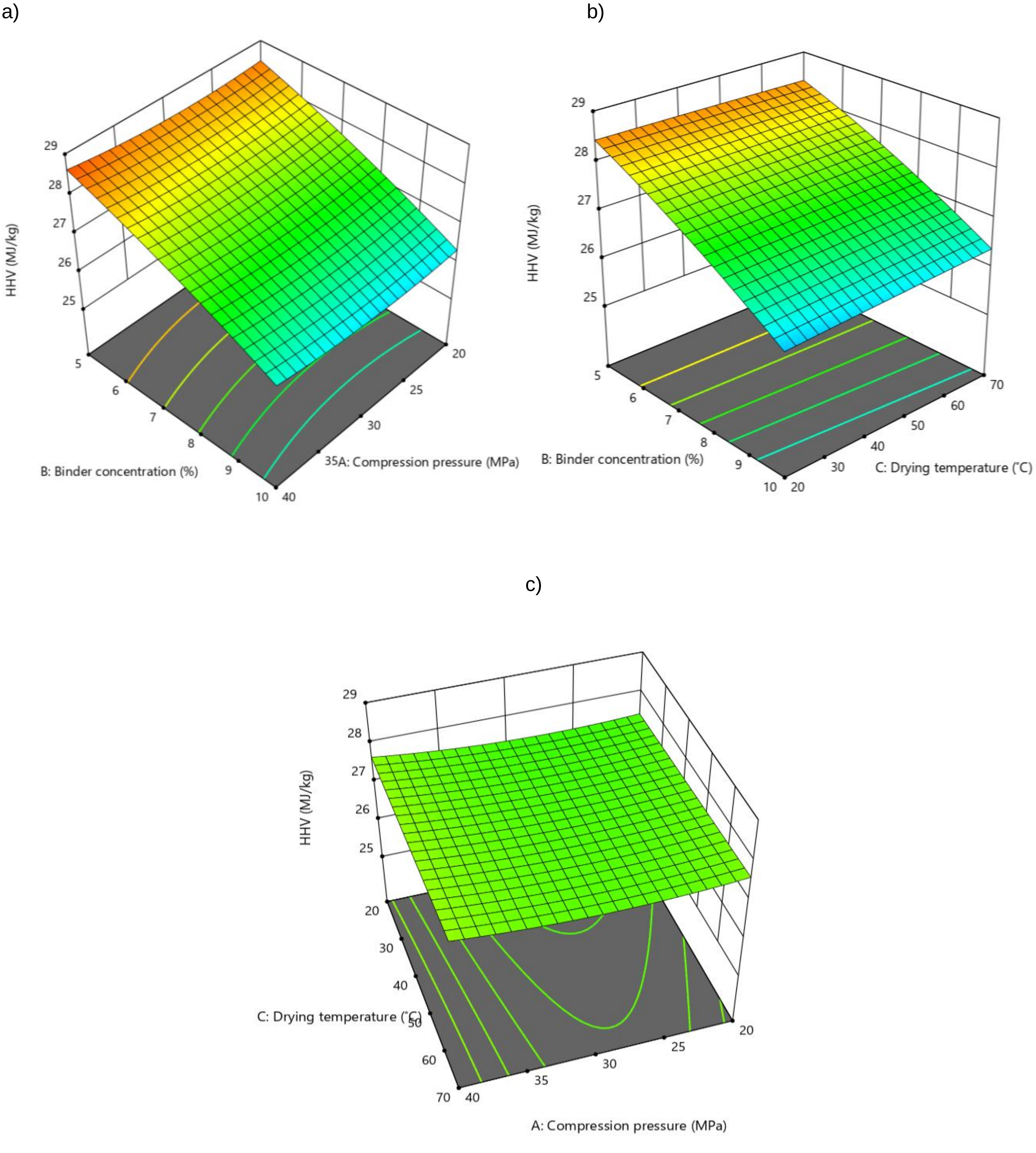


Figure 4.1: 3-D Response surface plot indicating the effect of a) compression pressure & binder concentration c) compression pressure & drying temperature b) binder concentration & drying temperature on the higher heating value.

4.4.2. The effect of process variables on the compressive strength

The ANOVA results show that all the studied factors had significant effects on the compressive strength model (**Table 4.7**). The high R^2 of 0.9776 and low CV of 0.8253 shows good precision and reliability of the quadratic model. The adequacy precision of 24.7474 is desirable as it is above 4, proving that the model is significant. The significant model terms for predicting compressive strength are A, B, AB, A^2. Therefore, the mathematical model in terms of compression pressure, binder concentration, and drying temperature is given by **Equation 4.2**.

$$\text{Compressive Strength} = 3.38152 - 0.076512\text{A} + 0.035568\text{B} + 0.007050\text{AB} + 0.001664\text{A}^2$$

Equation 4.2

Table 4.7: ANOVA and fit stats summary for compressive strength.

Factor	P-value	F value	Effect	Fit stats
Compression pressure (A)	0.0001	351.04	**Significant**	R^2=0.9776
Binder concentration (B)	0.0001	50.61	**Significant**	Adjusted R^2=0.9574
Drying temperature (C)	0.4873	0.5201	Insignificant	CV%=0.8253
AB	0.0108			Adeq precison=24.7474
AC	0.6518			
BC	0.3033			

4.4.2.1. Interactions between process variables on the compressive strength

The interaction of compression pressure from 20 to 40 MPa and binder concentration from 5 to 10% at a constant drying temperature of 45°C are shown in **Figure 4.2. a)**. There was a significant increase in the compressive strength as the compression pressure and binder concentration are increased. The figure revealed that there are significant effects between the compression pressure and binder concentration on the compressive strength. This is further supported by the ANOVA (P=0.0108) in **Table 4.7** and validates the existence of optimum conditions for compressive strength and binder concentration for maximum compressive strength. **Figure 4.2. b)** indicates the effects of compaction pressure from 20 to 40 MPa and drying temperature from 20 to 70°C on the compressive strength at a constant binder concentration of 7.5%, but there was no interaction between the variables. This can be attributed to the variables not meeting the significance test (p=0.6518) by ANOVA in **Table 4.7**. Similarly, the interaction between binder concentration from 5 to 10% and the drying temperature 20 to 70°C, held at 30 MPa compression pressure shown in **Figure 4.1. c)** was insignificant. The consistency is also observed in their individual effects on the compressive strength which did not meet the significance (p>0.05) as well as the significance (p=0.3033) of variables interaction in **Table 4.7**.

4.4.2.2. The influence of process variables on the compressive strength

The compressive strength obtained from densification ranges from 3.45 to 6.11 N/mm^2. The effects of the briquetting process variables on the resulting compressive strength are illustrated in the 3-D surface plots shown in **Figure 4.4** and the correlation is linked to the ANOVA results on the individual factors in **Table 4.7**, where only compression pressure and binder concentration show a statistically significant effect on the compressive strength, owing to the p-value of < 0.0001 and F-value of 351.04 for compression pressure, a p-value of <0.0001 and F-value of 50.61 for binder concentration, and p-value of 0.4873 and F-value of 0.5201 for drying temperature. The compression pressure on the compressive strength shows a significant effect, an increase in compression pressure from 20 to 40 MPa increases the compressive strength from 3.45-6.11 N/mm^2 (**Figure 4.4**). Correspondingly, binder concentration has a significant effect on the compressive strength. Particularly, increasing binder concentration increased the compressive strength as illustrated in **Figure 4.4**. The increase in compressive strength can be attributed to the fact that increasing the compressive pressure and the binder concentration create contact between surfaces which reduces the volume of the pores and all the voids within the material are filled by binder. Hence, creating stronger inter-particle bonds resulting in stable and firm solid briquettes (Helwani et al., 2018; Katimbo et al., 2014). The observation agrees with the study by Mitchual et al. (2013) on hardwood spices (*C. mildbreadii*) briquettes where the compressive strength increased from 1.30 to 12.45 N/mm^2. Similarly, Ujjinappa and Sreepathi (2018) on pongamia (Pongamia pinnata) shell briquettes where the compressive strength increases from 6.26 to 20.18 N/mm^2 with an increase in compression pressure and binder concentration. Conversely, the drying temperature showed no statistically significant effect on the compressive strength (p-value of 0.5201 and a low F-value of 0.4873) (**Table 4.7**). This could be because, in this study, the drying temperature ranged from 20-70°C within which the drying temperature could be less impactful on the compressive strength (**Figure 4.4**) and the influence of the drying temperature on the compressive strength is known to be obtained at higher temperatures (>80°C) (Tabakaev et al., 2017; Tanui et al., 2018). A similar trend on the peat briquettes showed little/no effect on the compressive strength when drying temperature is increased from 20-80°C and a decrease in compressive strength was only noticed at higher drying temperature (>80°C).

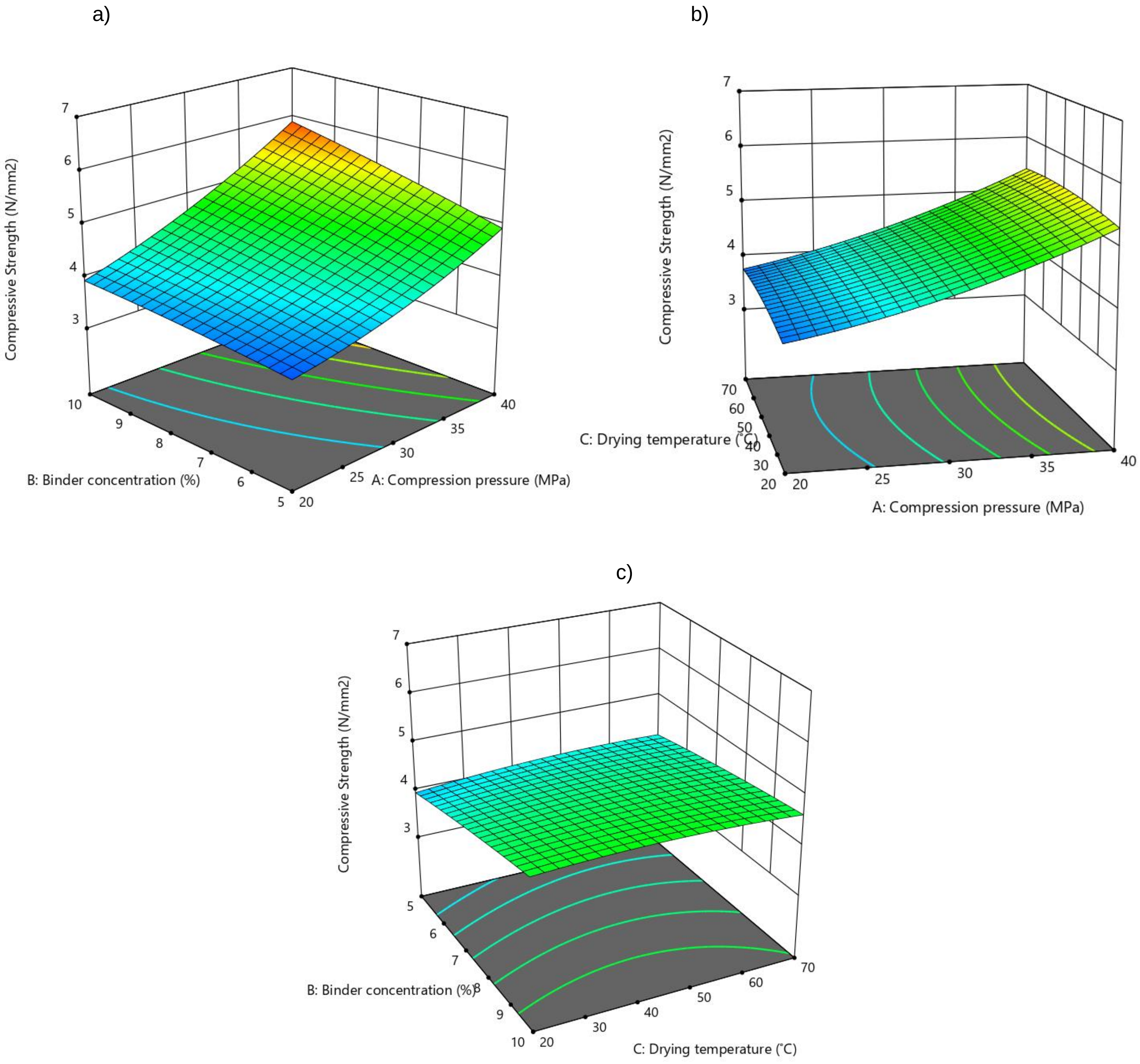


Figure 4.2: 3-D Response surface plot indicating the effect of a) compression pressure & binder concentration c) compression pressure & drying temperature b) binder concentration & drying temperature on the compressive strength.

4.4.3. The effect of process variables on density

The ANOVA results in **Table 4.8** shows the significant model terms for HHV. The results show high R^2 and low CV of 0.9252 and 2.25 respectively, which indicates good precision and reliability of the quadratic model. The adequacy precision is desirable as it is above 4 (39.4336) verifying the significance of the model. The density had a quadratic relationship with factors A, B, AB, A^2 and by removing terms that are not significant the model was reduced, and the final equation is obtained as follows:

$$\text{Density} = -155.07951 + 26.37835\text{A} + 36.89090\text{B} - 0.460000\text{AB} - 0.175344\text{A}^2 \quad \textbf{Equation 4.3}$$

Table 4.8: ANOVA and fit stats summary for density.

Factor	P-value	F value	Effect	Fit stats
Compression pressure (A)	0.0001	938.53	**Significant**	R^2=0.9814
Binder concentration (B)	0.0001	41.33	**Significant**	Adjusted R^2=0.9252
Drying temperature (C)	0.1228	2.84	Insignificant	CV%=2.25
AB	0.0471			Adq precison=39.4336
AC	0.6002			
BC	0.6002			

4.4.3.1. Interactions between process variables on the density

There is an increase in density as the compression pressure and binder concentration increases. **Figure 4-3. a)** shows interaction between compression pressure from 20 to 40 MPa and binder concentration from 5 to 10% at constant drying temperature of 45°C for density. The figure shows that the relationship between the two variables is linear and directly proportional to the density. Consequently, the interaction of the variables was significant as validated by the ANOVA (P=0.0471) in **Table 4-8**. Their individual significance ($p<0.05$) confirms that there exist conditions for these two variables to produce a maximum density. On the other hand, **Figure 4.3. b)** illustrates the relationship of compression pressure from 20 to 40M Pa and drying temperature from 20 to 70°C held at binder concentration of 7.5%. Although the compaction pressure showed an effect the density, the drying temperature had no effect as a result there was no interaction between the two variables. This is further validated the significance test p=0.6002(p>0.05) in **Table 4.8**. Likewise, an interaction between binder concentration and drying temperature showed no significance (**Figure 4. c)**), owing to the ANOVA p=0.05 (0.6002) in **Table 4.8**.

4.4.3.2. The influence of process variables on the density

The density obtained through the densification process ranged from 420 to 788 kg/m^3. **Figure 4.5** shows the 3D surface plot of the effects of compression pressure, binder concentration, and drying temperature on the density. **Table 4.8** results show that compression pressure is the most effective factor on the density of briquettes as indicated by the larger F-value of 938.53 and smaller p-value of <0.0001 followed by binder concentration (F-value of 41.33 and p-value of <0.0001). From **Figure 4.5** the density shows a significant increase when compression pressure increased from 20 to 40 MPa. Consequently, increasing the compression pressure causes particles of the material to be closely packed due to void ratio reduction and deformation of particles resulting in increased density (Mitchual et al., 2013; Tarasov et al., 2012). Also, the density results with an increase in compression pressure from this study are consistent with findings by Mitchual et al. (2013) that the densities from compression pressure of 10-50 MPa ranged from 386 to 658 kg/m^{3,} respectively. Furthermore, the binder concentration indicated an influence in the density of the briquettes. As indicated in **Figure 4.5** the density increases with increased binder concentration from 5 to 10%. The increment of density when binder concentration is increased can be explained by the addition of an ever-rising amount of higher-density binder than the actual material (Tanui et al. 2018; Tarasov et al., 2012). Ujjinappa and Sreepathi (2018) and Zubairu and Gana (2014) also observed an increment in density from 947 to 1023 kg/m^3 on hardwood spices (C. *mildbreadii*) briquettes and from 358.3 to 425.7 kg/m3 respectively on con-cobs briquettes when binder concentration was increased from 10-30%. On the contrary, in this study, the drying temperature shows no statistically significant effect on the density with a very low F-value of 2.84 and a p-value greater than 0.005 (0.1228) (**Table 4.8**). **Figure 4.5. c)** shows that the drying temperature increments had little/no effect on the density. Studies by Lela et al. (2016) and Tanui et al. (2018) also observed no statistically significant effect on the density when the drying temperature was increased from 22.5 to 100°C on briquettes from and sawdust and eucalyptus.

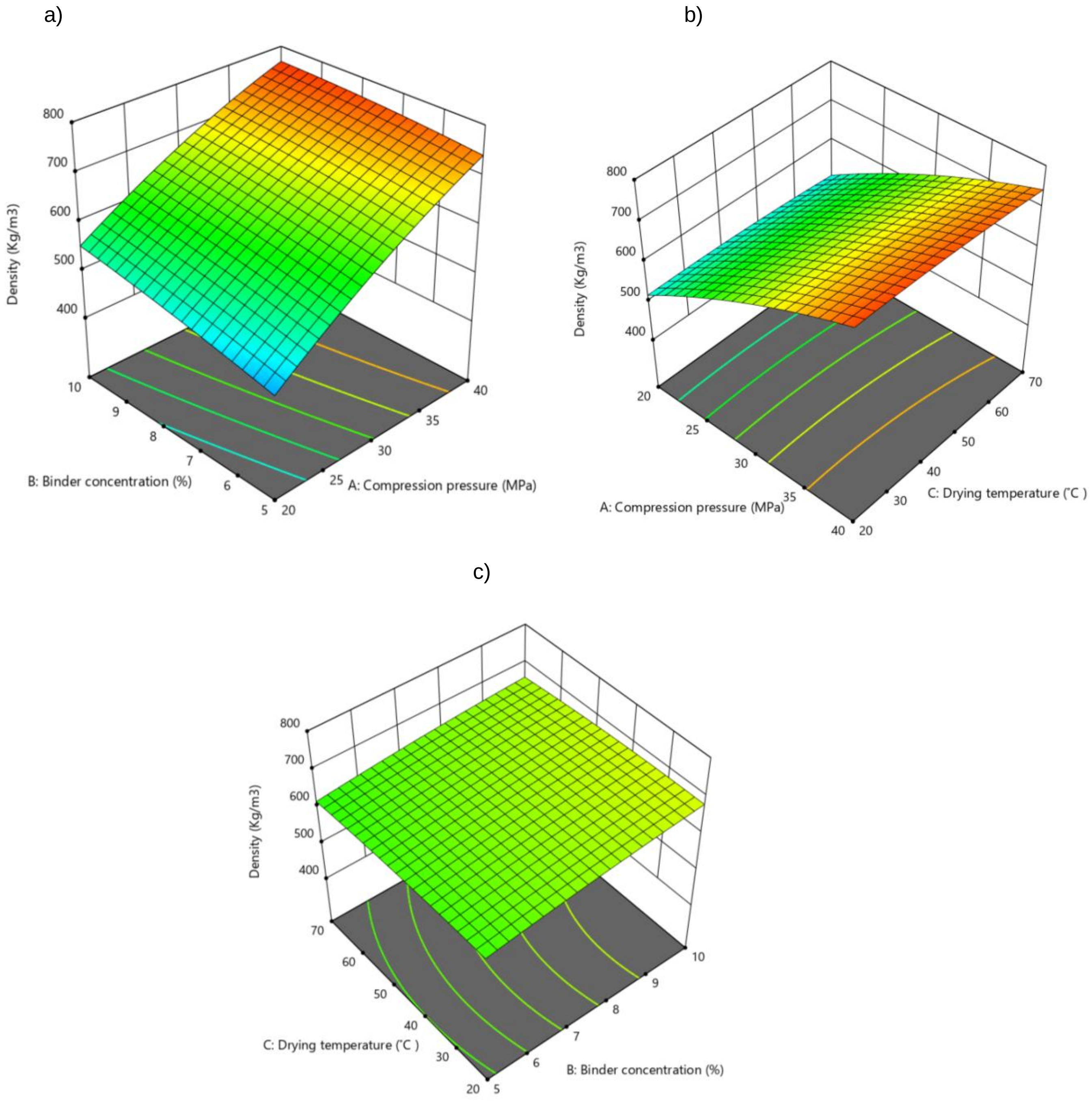


Figure 4.3*:* 3-D Response surface plot indicating the effect of a) compression pressure & binder concentration c) compression pressure & drying temperature b) binder concentration & drying temperature on the density.

4.4.4. The effect of process variables on durability

All the studied factors had a significant effect on the durability as indicated in **Table 4.9**. A high R^2 of 0.9831 and a low CV of 0.1864 validated the quadratic model's reliability and precision. Also, the model was confirmed with a desirable adeq precision of 27.5857. The factors A, B, C, AB, and BC were significant model terms for durability. Therefore, the mathematical model for the durability in terms of compression pressure, binder concentration, and drying temperature is represented by **Equation 4.4**.

$$\mathrm{Durability} = 98.63656 + 0.031501\mathrm{A} - 0.750731\mathrm{B} + 0.013729 + 0.013000\mathrm{AB} + 0.002400\mathrm{BC}$$

Equation 4.4

Table 4.9: ANOVA and fit stats summary for durability.

Factor	P-value	F value	Effect	Fit stats
Compression pressure (A)	0.0001	387.19	**Significant**	R^2=0.9831
Binder concentration (B)	0.0001	97.93	**Significant**	Adjusted R^2=0.9678
Drying temperature (C)	0.0049	12.91	**Significant**	CV%=0.18645
AB	0.0003			Adq precison=27.5857
AC	0.4279			
BC	0.0329			

4.4.4.1. Interactions between process variables on the durability

The interaction between the compaction pressure and drying temperature is significant $p>0.05$ (0.0003) confirmed by the ANOVA in **Table 4.9**. The 3-D surface plot shown in **Figure 4.4. a)** shows the interaction of compaction pressure from 20 to 40 MPa and binder concentration from 5 to 10% on the durability at a constant drying temperature of 45°C. There is a linear increase on the durability when the compression pressure and binder concentration is increased and its individual significance $p<0.05$ further confirms and the Equation 4-4 represents that. Similarly, there is an interaction between binder concentration and drying temperature on the durability from 5 to 10% and 20 to 70°C respectively, validated by the $p<0.05$ (0.0329) in **Table 4.9**. Noticeably, **Figure 4.4. b)** shows an increase on the durability when binder concentration increases while increasing the drying temperature decreases the durability. This implies that keeping the temperatures up to 70°C reduces the chance of maximising the durability using the set conditions. The results in **Table 4.9** and **Figure 4.4. c)** imply that there is no significant interaction between the compaction pressure from 20 to 40 MPa and drying temperature from on the durability at a constant binder concentration of 7.5%, owing to its $p>0.05$ (0.4279).

4.4.4.2. The influence of process variables on the durability

The effects of compression pressure, binder concentration, and drying temperature are shown in the 3D surface plots illustrated in **Figure 4.6**. **Table 4.9** represents the ANOVA results for density. The ANOVA results in the table show that all three factors have a significant effect on the durability of briquettes which is validated by their p-values that are below 0.05 and larger F-values (**Table 4.9**). From **Figure 4.6** it can be observed that increasing the compression pressure from 20 to 40 MPa increases the durability of briquettes from 97-100%. It is attributed to the fact that high pressure (>10 MPa) causes particles to be close together and can improve the bonding forces in the material (Tabakaev et al., 2017; Tanui et al., 2018). This trend is consistent with the study by Tarasov et al. (2012) and Jezerska et al. (2014) that durability increases with increasing pressure. They observed a durability increase on native wood and rice straw briquettes from 93.6 to 98% and 58 to 98.2% respectively when the pressure is increased. Similarly, the binder concentration indicated an influence on the durability of the briquettes. As seen in **Figure 4.6** the durability increases with increasing binder concentration (5 to 10%). This attributed to the fact increasing the binder concentration increases the chances of the inter-particles to be more bonded together to form a solid and stable briquette that can handle storage and transportation (Sotannde et al., 2009). Jezerska et al. (2014) observed the durability increasing from 70-99.2% when the starch binder was increased from 5 to 20% on spruce sawdust briquettes. Furthermore, it can be seen that the drying temperature also had a significant influence on the durability of the briquettes. Increasing the drying temperature from 20 to 70°C decreased the durability to 97%. The decrease in durability could be explained by the fact that higher drying temperatures result in rapid release of evaporating moisture and cracks forming in the surface of the briquettes making the briquettes too dry and increasing fine particles to fall of (Tabakaev et al., 2017). The results are consistent with the study by Said et al., (2015b) on rice straw briquettes where the durability reached up to 98.20% when the temperature was kept at <50°C, this confirms that strong durable briquettes are better achieved at much lower temperatures.

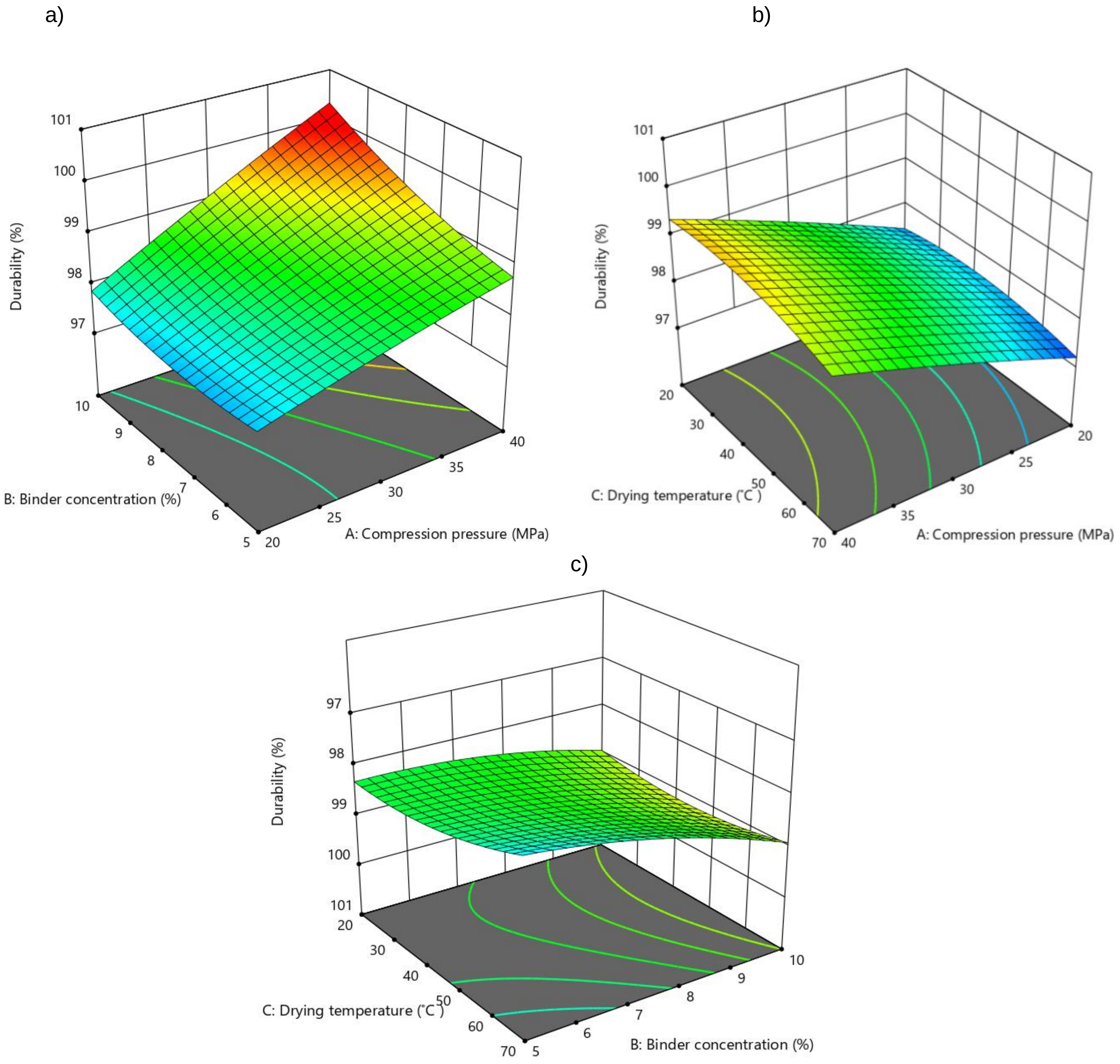


Figure 4.4: 3-D Response surface plot indicating the effect of a) compression pressure & binder concentration c) compression pressure & drying temperature b) binder concentration & drying temperature on the durability.

4.4.5. Optimisation and validation

According to the experimental results obtained by the response surface method, optimisation of briquetting process parameters on CCS briquettes was successfully performed and the average optimum briquetting conditions were suggested as follows: compression pressure (40MPa), binder concentration (8.74%) and drying temperature (21.6°C). At these conditions, the HHV, compressive strength, density, and durability as predicted by the respective developed models are 30 MJ/kg, 5.76 N/mm^2, 781.11 m^3/kg, and 98.62% respectively.

The reliability of the developed models was also verified by preparing CCS briquettes under the suggested optimum briquetting conditions. These conditions were assessed for HHV, compressive strength, density, and durability, and the mean values were found to be 27.32 MJ/kg, 5.48 N/mm^2, 770.40 m^3/kg, and 98.87 % respectively. These were compared with the predicted values from developed models. Menya et al. (2020) mentioned that for the reliability of the predictive capability of the developed models, the experimental values should lie within the range of values for 95% prediction interval (PI). The experimental values obtained are in close agreement with the predicted values, falling within the 95% prediction interval (**Table 4.10**). The experimental and predicted values were significant with considerable small standard deviations, of only 0.19, 0.23, 1.04, and 0.14 for HHV, compressive strength, density, and durability respectively which further confirms the good correlation between the experimental and predicted values.

Table 4.10: Validation experiments for the proposed models.

	Pressure (MPa)	**Binder (%)**	**Drying temp (°C)**	**HHV (MJ/kg)**	**Strength (N/mm^2)**	**Density (m^3/kg)**	**Durability (%)**
Predicted value (95% PI)	40.00	8.74	21.60	30.00	5.76	781.11	98.62
Experimental value							
Run 1	40.00	8.74	21.60	27.11	5.42	769.23	98.80
Run 2	40.00	8.74	21.60	27.48	5.73	770.75	99.03
Run 3	40.00	8.74	21.60	27.37	5.28	771.22	98.79
Mean Value	-	-	-	27.32	5.48	770.40	98.87
Std dev	-	-	-	0.19	0.23	1.04	0.14

4.5. Characterisation of briquettes

The CCS briquettes produced from optimised conditions were assessed for proximate analysis and burning characteristics. The burning characteristics were based on the time it took to boil 1L of water and the time it took to extinguish (burn into ashes). The results are shown in **Table 4.11**.

Table 4.11: Proximate analysis and burning characteristics results.

Experimental values	**Time taken to (min)**	**Proximate analysis (wt. %)**			
	Boil	Burn to ashes	Volatile matter	Fixed carbon	Ash content
Run 1	13:11	50:02	27.17	55.53	10.15
Run 1	12:02	55:10	27.33	55.67	10.15
Mean values	12:57	52:36	27.25	55.6	10.15

4.5.1. Proximate analysis

From the proximate analysis, the average volatile matter of optimised briquettes was found to be 27.25 wt. %. The addition of the binder increased the volatile matter (from 21.19 to 27.25) in comparison with the biochar represented in **Table 4.4**. The increase in volatile matter reduced the fixed carbon to 55.6 wt. %. These results agree with the values reported in the literature by Tabakaev et al. (2017) and Helwani et al. (2018) where the volatile matter for carbonised peat and empty fruit brunches decreased from 23.2 to 19.4% and 24.16 to 21.48% respectively. A low (<30%) volatile matter is favourable during combustion of the biomass briquette as it will produce less/zero smoke and will serve as an environmentally friendly biofuel (Ifa et al., 2020). According to Zanella et al. (2016), starch binders have a high volatile matter (approx. 80-95 wt. %). Thus, its addition causes an increase in the volatile matter of the product. The volatile matter in this study was found to be within the range of volatile matter for carbonised biomass (<30 wt. %) (Borowski et al., 2017). The fixed carbon which was found to be 55.6% is not directly influenced by the addition of the binder but due to changes in the volatile matter and ash content (Hasan et al., 2015). Regarding the ash content, it is noticed that it has slightly decreased from 13.86 to 10.15 wt. %. This can be explained by the fact that corn starch compositions have mostly volatiles and little to no ash which may have caused a slight decrease in ash content when added during densification (Zanella et al., 2016). These results are consistent with the study by Tabakaev et al. (2017) when 5% of starch was added, the ash content decreased from 22.9 to 18.9 wt. % for carbonised peat briquettes. The ash content obtained in this study is within the recommended range (5-40 wt. %) for biomass solid fuels (Ajimotokan et al., 2019).

4.5.2. Burning characteristics

The average time it took for the 1L of water to boil and the briquettes to extinguish was found to be 12:57 and 52:56 mins, respectively (**Table 4.11**). It was observed that the briquettes were burning with a yellow/orange flame (**Figure 5.A**), no sparks were observed, there was no smell and there was no/little smoke during burning. The results obtained in this study (**Table 4.11**) for the average time for briquettes to extinguish were higher than some values reported in the literature on carbonised biomass briquettes (18 to 33.3 minutes) (Tamilvanan, 2013; Kabok et al., 2018) but were consistent with the ones (25.4 to 68 minutes) reported by (Onchieku et al., 2012) and (Waweru & Chirchir, 2017). Briquettes are considered better with longer burning times, which is related to higher density briquettes (~>600 m^3/kg) and shapes that increase airflow rate and reduce the packing factor (Kabok et al., 2018). The burning properties of the briquettes produced in this study show that they have better qualities to be used as energy fuels.

4.6. Chapter summary

In this chapter, the physical and chemical compositions of biochar were accessed via HHV, proximate and ultimate analysis to determine its energy content quality. The biochar produced using slow pyrolysis at 400°C had an average HHV of 28.89 MJ/kg which is an increase of 71.96% from the biomass feedstock. The results were comparable to those of other biochars produced from biomass using pyrolysis with HHV of 28.77 and 27.51 MJ/kg (Angin, 2013; Bazargan et al., 2014). The briquettes produced from optimised conditions represented in **Table 4.10** shows that the HHV is comparable to that of South African bituminous A grade coal used for domestic and industrial purposes (24.5-33 MJ/kg) (Steyn & Minnitt, 2010; IGC GIFT, 2016; John Thompson, 2019). To maximise the production of high-quality CCS briquettes in terms of energy contents while obtaining high strength and density, the effects of compaction pressure, binder concentration, and the drying temperature were investigated. The results showed that the HHV (25.5-28.81 MJ/kg) of the briquettes were greatly influenced by the binder concentration ($p<0.05$) while the compressive strength (3.45-6.11 N/mm^2) and density (420-788 kg/m^3) of the briquettes were both influenced by compaction pressure and binder concentration ($p<0.05$). Lastly, the durability (97-100%) of the briquettes shows it was influenced by all 3 factors ($p<0.05$). Also, the compressive strength, density, and durability of produced briquettes shown in **Table 4.10** are comparable to that of domestic charred bio-briquettes (Sánchez et al., 2014; Borowski et al., 2017). In conclusion, the HHV, strength, density, and durability of charred briquettes were successfully optimised. Also, considering the assessed proximate analysis and burning characteristics in **Table 4-10** CCS briquettes have a great potential to be used as heating and cooking solid fuel when the optimum conditions are carefully studied.

CHAPTER FIVE

5. PROCESS DEVELOPMENT AND ECONOMIC ANALYSIS

5.1. Introduction

Briquettes are expected to relieve the ever-increasing South Africa's energy demands. Thus, a detailed and critical techno-economic evaluation of carbonised biomass briquette production plant is essential. To determine the prospect of developing an efficient production process, process development and economic assessment are necessary. There is a dearth in the literature on the process modelling and economic assessment of carbonised biomass, and more specifically, carbonised corn-stover (CCS). This chapter aims to conduct a techno-economic analysis of a briquette production plant in South Africa. The experimental optimum conditions for biochar and briquette production from corn-stover (CS) detailed in chapter 4 were used to develop a process design and economic evaluation of the scale-up plant. Process development was demonstrated using a process flow diagram (PFD) for the slow pyrolysis section and SuperPro Designer® for the briquette production section. The equipment prices, sizes and data information for the process design and simulations were obtained from Alibaba group® and literature data. The process' economic evaluation was based on the discounted payback period (DPBP), net present value (NPV) and discounted cash flow rate of return (DCFROR).

5.2. Process development

5.2.1. Design overview

In this study, slow pyrolysis was used to convert biomass to biochar and subsequently densify into briquettes. The considered main operation production capacity of the process was 550 kg/h in a semi-batch process. This is an average production capacity for small-scale briquetting plants (Felfi et al., 2005; Sahoo et al., 2019). South Africa is a developing country and production of carbonised biomass is still in its infancy stage, hence, a lower production rate and batch or semi-batch is attractive.

5.2.2. Raw material

Corn-stover was used as the feedstock in this study owing to the fact that maize residue in is readily available in South Africa (Batidzirai et al. 2016). The CS moisture content of ~10 wt. %, was chosen as it is the conventionally adopted composition in the pyrolysis of agricultural residues for both operational and conceptual processes (Zanella et al., 2016).

Another raw material used in this study, corn-starch, was chosen as a binder because it is produced locally in South Africa by different Agric-processing plants and is therefore affordable, relatively abundant, and available as waste as well. Also, starch has been shown to have good binding properties for carbonised biomass (Zanella et al., 2016; Borowski et al., 2017)

5.2.3. Plant processing time

Conventionally, briquetting plants are operated 8-16 hours a day for 300 days a year (Islam et al., 2003; Felfi et al., 2005; Sahoo et al., 2019). In this, study an operating time of 10 hours a day for 300 days was adopted.

5.2.4. Targeted products

Briquette production is in two parts, namely slow pyrolysis, and the briquetting sections. In the slow pyrolysis section, the main targeted product is biochar with a production yield of ~46.11 wt. % and an average heating value of 27.32 MJ/kg adapted from the experimental results (Chapter 4). This production yield and HHV is expected for a slow pyrolysis process when targeting biochar as the main product (Elkhalifa et al., 2019; Park et al., 2014). In the briquetting section, the targeted product is densified biochar (briquettes) comparable to conventional charcoal or coal in terms of quality but with better greenhouse gas emissions.

5.2.5. Location

In this study, it is assumed that the plant will be in one of the top 3 maize producers provinces in South Africa, namely Mpumalanga, Free state, and Northern Cape (Galal, 2020). It is assumed that the closeness of the plant to the farms and ready availability of the feedstock will ensure sustainability.

5.2.6. Development of process flow diagram (Base case)

The research findings in this study and information from slow pyrolysis and briquetting plants were used to develop the process flow diagrams (PFDs). PFDs are known to show the flow plant processes and the relationships between unit equipment. In this study, the flowsheet diagram contains the slow pyrolysis plant which produces biochar as its main product as well as bio-oil and biogas as by-products. The general production of carbonised briquettes is assumed to be done using electricity from the grid and is considered the base case for this study. It also comprises the briquetting plant which densifies the biochar from pyrolysis into briquettes (**Figure 5.1**).

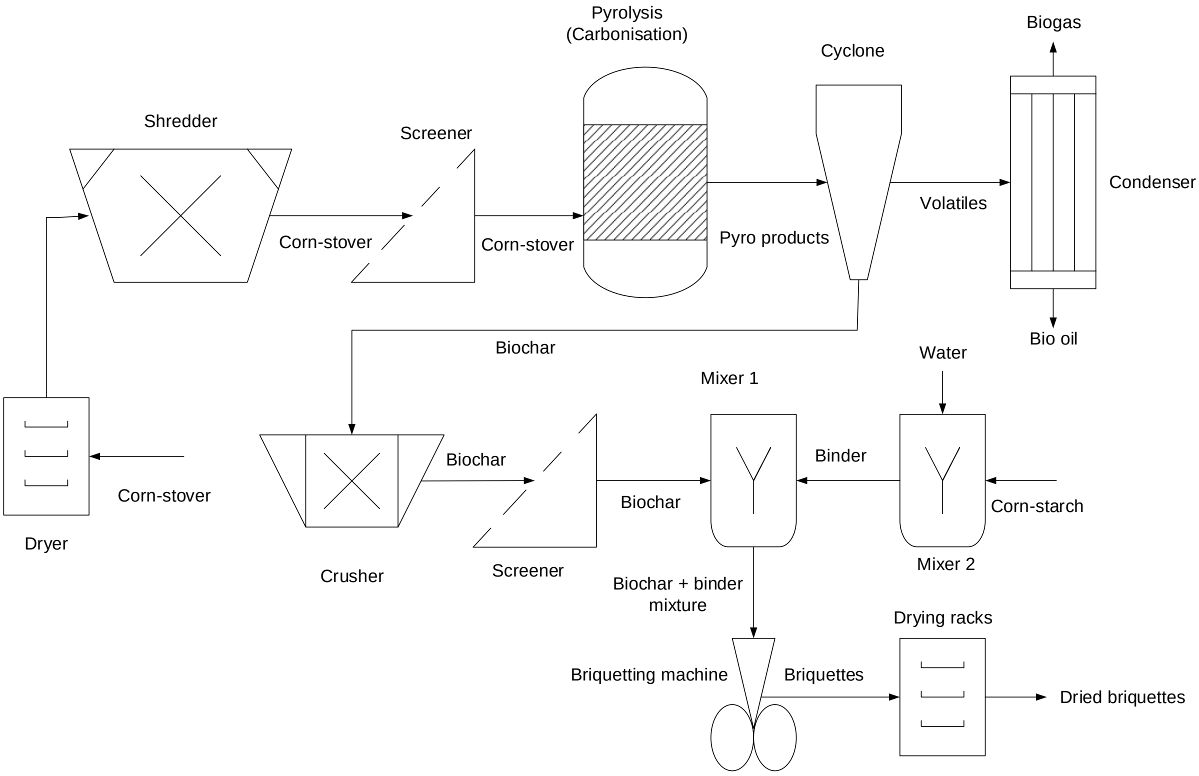


Figure 5.1: PFD for slow pyrolysis and briquetting production system.

5.2.7. Slow pyrolysis (Carbonisation) section

As a conventional hypothesis, the base case scenario proposes a scale-up plant that attains the same performance as the pyrolysis pilot unit in terms of quality discussed in chapter 4, thus discarding the beneficial scale effect. The base case scenario was adapted from previous studies (Felfi et al., 2005; Severy et al., 2018; Sahoo et al., 2019). The pyrolysis section consists of a shredder, dryer, and pyrolysis reactor system. The PFD for the base case of the slow pyrolysis section is shown in **Figure 5.2**.

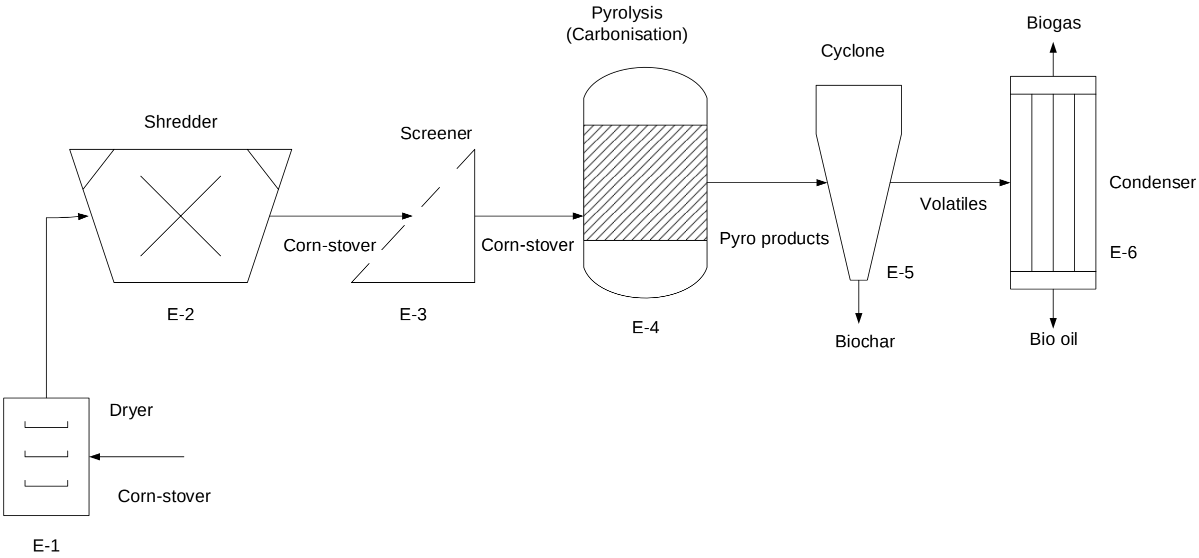


Figure 5.2: PFD for pyrolysis section.

5.2.7.1. Selection of operating conditions

A dryer (E-1) was used to dehydrate CS at 80-120°C to achieve a moisture content of less than 10 wt. %. In the shredder (E-2), CS was pulverised and then sifted into a particle size of ~4 mm using a screener (E-3) (**Figure 5.2**). CS was then carbonised in the pyrolysis reactor (E-4) at temperature and pressure of 400°C and 100 kPa respectively, to produce high-quality biochar with bio-oil and gas as by-products. The reactor operating conditions chosen are based on experimental data from the current study (Chapter 4). The discharge from the reactor was then cooled down for 2 hours. The biochar product was collected in an airtight container (E-5) while the tar-loaded vapours were collected separately (E-6) (**Figure 5.2**).

5.2.7.2. Mass balance and yield product distribution results

The reactor product distribution considered for the developed process was based on yields from the experimental data in this study as well as modification from the study by Sahoo et al. (2019). Studies by Manyuchi et al. (2016) and Rizzo et al. (2019) were referred to, so as to provide necessary additional information. The input-output structure in **Figure 5.3** shows the overall process streams.

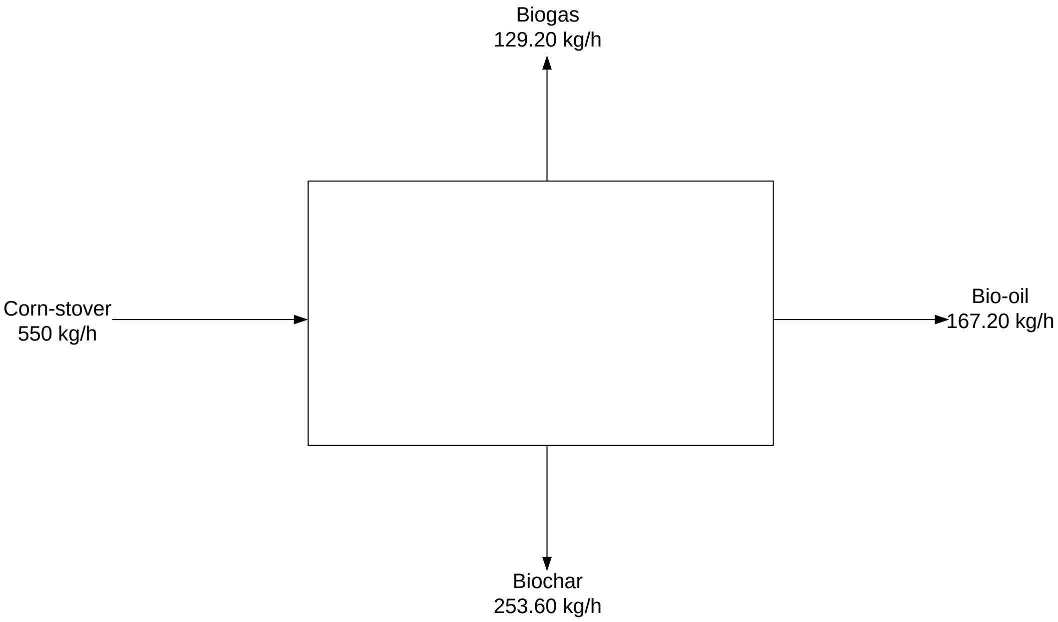


Figure 5.3: Mass balance of the pyrolysis section.

The mass balance and yield distribution of the pyrolysis reactor is shown in **Table 5.1**.

Table 5.1: Mass balance of the pyrolysis section.

Stream No	**Corn-stover**	**Char**	**Oil**	**Gas**
Yield (wt. %)	-	46.11	30.4	23.49
Mass flow (kg/h)	550	253.61	167.2	129.20
Temperature (˚C)	25	400	40	-
Pressure (kPa)	100	100	100	100

5.2.7.3. Energy requirements

In this study, the pyrolysis section has not been modelled in SuperPro Designer® but developed by process diagram for its mass balances as illustrated in section 5.2.7.2. The power requirements of each unit equipment which is based on the scale and equipment capacity have been considered for economic evaluation in section 5.3. The power requirements of each pyrolysis section equipment are shown in **Table 5.2**.

Table 5.2: Power requirements for the pyrolysis section.

Equipment	Power required (kW)	Reference
Dryer	15	Alibaba Groupr®
Shredder	15	Alibaba Groupr®
Pyrolysis system	50	Boston Machinery (2019)
Total	80	

5.2.8. Briquetting section

The purpose of the briquetting section in this study is to densify the CCS into briquettes. It is assumed that the briquetting section will operate at optimum conditions determined in this study (Chapter 4). The equipment that makes the briquetting section is a grinder, screener, two mixers, briquetting machine, and drying rack. The PFD of the briquetting section is shown in **Figure 5.4**.

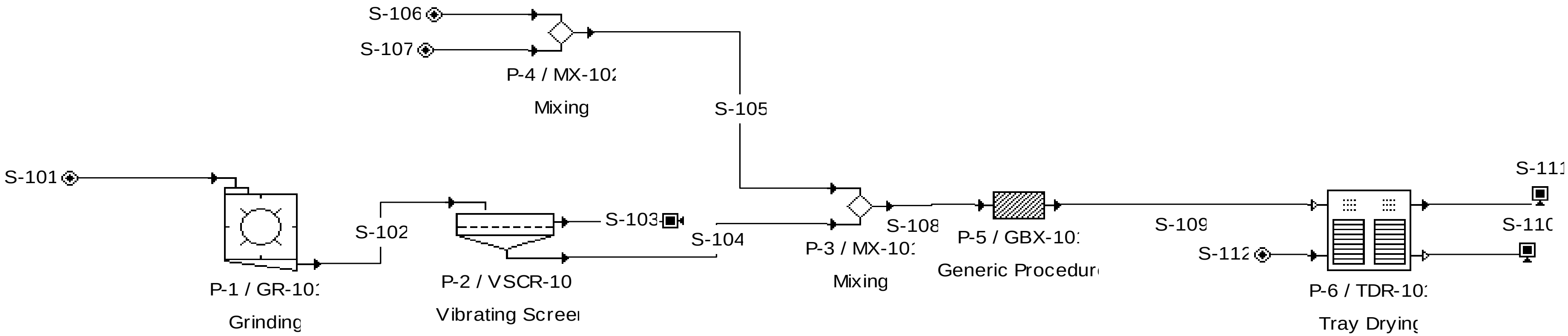


Figure 5.4:PFD for briquetting section.

In this study, SuperPro Designer® was used to model the proposed briquetting process. It has been widely used for the simulation of simple pharmaceutical, biotech, Chemical engineering, and agricultural chemical processes (Mocke, 2013; Petrides et al., 2014). It was found suitable to model briquetting processes due to its ease to modify a wide range of equipment and enables the user to model batch processes in greater detail.

5.2.8.1. Selection of operating conditions

The briquetting section begins with grinding of the material, biochar is crushed with a grinding machine (P-1/GR-101) and screened using the screener (P-4/MX-102) to a particle size less than 2 mm, which is the preferable size for carbonised briquettes (Wilson et al., 2016). A mixer (P-2/VSCR-101) heated to approximately 80°C was used to activate and form a binder using water and corn starch. In another mixer (P-3/MX-101) the starch binder and biochar are mixed (3:2 [binder: char]). Moreover, a briquetting machine (P-5/GBX-101) at a pressure of 40 MPa (optimum condition obtained in Chapter 4) was used to densify the prepared biochar and binder mixture to form biochar briquettes. The briquettes were placed in a drying rack (P-6/TDR-101) and sun-dried for at least 24 hours or at 30°C in a drier. The briquettes were then packaged. The design basis and operation conditions for each piece of equipment in this section are summarised in **Table 5.3**.

Table 5.3: Process simulation design basis and operation conditions for the briquetting section.

Equipment	Operation	Temperature (˚C)	Pressure (MPa)	Conditions	Unit ID
Crusher	Crushing	20	0.1		P-1
Screener	Screening	20	0.1	Particle size of less <2 mm	P-2
Mixer 1	Mixing	20	0.1	Binder concentration: 8.74%	P-3
Mixer 2	Mixing	80	0.1	Ratio of 3:2 Binder: Char)	P-4
Briquetting machine	Densification	20	40	Holding time: 30 seconds	P-5
Drying racks	Drying	21.6	0.1	Drying for 24 hours at 20	P-6

For the simulation in SuperPro Designer®, corn starch, biochar and briquettes were manually defined and were regarded as non-conventional components in this study, as they are not originally defined in the software. Also, briquetting machine was regarded as non-conventional equipment which was selected as a generic box. Recipe operation conditions were used.

5.2.8.2. Mass and energy outputs

After simulation of the briquetting process, a stream summary was generated. The composition of all inlet and outlet streams is presented in **Table 5.4**. The capacity of all process equipment is suggested and supported by quotations of required capacity from individual manufacturers for ease of cost.

Table 5.4: Mass balance of stream S-101 to S-105 for the briquetting section.

Stream No	**S-101**	**S-102**	**S-103**	**S-104**	**S-105**
Total mass (kg/h)	253.61	253.61	2.54	251.07	418.81
Temperature (°C)	25.00	25.00	25.00	25.00	25.00
Pressure (MPa)	0.10	0.10	0.10	0.10	0.10
Total Volume (L/h)	254.96	254.96	2.55	252.41	421.04
Biochar	253.61	253.61	2.54	251.07	0.00
Starch	-	-	-	-	38.40
Water	-	-	-	-	380.41

Table 5.5: Mass balance of stream S-106 to S-110 for the briquetting section.

Stream No	**S-106**	**S-107**	**S-108**	**S-109**	**S-110**
Total mass (kg/h)	38.40	380.41	669.88	669.88	669.88
Temperature (°C)	25.00	25.00	25.00	25.00	25.00
Pressure (MPa)	0.10	0.10	0.10	0.10	0.10
Total Volume (L/h)	38.60	382.44	673.45	673.45	673.45
Biochar	-	-	251.07	251.07	251.07
Starch	38.40	-	38.40	38.40	38.40
Water	-	380.41	380.41	380.41	380.41

Table 5.6: Energy requirements for briquetting equipment.

Equipment	Power Required (kW)	References
Crusher	11	Alibaba Group®
Vibrating screen	0.5	Alibaba Group®
Mixer 1	20	Alibaba Group®
Mixer 2	11	Alibaba Group®
Briquetting machine	17	Alibaba Group®
Total	59.5	

5.2.9. Addition of gasifier-based generator (GBG) (Scenario 2)

The base case scenario of briquette production suggests the use of electricity from the grid to produce briquettes. However, a second scenario based on energy-saving evaluation suggests addition of a gasifier-based generator that will use corn cob as feedstock is proposed to supplement electricity by generating electricity from biomass. This case which is adapted from the study by Sahoo et al. (2019) does not change the PFD system of the process but will aid in evaluating energy saving costs.

Table 5.7: Energy requirements for gasifier-based generator.

Equipment	Operation	Output power (kW)	Mass flow (kg/h)	Reference
Gasifier-based generator	Generates electricity	80	90	Alibaba Groupr®

5.3. Discussion

5.3.1. Pyrolysis section

The 550 kg/h of CS being fed to the pyrolysis reactor yielded 46.11% (253.61 kg/h) of biochar. This leaves the bio-oil and biogas to a mass and yield of 167.2 kg/h (30.4%) and 129.20 kg/h (23.49%) respectively. The results show that at 400°C biochar had the highest yield, and this can be attributed to lower heating rates and lower to moderate temperatures (400-450°C) caused by secondary cracking reactions (Azuara et al., 2016). Previous studies showed similar results where they reported higher biochar yields of 31 to 52% around 400°C for corn-stover, rice husk & sawdust, co-biomass, and coconut shell (Capunitan & Capareda, 2012; Waghmare et al., 2016; Hanif et al., 2016: Sarkar & Wang, 2020). These wide range of biochar yield can be explained by the fact that biochar production is not only influenced by the type of feedstock but is also influenced by the particle size of the biomass, heating rate, lignin content and ash content (Demirbas, 2004).

In relation to energy usage in the pyrolysis section, the pyrolysis reactor system accounts for 62.5% of the overall pyrolysis process power requirements. This is due to the energy intensity of pyrolysing the biomass at a temperature of 400°C and which is expected to increase even further if higher temperatures are used. A similar trend was observed in a study by Sahoo et al. (2019) on the production of biochar to produce briquettes from woodchips where the torrefaction section contributed the most energy usage of about 90% overall. Therefore, if biochar is produced at optimum conditions targeted at the desired final product quality, energy usage can be reduced. In doing so, using higher temperatures could be avoided. Moreover, it is necessary to carefully design the pyrolysis system so to minimise the requirements for the external heat supply and effectively operate the pyrolysis process (Lee et al., 2013). Alternatively, the by-products of the pyrolysis system could be utilised to produce energy within the system (Pawar et al., 2020)

5.3.2. Briquetting section

A total mass of 253.61 kg/h of biochar, 380 kg/h of water and 38.40 kg/h of corn-starch were used to form a total mass of 669.88 kg/h of wet briquettes. As these briquettes were completely dried, the total mass of the briquettes was ~ 300 kg/h. It was observed that the total mass of the briquettes reduced by 44.78% from wet briquettes to dry briquettes. It is assumed that drying the briquettes has the potential of reducing the moisture content from 10% to almost 5 to 0% which affects the final mass of the briquettes (Felfli et al., 2005). Moreover, Previous studies by Sahoo et al. (2019) on the pyrolysis and briquetting of woodchips reported slightly different results for biomass pyrolysed at 400 °C. A mass balance of 768 kg/h of biochar produced a total mass of briquettes of 700 kg/h. The authors attributed the cause to the decrease in the moisture content from 10 to 0.6%. The variation in these two studies can be due to the different binding materials used to produce the briquettes as well the different types of feedstocks used to cause the disparity in the total mass balance. In this study, the corn-starch contributed to the final product of the briquettes which slightly increased the mass while all the total water content was dried out and not accounted for in the final product. In terms of energy usage of the briquetting section, mixer 1 (P-4/MX-102) accounts for 33.61% of the overall process power requirements which is attributed to the addition of the heating element responsible to activate the binder during mixing. The rest of the power requirements are distributed to the remaining equipment. It can be concluded that to reduce energy costs it is very essential to know the temperature at which the used binder activates.

5.4. Economic analysis

To perform an economic analysis, the first step required is to estimate the total capital investment (TCI) and the total manufacturing costs (TMC). These costs are associated with the day-to-day operation as well as the construction of the plant. Thereafter a profitability analysis was used to determine the viability of the plant. The methods and assumptions required to assess the economic feasibility of briquetting process are described in the next section.

5.4.1. Estimation of capital cost

The sum of the fixed capital cost (FCC) and working capital cost (WCC) is the TCI of a plant. According to Sinnot (2005), the total costs of the plant ready for the start-up is represented by the FCC which considers the total installed costs of equipment, contingencies and fees, and auxiliary facility costs. For this study, all utilities will be purchased from public local suppliers at a fixed price hence the auxiliary and facilities will not be considered. Then WCC represents the additional investment required over the FCC until income is earned when starting and operating the plant.

The approach used for TCI estimation in this study is the sum of the installed cost of all equipment of the main process which was adapted from the studies of Islam et al. (2003), Rizzo et al. (2019), and Sahoo et al. (2019). An equipment cost estimate (pyrolysis and briquetting sections) was based on the design and the quotation of individual components obtained from different manufacturers.

5.4.2. Estimation of total manufacturing costs (TMC)

The raw materials, utilities, operating labour, and the fixed capital need to be known to determine the TMC. The quantity of raw materials and utilities for determining the required variable costs for this study are shown in tables presented in section 5.2.6. The utilities in this study are water and electricity and they are purchased based on consumption. Moreover, the operating labour costs are based on 10 operating hours for 300 days and the amount of labour required was adapted from a study by Sahoo et al. (2019) which suggested two operators are needed for a small briquetting plant. The cost data assumptions for determining the TMC are shown in **Table 5.8**.

Table 5.8: Economic assumptions.

Unit	**$/ Unit**	**Reference**
Raw material		
Corn Stover ($/ton)	40	Wright et al. (2010)
Corn starch ($/ton)	45	Alibaba Groupr® (2019)
Corn cobs[a] ($/ton)	40	Brigagao et al. (2019)
Water ($/L)	0.0087	City of Cape (2019)
Product		
Briquettes ($/ton)	650	Alibaba Groupr® (2019)
Bio-oil ($/L)	0.4	Wang & Jan (2018)
Biochar ($/ton)	50	Alibaba Groupr®
Utilities		
Water ($/L)	0.0087	City of Cape (2019)
Electricity ($/kWh)	0.15	City of Cape (2019)
Labour		
Operator salary ($/Month)	388	PayScale (2019)

a- to be used for second scenario

The cost factors for estimating the manufacturing cost are estimated from equations with multiplication factors reported by Turton et al. (2013). **Table 5.9** shows a summary of the cost factors used to estimate the TMC of the briquetting plant.

Table 5.9: Cost factors from Turton et al. (2013).

Cost items	**Values for cost factors**
Direct Manufacturing cost	
Raw material	C_{RM}
Utilities	C_{UL}
Waste treatment	C_{WT}
Operating labour	C_{OL}
Direct supervisory labour	$0.18C_{OL}$
Maintenance and repairs	0.06FCC
Operating supplies	0.009FCC
Labour charges	$0.15C_{OL}$
Patents and royalties	0.03TMC
Fixed Manufacturing costs	
Depreciation	0.1FCC
Local taxes and insurances	0.032FCC
Plant overhead	0.6(1. d+1.e+1. f)
General manufacturing costs	
Administration costs	$0.15C_{OL}$
Distribution and selling cost	0.11TMC
Research and development	0.05TMC
Total Manufacturing cost = $\mathbf{1.014(C_{RM} + C_{UT} + C_{WT}) + 2.09C_{OL} + 0.023FCC + DEPC}$	

5.4.3. Estimation of revenue

The generated revenue in this study is from sales of briquettes and bio-oil. Their selling prices are based on their qualities. The briquettes selling price of $650 was based on briquette prices that have similar qualities to the one from this study (Alibaba Groupr®, 2019). The bio-oil produced will be sold without any upgrading and its selling price was adapted from a study by Wang and Jan et al. (2018) where refined bio-oil was sold at $0.55/litre, for this study the price was reduced by 15% ($0.4/litre) due to its un-upgraded quality. The selling price of each product is shown in **Table 5.8**.

5.4.4. Profitability analysis

The profitability of an investment can be assessed based on assumptions and profitability criteria after the TCI and TMC of a project have been estimated. The criteria used in this study are discounted payback period (DPBP), net present value (NPV) and discounted cash flow rate of return (DCFROR). These evaluations were conducted on a Microsoft Excel spreadsheet.

5.4.4.1. Main investment assumptions

A profitability analysis based on the discounted cash flow technique that included the project life, start-up period, depreciation method, discount rate and taxation rate was done to provide a greater view of the viability of the project over the whole project life (Seider et al., 2004). Chemical plant life projects used for profitability analysis are typically 10, 12, and 15 years (Turton et al., 2013). In this study, reasonable profitability at the minimum project life is expected since the evaluated project is a small plant hence a project life of 10 years was assumed. The plant was assumed to be constructed and start-up within 2 years. The first and second year of construction will be spread out by 60% and 40% of the total fixed capital that does not include the land. It was assumed that the WCC is 15% of the FCC. The simplest and most used depreciation method is the straight-line method. Therefore, a straight-line depreciation was assumed over the first five years after project start-up and a salvage value of zero (Seider et al., 2004; Turton et al., 2010). In this study, a taxation rate of 28% was used (South African Revenue Services, 2019). The desired discounted rate of 10% was used (Turton et al., 2013). Lastly, an average conversion rate of R15.13= 1USD (average exchange rate in 2019) for all cases was used.

5.5. Results and discussion

5.5.1. Total capital investment

The total purchased cost of the listed equipment of the base case scenario for the briquette production process is \$84 255. **Table 5.10** shows that the major contributor to the total purchased cost is the pyrolysis system at 63.74% which includes the condenser and gas tower. The high installed cost of \$53 700 for the pyrolysis system was expected and this is due to the reactor size and operating temperature which normally requires materials of construction that can resist the required temperature. The purchased cost of briquette machine was estimated to be \$10 800, and it is the second contributor at 12.82% of the total purchased cost. This can be attributed to the production rate of the briquette machine. This trend agrees with Felfli et al. (2005) and Sahoo et al. (2019) who reported the combined purchase cost of the pyrolysis system and briquette machine contributes to the total purchase cost at 89.02% and 73.43% % respectively.

Table 5.10: Total capital investment for base case.

Unit item	Purchase cost ($)
Shredder	5000
Dryer	4000
Pyrolysis system	53 700
Crusher	1105
Vibrating screen	1200
Mixer 1	2000
Mixer 2	5000
Briquetting machine	10 800
Drying racks	900
Bio-oil storage tank	550
Total purchase cost, C_P	84 255
Total bare module cost, $C_{BM\text{-}list}=3.63C_P$	305 845.65
Total installation, $C_{BM}=1.25C_{BM\text{-}list}$	382 307.06
Contingency and fee cost, $C_{FC}=0.18C_{BM}$	68 815.27
Fixed capital, $FCC=C_{BM}+C_{FC}$	451 122.33
Working Capital, WCC=0.15FCC	67 668.35
Total Capital investment TCI=FCC+WCC	518 790.68

From **Table 5.10** it can be observed that to account for all unlisted equipment, an extra 25% of all the listed bare module costs was assumed, to calculate the FCC which was estimated to be $451 122.33. Thereafter the WCC was determined to be $67 668.35 assuming 15% of the FCC. Hence, it can be concluded that the required TCI of the base case for briquette production will be $518 790.68.

5.5.2. Total manufacturing cost

Table 5.11: Total manufacturing cost.

Cost items	Manufacturing costs ($)
Direct manufacturing cost	
• Raw materials	81 064.14
• Utilities	59 268.89
• Waste treatment	0
• Operating labour	9312
• Direct supervisory labour	1676.16
• Maintenance and repairs	31 127.4
• Operating supplies	4669.12
• Labour charges	1396.8
• Patents and royalties	0
Fixed manufacturing costs	
• Depreciation	51 879.07
• Local taxes and insurances	16 601.30
• Plant overhead	5587.2
General manufacturing costs	
• Administration costs	1396.8
• Distribution and selling cost	29 037.68
Total production cost	212 099.84
Total manufacturing cost	224 149.98

The breakdown of TMC for the briquette production process is illustrated in **Figure 5.5**. The direct, fixed, and general expenses were found to constitute 64, 25 and 11% respectively. It can be observed that the direct manufacturing costs (DMC) ($188 514.14) are the highest contributor to the TMC. The high DMC is due to the high cost of raw materials and utility demand of $81 064.14 and $ 52 368.89, respectively. The high raw material and utility demand can be attributed to the amount required to drive the process. Similar results were reported by Felfli et al. (2005) who observed that raw material and utility costs contributed approximately 25 and 19% to the DMC, respectively. Whereas Wilson (2016) reported that raw material and utilities combined contributed about 23.30% in the DMC while operating supplies and labour charges consume about 66.62% combined. This could be attributed to the fact that the raw material and utilities might have been sourced for free or at a very lower cost causing the operating supplies and labour charges to be higher in DMC. Consequently, the fixed manufacturing costs (FMC) are the second contributor at $ 74 067.57 to the TMC which is largely due to local taxes and plant overhead in this study. While general manufacturing expenses (GME) are the lowest contributor to the TMC at $30 434.48 which includes administration, distribution, and selling costs. Hence, the briquette production process requires a TMC of $224 149.99. From **Table 5.11**, it can be concluded that to minimise the DMC which contributes largely to the TMC, the utility usage such as electricity and water needs to be kept as minimum as possible through careful saving because it can contribute a substantial amount of charges in the TMC (Triphathi et al., 1998).

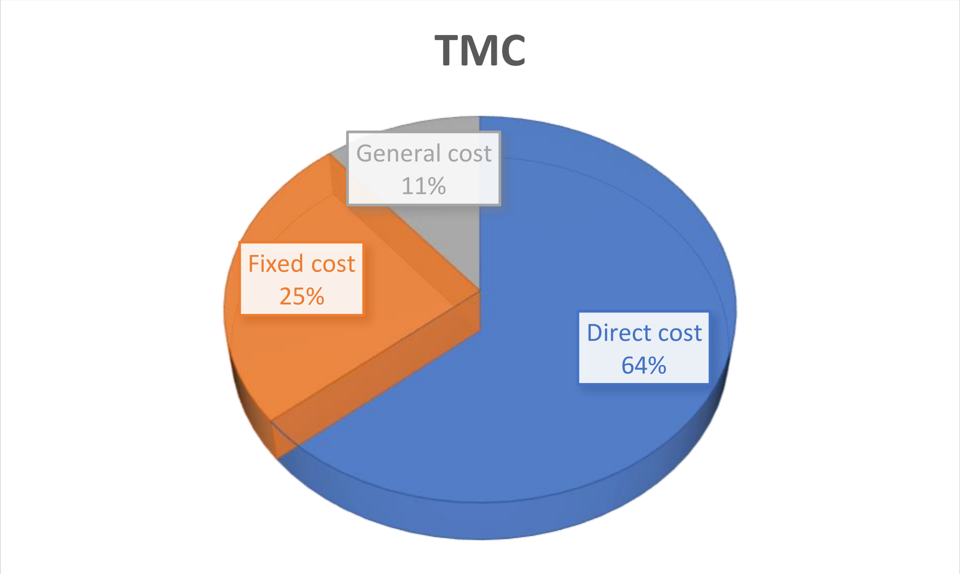


Figure 5.5: Breakdown of TMC.

5.5.3. Revenue generated

The total annual sales for the base case scenario were determined to be $685 348.69 as shown in **Table 5.12**.

Table 5.12: Generated revenue

Product	Annual revenue ($/y)
Briquette	585 028.69
Biooil	100 320
Total revenue ($)	685 348.69

The results indicate that the highest contributor to the revenue generated is the briquettes at $585 028.69 which is 85.36% of the total annual sales (**Table 5.12**). This can be attributed to its high selling price of $650/ton, which is due to the quality achieved in this study. Therefore, it can be concluded that the annual sales are dependent on the amount and quality of the briquettes produced. This can be corroborated by study reported by Felfli et al. (2005) who showed that the quality of briquettes significantly increases the revenue by 19.3% after briquettes undergo carbonisation. Also, Sahoo (2019) reported the minimum selling price of non-carbonised woodchips briquettes was $161.5/MT while the minimum selling price of the briquetted woodchips increased the revenue by 69.85% after carbonisation.

Table 5.12 and **Figure 5.6** also show that bio-oil contributes the least to the revenue stream. The total annual sales for bio-oil were found to be $100 320 which is 14.64% of the total generated revenue and that can be attributed to its low production rate and low selling price as compared to the biochar used to produce briquettes. The low production rate and quality are expected, as the main aim of the slow pyrolysis section is to produce a high volume of quality biochar (Tripathi et al., 2016).

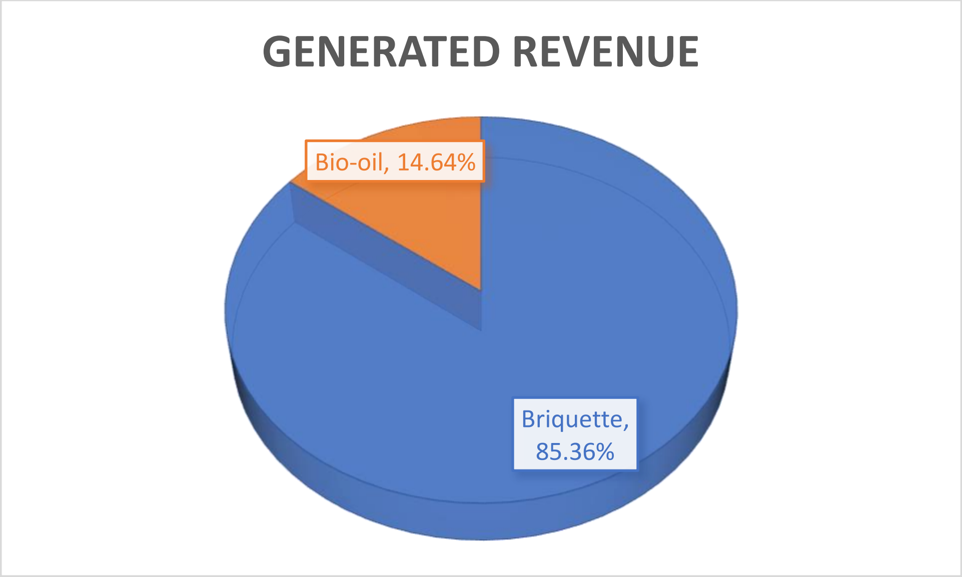


Figure 5.6: Generated revenue distribution.

5.5.4. Profitability analysis

5.5.4.1. Base case scenario analysis

The results of profitability indicators (PI) for the base case scenario for this study at a discount rate of 10% are shown in **Table 5.13** and **Figure 5.6**.

Table 5.13: Economic indicators for base case scenario.

PI	This Study	Felfli. (2005)	Ifa. (2020)	Segnar et al. (2013)
DPBP (years)	2.67	-	3.42	2.50
NPV ($)	1 612 122.34	-	611230	8693.70
DCFROR (%)	53.10	48	23.55	230

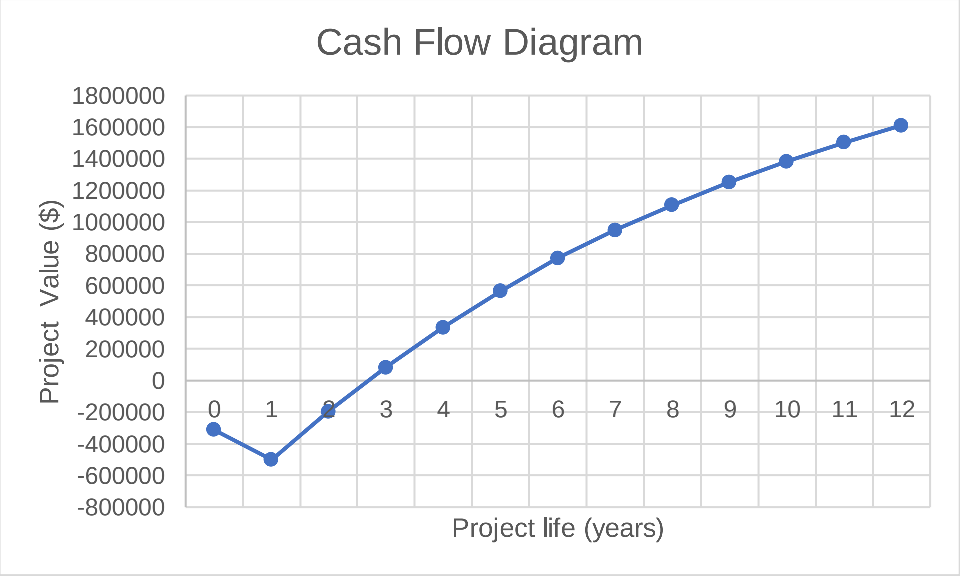


Figure 5.7: Cumulative cash flow diagram.

From **Table 5.13** the DCFROR and the NPV for the base case scenario was determined to be 53.1% and $1 612 122.34, respectively. A Higher DCFROR of 48% was observed in the study by Felfli et al. (2005) for carbonised briquettes from various biomass. However, Ifa (2020) observed a slightly lower DCFROR of 23.55% in the production of bio-briquettes from cashew nutshell waste. Although these studies are all profitable, their disparities can be due to cost of feedstock, fixed cost as well as the selling price (Felfli et al, 2005; Sahoo et al, 2019). In this study the DCFROR is higher than the desired discount rate (>30%) and the NPV is greater than zero. Hence, the base case scenario is considered economically profitable. The attractiveness can be attributed to high revenue profits from the sales of briquettes, and the fact that bio-oil adds to the revenue stream. Likewise, the DPBP of 2.64 years meets the desired requirements of less than 4 years which proves the base case scenario to be favourable and can increase the attractiveness to investors. The DPBP of the base case scenario is comparable to the study by Sengar et al. (2013) who obtained a DPBP of 2.5 years for carbonised rice rusk briquette production and Ifa (2020) who obtained a DPBP of 3.42 years for bio-briquettes from cashew nutshell waste.

5.5.4.2. Comparison of scenarios

In thus study, the base scenario evaluated in section 5.2.6 was compared with a second scenario of installing a GBG to generate electricity using corn cobs as feedstock for the GBG (section 5.2.9). The comparison between the scenarios was performed based on the TCI, total production costs (TPC), revenue, and profitability (PI).

Table 5.14: Comparison of base case scenario and scenario 2.

Scenario	Base case	Scenario 2
TCI ($/y)	518 790.68	672 725.37
TPC ($/y)	212 099.84	202 559.75
Revenue ($/y)	685 348.69	687 298.69
DCFROR (%)	53.10	44.10
NPV ($)	1 612 122.34	1 542 340.44
DPBP (years)	2.67	3.14

From **Table 5.14**, the TCI of $672 725.37 will be required if the GBG is added which is 22.88% higher than base case. The increase is due to the additional equipment required which increases the TCI. Regarding the TPC, **Table 5.14** shows that production costs of the base case decreased by 4.50% when the GBG is added. Even though the raw material cost increased by 11.76 %. The decrease is due to a significant reduction in utilities particularly electricity costs by 61.58% from power generated by the GBG. Evaluation of revenue generation shows that adding the GBG to the base case scenario slightly increased the revenue by 0.28 % due to additional biochar (corn cob) sales. In terms of profitability, the base case is higher than the second scenario with a DCFROR of 53.1% and 44.1% respectively. This trend is seen in the studies by Felfi et al. (2005) and Segnar et al. (2013) where they observed high DCFROR of 48% and 230% respectively when using electricity on the grid and a study by Sahoo et al. (2019) of 19.8% to 15.2% while using electricity from the GBG. This can be attributed to the addition of equipment involved when using GBG which increases the TCI as shown in the table leading to a decrease in DCFROR and an increase in DPBP. Therefore, it can be concluded that the inclusion of the GBG will depend on the goals and the environment surrounding the project involved.

5.6. Chapter summary

This study aimed to optimise and assess the technical and economic profitability of the briquette production process from CCS. The mass and energy balances from the overall process were determined using PFD and software simulation in conjunction with equipment prices, sizes, and data from Alibaba Group® and literature. 550 kg/h of CS was converted to biochar to a mass and yield of 253.61 kg/h and 46.11% respectively. The energy requirement showed that the pyrolysis reactor consumed 62.5% of the overall pyrolysis process power requirements. The biochar was able to generate 300 kg/h of dry briquettes. The energy requirements for the briquettes section showed that the binder mixing section accounted for

33.61% of overall briquette section power requirements. Using the exact temperature required for binder activation is vital to energy-saving contribution.

The base case scenario and scenario 2 were found to be economically feasible with a DBPB <4 years and DCFROR >30%. The addition of GBG was found to slightly increase the revenue by 0.28 %. However, it was also found that using the GBG increased the DPBP and decreased DCFROR in comparison with the base case scenario from 2.67 years to 3.14 years and 53.10 and 44.10% respectively. Although both scenarios are seen to be technical and economically profitable, the goals and environmental surroundings of the project will decide the necessity of either scenario.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Impact of the study

This study shows that corn-stover (CS) biomass when carbonised via slow pyrolysis can significantly reduce the costs for ash disposal which is already a problem with coal and demonstrates the sustainability of the resulting fuel. Its high calorific capacity in the form of carbonised briquettes can significantly reduce the fuel consumption for heat supply and provide a decrease in costs for its transportation in comparison with the raw material. The produced carbonised CS briquettes at the relevant market price were found to be feasible technical and economically to be considered as a suitable solid fuel comparable with conventional charcoal and coal. These carbonised CS briquettes can contribute significantly to the environment by reducing the dependence on firewood and other unclean fuel sources and manage waste in South Africa and other developing countries.

6.2. Conclusions

This study shows that raw CS under optimised slow pyrolysis conditions produced high-quality biochar with an HHV of 28.89 MJ/kg comparable to those of other biochars produced from biomass using pyrolysis which was converted into briquettes. The CCS briquette's effect of compaction pressure, binder concentration, and the drying temperature was investigated and was optimised successfully in terms of HHV while obtaining high strength and density. The briquettes produced to show that the HHV, as well as the compressive strength, density, and durability, is comparable to that of South African bituminous A grade coal. The briquettes were smokeless with low ash and volatile matter content which are suitable for domestic and industrial purposes. The technical and economic analysis of briquette production plant in South Africa from CCS was evaluated. This study shows that process development of CCS briquettes using PFD was successfully developed and was found to be economically feasible with a DBPB <4 years, high positive NPV and DCFROR >30%. Therefore, this can conclude that it is economically possible to produce and sell CCS briquettes that will contribute to relieving South Africa ever-increasing energy demands.

6.3. Future work

Recommendations for future studies are as follows:

- Research should be done to focus on the characterisation of all slow pyrolysis products (bio-oil and biogas) for possible simulation requirements.
- Implementation of the existing regulations for a sustainable biochar sector in South Africa needs to consider CCS briquette.

- Employ simulation techniques that can incorporate both slow pyrolysis and briquetting production.
- More research should be focused on upgrading slow pyrolysis by-products to give a more defined economic perspective of all products.
- Investigate more scenarios where the bio-oil and biogas by-products can be used as energy sources to supplement or replace electricity

7. REFERENCE LIST

Abbas, M.M. 2014. Alternative material use of fast pyrolysis char and its impact on the bioliq® process chain. Msc thesis. Tecnico LISBOA, Portugal.

Acheampong, B.B. 2016. Biomass and Bioenergy Strength properties and calorific values of sawdust-briquettes as wood-residue energy generation source from tropical hardwoods of different densities. *Biomass and Bioenergy*, 85: 144–152.

Ahmed, S.A., Kumari, A. & Mandavgane, K. 2014. A Review on Briquettes as an Alternative Fuel. *International Journal of Innovations in Engineering and Technology (IJIET)*, 3(4):139.

Ajimotokana, H.A., Ehindero, A.O., Ajao K.S., Adeleke, A.A., Ikubanni, P.P., Shuaib-Babata, Y.L. 2019. Combustion characteristics of fuel briquettes made from charcoal particles and sawdust agglomerates. *Scientific African*, 6: 2468-2276.

Akubo, K., Nahil, M.A. & Williams, P.T. 2019. Pyrolysis-catalytic steam reforming of agricultural biomass wastes and biomass components for production of hydrogen/syngas. *Journal of the Energy Institute*, 92(6): 1987–1996.

Al Arni, S. 2018. Comparison of slow and fast pyrolysis for converting biomass into fuel. *Renewable Energy*, 124: 197–201.

Alanya-Rosenbaum, S. & Bergman, R.D. 2019. Life-cycle impact and exergy based resource use assessment of torrefied and non-torrefied briquette use for heat and electricity generation. *Journal of Cleaner Production*, 233: 918–931.

Alibaba Groupr®. 2018. https://www.alibaba.com [24/08/2019]

Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M., Usman, A.R.A. 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. *Bioresource Technology*, 131:374–379.

Angin, D. 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource Technology*, 128: 593–597.

Antwi-Boasiako, C.; Acheampong, B.B. 2016. Strength properties and calorific values of sawdust-briquettes as wood-residue energy generation source from tropical hardwoods of different densities. *Biomass Bioenergy*, 85: 144–152.

Anukam, A.I., Goso, B.P., Okoh, O.O. & Mamphweli, S.N. 2017. Studies on Characterization of Corn Cob for Application in a Gasification Process for Energy Production. *Journal of Chemistry*, 2017.

Anwar, Z., Gulfraz, M. & Irshad, M. 2014. Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: A brief review. *Journal of Radiation Research and Applied Sciences*, 7(2): 163–173.

Aransiola, E.F., Oyewusi, T.F., Osunbitan, J.A. & Ogunjimi, L.A.O. 2019. Effect of binder type, binder concentration and compacting pressure on some physical properties of carbonized corncob briquette. *Energy Reports*, 5: 909–918.

Azuara, M., Baguer, B., Villacampa, J.I., Hedin, N. & Manyà, J.J. 2016. Influence of pressure and temperature on key physicochemical properties of corn stover-derived biochar. *Fuel*, 186: 525–533.

Bajwa, D.S., Peterson, T., Sharma, N., Shojaeiarani, J. & Bajwa, S.G. 2018. A review of densified solid biomass for energy production. *Renewable and Sustainable Energy Reviews*, 96: 296–305.

Balasubramani, P., Anbumalar, V., Nagarajan, M.S. & Prabu, P.M. 2016. Biomass briquette manufacturing system model for environment. *Journal of Alloys and Compounds*, 686: 859–865.

Barten, T.J. 2013. Evaluation and prediction of corn stover biomass and composition from commercially available corn hybrids. PhD thesis. Iowa State University, United states.

Basu, P. 2010. *Biomass gasification and pyrolysis: practical designs and theory*. Oxford: Elsevier.

Batidzirai, B., Valk, M., Wicke, B., Junginger, M., Daioglou, V., Euler, W. & Faaij, A.P.C. 2016. Current and future technical, economic and environmental feasibility of maize and wheat residues supply for biomass energy application: Illustrated for South Africa. *Biomass and Bioenergy*, 92: 106–129.

Bazargan, A., Rough, S.L. & McKay, G. 2014. Compaction of palm kernel shell biochars for application as solid fuel. *Biomass and Bioenergy*, 70: 489–497.

Belay, A. 2014. Comparative Analysis of Briquetting Most Viable Biomass Waste to Substitute Charcoal in Ethiopia. MSc thesis. Addis Ababa University. Ethiopia.

Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S. & Escaleira, L.A. 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, 76(5): 965–977.

Biswas, B., Pandey, N., Bisht, Y., Singh, R., Kumar, J. & Bhaskar, T. 2017. Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk. *Bioresource Technology*, 237: 57–63.

Borowski, G., Stępniewski, W. & Wójcik-Oliveira, K. 2017. Effect of starch binder on charcoal briquette properties. *International Agrophysics*, 31(4): 571–574.

Boston Machinary. 2019. http://www.bostonmachinery.com/[23/03/2019]

Brand, M.A., Jacinto, R.C., Antunes, R. & da Cunha, A.B. 2017. Production of briquettes as a tool to optimize the use of waste from rice cultivation and industrial processing. *Renewable Energy*, 111: 116–123.

Bridgwater, A. V. 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, 38: 68–94.

Brigagão, G.V., de Queiroz Fernandes Araújo, O., de Medeiros, J.L., Mikulcic, H. & Duic, N. 2019. A techno-economic analysis of thermochemical pathways for corncob-to-energy: Fast pyrolysis to bio-oil, gasification to methanol and combustion to electricity. *Fuel Processing Technology*, 193(April): 102–113.

Brown, Tristan R., Wright, M.M. & Brown, R.C. 2011. Estimating profitability of two biochar production scenarios: slow pyrolysis vs fast pyrolysis. *Biofuels, Bioproducts and Biorefining*, 5(1): 54–68.

Capunitan, J.A. & Capareda, S.C. 2012. Assessing the potential for biofuel production of corn stover pyrolysis using a pressurized batch reactor. *Fuel*, 95: 563–572.

Carrier, M., Hugo, T., Gorgens, J. & Knoetze, H. 2011. Comparison of slow and vacuum pyrolysis of sugar cane bagasse. *Journal of Analytical and Applied Pyrolysis*, 90(1): 18–26.

Cavallo, E. & Pampuro, N. 2017. Effects of compressing pressure on briquettes made from woody biomass. *Chemical Engineering Transactions*, 58: 517–522.

Chan, Y.H., Cheah, K.W., How, B.S., Loy, A.C.M., Shahbaz, M., Singh, H.K.G., Yusuf, N.R., Shuhaili, A.F.A., Yusup, S., Ghani, W.A.W.A.K., Rambli, J., Kansha, Y., Lam, H.L., Hong, B.H. & Ngan, S.L. 2019. An overview of biomass thermochemical conversion technologies in Malaysia. *Science of the Total Environment*, 680: 105–123.

Chaney, J.O. 2010. Combustion Characteristics of Biomass Briquettes. PhD thesis. University of Nottingham: England.

Chelgani, S.C. 2019. Investigating the occurrences of valuable trace elements in African coals as potential byproducts of coal and coal combustion products. *Journal of African Earth Sciences*, 150: 131–135.

Chen, W., Peng, J. & Bi, X.T. 2015. A state-of-the-art review of biomass torrefaction , densification and applications. *Renewable and Sustainable Energy Reviews*, 44: 847–866.

Chen, Y. 2012. Biomass to Fuels: Thermo-chemical or Bio-chemical Conversion? *Fermentation Technology*, 01(02): 7972.

Chen, Zhenyang, Niu, B., Zhang, L. & Xu, Z. 2018. Vacuum pyrolysis characteristics and parameter optimization of recycling organic materials from waste tantalum capacitors. *Journal of Hazardous Materials*, 342: 192–200.

Chirchir, D. K ., Nyaanga , D. M. & Githeko, J.M. 2013. Effect of Binder Types and Amount on. *International Journal of Engineering Research and Science and Technology*, 2(1): 12–20.

City of Cape Town, 2019. https://resource.capetown.gov.za/documentcentre/Documents/Financial%20documents/Electricity%20Consumptive%20Tariffs.pdf. [17/05/2019]

Clarkson, J. & Eckert, C. 2005. *Design process improvements*. London: Springer.

Collard, F.X. & Blin, J. 2014. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renewable and Sustainable Energy Reviews*, 38: 594–608.

Collard, F.X., Carrier, M. & Görgens, J.F. 2016. Fractionation of Lignocellulosic Material With Pyrolysis Processing. *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery*: 81–101.

Cong, H., Mašek, O., Zhao, L., Yao, Z., Meng, H., Hu, E. & Ma, T. 2018. Slow Pyrolysis Performance and Energy Balance of Corn Stover in Continuous Pyrolysis-Based Poly-Generation Systems. *Energy and Fuels*, 32(3): 3743–3750.

Czajczyńska, D., Anguilano, L., Ghazal, H., Krzyżyńska, R., Reynolds, A.J., Spencer, N. & Jouhara, H. 2017. Potential of pyrolysis processes in the waste management sector. *Thermal Science and Engineering Progress*, 3: 171–197.

Danje, S. 2011. Fast pyrolysis of corn residues for energy production. MEng thesis. Stellenbosch University, South Africa.

Davies, R.M. & Davies, O.A. 2013. Physical and combustion characteristics of briquettes made from water hyacinth and phytoplankton scum as binder. *Journal of Combustion*,:1-7.

Demirbas, A. 2004. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *Journal of Analytical and Applied Pyrolysis*, 72: 243–248.

Demirbas, A. 2004. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues*. Journal of Analytical and Applied Pyrolysis*, 72:243–248.

Dhyani, V. & Bhaskar, T. 2018. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renewable Energy*, 129: 695–716.

Dooley, K.L. 2015. Slow pyrolysis biochar from forestry residue and municipal and farm wastes : Characterization and their use in greenhouses as a soil amendment. Msc thesis. Memorial University of Newfoundland: Canada.

Elkhalifa, S., Al-Ansari, T., Mackey, H.R. & McKay, G. 2019. Food waste to biochars through pyrolysis: A review. *Resources, Conservation and Recycling*, 144: 310–320.

Emerhi, E.A. Physical and combustion properties of briquettes produced from sawdust of three hardwood species and different organic binders. *Advances in Applied Science Research*. 2: 236–246.

Essex, S. & de Groot, J. 2019. Understanding energy transitions: The changing versions of the modern infrastructure ideal and the 'energy underclass' in South Africa, 1860–2019. *Energy Policy*, 133: 110937.

Faizal, H.M., Latiff, Z.A., Wahid, M.A. & Darus, A.N. 2010. Physical and Combustion Characteristics of Biomass Residues from Palm Oil Mills. *New Aspects of Fluid Mechanics, Heat Transfer and Environment*, : 34–38.

Felfi, F.F., Luengo, C.A. & Rocha, J.D. 2005. Torrefied briquettes: technical and economic feasibility and perspectives in the Brazilian market. *Energy for Sustainable Development*, 9:23-29.

Gageanu, I., Cujbescu, D., Persu, C. & Voicu, G. 2018. Impact of using additives on quality of agricultural biomass pellets. *Engineering for Rural Development*, 17: 1632–1638.

Galal, S. 2020. Production of maize in South Africa from 2000 to 2020 https://www.statista.com/statistics/1134833/production-of-maize-in-south-africa/ [20/06/2020]

Gan, Y.Y., Ong, H.C., Ling, T.C., Chen, W.H. & Chong, C.T. 2019. Torrefaction of de-oiled Jatropha seed kernel biomass for solid fuel production. *Energy*, 170: 367–374.

Gebresas, A., Asmelash, H., Berhe, H. & Tesfay, T. 2015. Briquetting of Charcoal from Sesame Stalk. *Journal of Energy*, 2015: 1–6.

Gendek, A., Aniszewska, M., Malaťák, J. & Velebil, J. 2018. Evaluation of selected physical and mechanical properties of briquettes produced from cones of three coniferous tree species. *Biomass and Bioenergy*, 117: 173–179.

Gilvari, H., de Jong, W. & Schott, D.L. 2019. Quality parameters relevant for densification of bio-materials: Measuring methods and affecting factors—A review. *Biomass Bioenergy*. 120: 117–134.

Goh, C. S., Thran., D., Marchalddd, D & Bradley., D. 2013. Wood pellet market and trade: A global perspective. *Biofuels, Bioproducts and Biorefining*. 7 :24–42.

Goyal, H. B., Seal, D., and Saxena, R. C. 2008. Bio-fuels from thermochemical conversion of renewable resources: a review. *Renewable and Sustainable Energy Reviews*. 12, 504–517.

Grover, P. D & Mishra, S.K. 1996. Biomass Briquetting : Technology and Pratices.Regional wood energy development program in Asia, field document no. 46. Bangkok, Thailand: Food and Agriculture Organization of the United Nations; , (46).

Hakizimana, J. de D.K. & Kim, H.T. 2016. Peat briquette as an alternative to cooking fuel: A techno-economic viability assessment in Rwanda. *Energy*, 102: 453–464.

Hamid, M.F., Idroas, M.Y., Ishak, M.Z., Alauddin, Z.A.Z., Miskam, M.A. & Abdullah, M.K. 2016. An Experimental Study of Briquetting Process of Torrefied Rubber Seed Kernel and Palm Oil Shell. *BioMed Research International*, : 3–5.

Hanif, M.U., Capareda, S.C., Iqbal, H., Arazo, R.O. & Baig, M.A. 2016. Effects of pyrolysis temperature on product yields and energy recovery from co-feeding of cotton gin trash, cow manure, and microalgae: A simulation study. *PLOS ONE*, 11(4): e0152230.

Hasan, E.S., Jahiding, M., Mashuni, Ilmawati, W.O.S., Wati, W. & Sudiana, I.N. 2017. Proximate and the Calorific Value Analysis of Brown Coal for High-Calorie Hybrid Briquette Application. *Journal of Physics: Conference Series*, 846(1).

Haykiri-Acma, H & S.Yaman, S. 2010. Production of Smokeless Bio-briquettes from Hazelnut Shell. *Proceedings of the World Congress on Engineering and Computer Science*, II: 20–22.

He, X., Liu, Z., Niu, W., Yang, L., Zhou, T., Qin, D., Niu, Z. & Yuan, Q. 2018. Effects of pyrolysis temperature on the physicochemical properties of gas and biochar obtained from pyrolysis of crop residues. *Energy*, 143: 746–756.

Helwani, Z., Fatra, W., Arifin, L., Othman, M.R. & Syapsan. 2018. Effect of process variables on the calorific value and compressive strength of the briquettes made from high moisture Empty Fruit Bunches (EFB). *IOP Conference Series: Materials Science and Engineering*, 345(1).

Hiremath, R.B., Kumar, B., Balachandra, P., Ravindranath, N.H. & Raghunandan, B.N.

2009. Energy for Sustainable Development Decentralised renewable energy : Scope , relevance and applications in the Indian context. *ESD*, 13(1): 4–10.

Hornung, A., Apfelbacher, A. & Sagi, S. 2011. Intermediate pyrolysis: A sustainable biomass-to-energy concept-biothermal valorisation of biomass (BtVB) process. *Journal of Scientific and Industrial Research*, 70(8): 664–667.

Hu, X. & Gholizadeh, M. 2019. Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage. *Journal of Energy Chemistry*, 39: 109–143.

Huang, K., Kong, D.L., Lu, X.R., Feng, W.W., Liu, M.C. & Feng, Y.L. 2020. Lesser leaf herbivore damage and structural defense and greater nutrient concentrations for invasive alien plants: Evidence from 47 pairs of invasive and non-invasive plants. *Science of the Total Environment*, 723: 137829.

Ifa, L., Yani. S, Nurjannah Nurjannah, N., Darnengsih, D., Rusnaenah, A., Mel, M., Mahfud Mahfud, M. & Kusuma, H.S. 2020. Techno-economic analysis of bio-briquette from cashew nutshell waste. *Heliyon*, e05009.

IGC GIFT. Type, Distribution and Use of Coal in South Africa. Presented At 35th IGC GIFT Workshop, South Africa, 28 August 2016.

Islam, M.N., Kamrujjaman, K. & Ali, M.N. & Islam, S. 2003. An Investigation of the raw materials and products of the briquetting. *IRRAESND*, 19-20 December.

Islam, M.N., Ali, M.H. & Ahmad, I. 2017. Fixed bed slow pyrolysis of biomass solid waste for bio-char. *IOP Conference Series: Materials Science and Engineering*, 206(1).

Jackson, J., Turner, A., Mark, T. & Montross, M. 2016. Densification of biomass using a pilot scale flat ring roller pellet mill. *Fuel Processing Technology*, 148: 43–49.

Jezerska, L., Zajonc, O., Rozbroj, J., Vyletělek, J. & Zegzulka, J. 2014. Research on Effect of Spruce Sawdust with Added Starch on Flowability and Pelletization of the Material. *IERI Procedia*, 8: 154–163.

Ji, Y., Li, K., Liu, G., Shrestha, A. & Jing, J. 2018. Comparing greenhouse gas emissions of precast in-situ and conventional construction methods. *Journal of Cleaner Production*. 173: 124-134.

John Thompson (Pty) Ltd. 2019. Typical Analysis for Coal Grade C Smalls. John Thompson report [18/06/2019]

Kakooza, A.W. 2017. Appraisal of Food Residue (Waste) Based Fuel Briquettes in Domestic

Cooking Applications: a Case Study of Uganda. *M.Sc Thesis*.

Kaliyan, N. & Morey, R. V. 2009a. Densification characteristics of corn stover and switchgrass. *Transactions of the ASABE*, 52(3): 907–920.

Kaliyan, N. & Morey, R. V. 2009b. Factors affecting strength and durability of densified biomass products. *Biomass and Bioenergy*, 33(3): 337–359.

Kan, T., Strezov, V. & Evans, T.J. 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renewable and Sustainable Energy Reviews*, 57: 1126–1140.

Katimbo, A., Kiggundu, N., Kizito, S., Kivumbi, H.B. & Tumutegyereize, P. 2014. Potential of densification of mango waste and effect of binders on produced briquettes. *Agricultural Engineering International: CIGR Journal*, 16(4): 146–155.

Kaur, A., Kumar, A., Singh, P. & Kundu, K. 2017. Production, Analysis and Optimization of Low Cost Briquettes from Biomass Residues. *Advances in Research*, 12(4): 1–10.

Kebelmann, K., Hornung, A., Karsten, U. & Griffiths, G. 2013. Intermediate pyrolysis and product identification by TGA and Py-GC/MS of green microalgae and their extracted protein and lipid components. *Biomass and Bioenergy*, 49(0): 38–48.

Kers, J., Kulu, P., Aruniit, A., Laurmaa, V., Križan, P., Šooš, L. & Kask, Ü. 2010. Polümeersetest jäätmetest pressitud brikettide füüsikalismehaaniliste ja põlemiskarakteristikute määramine. *Estonian Journal of Engineering*, 16(4): 307–316.

Khan, Z., S. Yusup, M.M. Ahmad, V.S. Chok, Y. Uemura and K.M. Sabil, 2010. Review on hydrogen production technologies in Malaysia. *Internal Journal Engineering Technology*. 10: 111-118.

Klingenfeld, D., Lee, H. & Toft, M. 2008. Corn Stover As A Bioenergy Feedstock : Identifying And Overcoming Barriers For Corn Stover Harvest , Storage , And Transport Prepared by : National Commission on Energy Policy Faculty Advisor :

Kongprasert, N., Wangphanich, P. & Jutilarptavorn, A. 2019. Charcoal briquettes from Madan wood waste as an alternative energy in Thailand. *Procedia Manufacturing*, 30: 128–135.

Križan, P., Matúš, M. & Beniak, J. 2016. Relationship between compacting pressure and conditions in pressing chamber during biomass pressing. *Acta Polytechnica*, 56(1): 33–40.

Kumar, V.G. & Lakshmishri, R. 2017. Utilisation of response surface methodology for modelling and optimization of tablet compression process. *Journal of young pharmacists*. 9(3): 417-421.

Kunkes, E.L., Simonetti, D.A., West, R.M., Serrano-Ruiz, J.C., Gartner, C.A., and Dumesic, J.A. 2008. Catalytic conversion of biomass to monofuctional hydrocarbons and targeted liquid-fuels classes. Science. 322 (5900): 417-421.

Laird, D.A., Rogovska, N.P., Garcia-Perez, M., Collins, H.P., Streubel, J.D. & Smith, M. 2010. Chapter 16: Pyrolysis and Biochar-Opportunities for Distributed Production and Soil Quality Enhancement. Biofuels, Bioenergy and Biorefinary, :257–281.

Lee, Y., Eum, P., Ryu, C., Park, Y., Jung, J. & Hyun. 2013. Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1. *Bioresource Technology,* 130: 345-350.

Lee, Y., Park, J., Ryu, C., Gang, K.S., Yang, W., Park, Y.K., Jung, J. & Hyun, S. 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500°C. *Bioresource Technology*, 148: 196–201.

Lela, B., Barišić, M. & Nižetić, S. 2016. Cardboard/sawdust briquettes as biomass fuel: Physical-mechanical and thermal characteristics. *Waste Management*, 47: 236–245.

Limayem, A. & Ricke, S.C. 2012. Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects. *Progress in Energy and Combustion Science*, 38(4): 449–467.

Lin, Y., and Tanaka, S. 2006. Ethanol fermentation from biomass resources: Current state and prospects. *Applied. Microbiology and Biotechnology*. 69: 627-642.

Liu, X., Zhang, Yang, Li, Z., Feng, R. & Zhang, Yaozhong. 2014. Characterization of corncob-derived biochar and pyrolysis kinetics in comparison with corn stalk and sawdust. *Bioresource Technology*, 170: 76–82.

Liu, Z. & Han, G. 2015. Production of solid fuel biochar from waste biomass by low temperature pyrolysis. *Fuel*, 158: 159–165.

Liu, Zhaoxia, Niu, W., Chu, H., Zhou, T. & Niu, Z. 2018. Effect of the Carbonization Temperature on the Properties of Biochar Produced from the Pyrolysis of Crop Residues. *BioResources*, 13(2): 3429–3446.

Ma, C., Yu, J., Wang, B., Song, Z., Xiang, J., Hu, S., Su, S. & Sun, L. 2017. Catalytic pyrolysis of flame retarded high impact polystyrene over various solid acid catalysts. *Fuel Processing Technology*, 155: 32–41.

Mabizela, P.S. 2014.Characterization and computer simulation of corn stover/ coal blends for co-gasification in a downdraft gasifier. MSc thesis. University of Fort Hare, South Africa.

Machado, N.T., de Castro, D.A.R., Santos, M.C., Araújo, M.E., Lüder, U., Herklotz, L., Werner, M., Mumme, J. & Hoffmann, T. 2018. Process analysis of hydrothermal carbonization of corn Stover with subcritical H2O. *Journal of Supercritical Fluids*, 136: 110–122.

Mahmood, A.S.N., Brammer, J.G., Hornung, A., Steele, A., Poulston, S. 2013. The intermediate pyrolysis and catalytic steam reforming of Brewers spent grain. *Journal of Analytical and Applied Pyrolysis*, 103: 328-342.

Malatji, P., Mamphweli, N.S. & Meincken, M. 2011. The technical pre-feasibility to use briquettes made from wood and agricultural waste for gasification in a downdraft gasifier for electricity generation. *Journal of Energy in Southern Africa*, 22(4): 2–7.

Mamvura, T.A., Pahla, G. & Muzenda, E. 2018. Torrefaction of waste biomass for application in energy production in South Africa. *South African Journal of Chemical Engineering*, 25: 1–12.

Manyuchi, M. M., Tichapondwa, S. M., Ikhu-Omoregbe, D. I. O. & Oyekola, O. O. 2016. Process Parameters Affecting the Production of Charcoal Briquettes from Lignocellulose Waste. *Lignocellulose*, 5: 86–93.

Mbandinga, M. A. B. 2015.Conversion of a batch biodiesel plant from homogeneous to heterogeneous catalysed process: modelling, optimisation, and techno-economic analysis. MTech Thesis. Cape Peninsula University of Technology, South Africa.

McKendry, P. 2002. Energy production from biomass (part 1): Overview of biomass. *Bioresource Technology*, 83(1): 37–46.

Mendoza-Martinez, C.L.; Sermyagina, E.; Carneiro, O.A.D.C.; Vakkilainen, E.; Cardoso, M. 2019. Production and characterization of coffee-pine wood residue briquettes as an alternative fuel for local firing systems in Brazil. *Biomass Bioenergy*, 123, 70–77.

Menya, E., Olupot, P.W., Storz, H., Lubwama, M., Kiros, Y. & John, M.J. 2020. Optimization of pyrolysis conditions for char production from rice husks and its characterization as a precursor for production of activated carbon. *Biomass Conversion and Biorefinery*, 10(1): 57–72.

Milhollin, R., Hoehne, J., Horner, J., Weber, S. & George, C. 2011. Feasiblity of Corn Stover in Missouri. Technical report: 1–86.

Mitchual, S.J., Frimpong-Mensah, K. & Darkwa, N.A. 2013. Effect of species, particle size and compacting pressure on relaxed density and compressive strength of fuel briquettes. *International Journal of Energy and Environmental Engineering*, 4(1): 1–6.

Mocke, F.J., 2013. Implementation of membrane technology in a base metal refinery. MEng thesis. North-West University, South Africa.

Mohan, D., Pittman, C.U. & Steele, P.H. 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy and Fuels*, 20(3): 848–889.

Mohlala, L.M., Bodunrin, M.O., Awosusi, A.A., Daramola, M.O., Cele, N.P. & Olubambi, P.A. 2016. Beneficiation of corncob and sugarcane bagasse for energy generation and materials development in Nigeria and South Africa: A short overview. *Alexandria Engineering Journal*, 55(3): 3025–3036.

Moneim, M.A., El Naggar, A.M.A., El Sayed, H.A., Mostafa, M.S., Khalil, N.M. & Hassan, M.E.D. 2018. Direct conversion of an agricultural solid waste to hydrocarbon gases via the pyrolysis technique. *Egyptian Journal of Petroleum*, 27(4): 991–995.

Naqvi, S.R., Jamshaid, S., Naqvi, M., Farooq, W., Niazi, M.B.K., Aman, Z., Zubair, M., Ali, M., Shahbaz, M., Inayat, A. & Afzal, W. 2018. Potential of biomass for bioenergy in Pakistan based on present case and future perspectives. *Renewable and Sustainable Energy Reviews*, 81: 1247–1258.

NCPC-SA. 2019. Engergy Management 101. Cape Town: Eskom Brankenfell.

Ndindeng, S.A., Mbassi, J.E.G., Mbacham, W.F., Manful, J., Graham-Acquaah, S., Moreira, J., Dossou, J. & Futakuchi, K. 2015. Quality optimization in briquettes made from rice milling by-products. *Energy for Sustainable Development*, 29: 24–31.

Nizami, A.S., Rehan, M., Waqas, M., Naqvi, M., Ouda, O.K.M., Shahzad, K., Miandad, R., Khan, M.Z., Syamsiro, M., Ismail, I.M.I. & Pant, D. 2017. Waste biorefineries: Enabling circular economies in developing countries. *Bioresource Technology*, 241: 1101–1117.

Nsamba, H.K., Hale, S.E., Cornelissen, G. & Bachmann, R.T. 2015. Sustainable Technologies for Small-Scale Biochar Production — A Review., : 10–31.

Okot, D.K., Bilsborrow, P.E. & Phan, A.N. 2018. Effects of operating parameters on maize COB briquette quality. *Biomass and Bioenergy*, 112(October 2017): 61–72. https://doi.org/10.1016/j.biombioe.2018.02.015.

Okot, D.K., Bilsborrow, P.E. & Phan, A.N. 2019. Briquetting characteristics of bean straw-maize cob blend. *Biomass and Bioenergy*, 126(September 2018): 150–158.

Oladeji J.T. 2015. Theoretical Aspects of Biomass Briquetting : A Review Study. *Journal of Energy Technologies and Policy*, 5(3): 72–82.

Onchieku, J.M., Chikamai, B.N. & Rao, M.S. 2012. Optimum Parameters for the Formulation of Charcoal Briquettes Using Bagasse and Clay as Binder. *European Journal of Sustainable Development*, 1(3): 477.

Park, J., Lee, Y., Ryu, C. & Park, Y.K. 2014. Slow pyrolysis of rice straw: Analysis of products properties, carbon and energy yields. *Bioresource Technology*, 155: 63–70.

Pawar, A Panwar. N.L, & Salvi, B.L. 2020. Comprehensive review on pyrolytic oil production, upgrading and its utilization. *Journal of Material Cycles and Waste Management*, 22:1712–1722.

Payscale, 2019. https://www.payscale.com [12/09/2019].

Petrides, D.; Carmichael, D.; Siletti, C.; Koulouris, A. 2014. Biopharmaceutical Process Optimization with Simulation and Scheduling Tools. *Bioengineering*, 1:154-187.

Pietsch, W. 2002. Agglomeration theories: Estimation of agglomerate strength. *Agglomeration processes*: 70–75.

Pilusa, T.J., Huberts, R. & Muzenda, E. 2013. Emissions analysis from combustion of eco-fuel briquettes for domestic applications. *Journal of Energy in Southern Africa*, 24(4): 30–36.

Pollet, B.G., Staffell, I. & Adamson, K.A. 2015. Current energy landscape in the Republic of South Africa. *International Journal of Hydrogen Energy*, 40(46): 16685–16701.

Poudel, J. & Oh, S.C. 2014. Effect of torrefaction on the properties of corn stalk to enhance solid fuel qualities. *Energies*, 7(9): 5586–5600.

Pourkarimi, S., Hallajisani, A., Alizadehdakhel, A. & Nouralishahi, A. 2019. Biofuel production through micro- and macroalgae pyrolysis – A review of pyrolysis methods and process parameters. *Journal of Analytical and Applied Pyrolysis*.: 1–19

Pradhan, P., Arora, A. & Mahajani, S.M. 2018. Pilot scale evaluation of fuel pellets production from garden waste biomass. *Energy for Sustainable Development*, 43: 1–14.

Pratama, A. H., Yusup, S., Shahbaz, M. & Onoja, D. 2016. Bottom ash characterization and its catalytic potential in biomass gasification. *Procedia Engineering.* 148: 432–436

Qiao, X., Zhao, C., Shao, Q. & Hassan, M. 2018. Structural Characterization of Corn Stover Lignin after Hydrogen Peroxide Presoaking Prior to Ammonia Fiber Expansion Pretreatment. *Energy and Fuels*, 32(5): 6022–6030.

Quispe, I., Navia, R. & Kahhat, R. 2017. Energy potential from rice husk through direct combustion and fast pyrolysis: A review. *Waste Management*, 59: 200–210.

Rafiq, M.K., Bachmann, R.T., Rafiq, M.T., Shang, Z., Joseph, S. & Long, R.L. 2016. Influence of pyrolysis temperature on physico-chemical properties of corn stover (zea mays l.) biochar and feasibility for carbon capture and energy balance. *PLoS ONE*, 11(6): 1–17.

Rizzo, A.M., Pettorali, M., Nistric, R. & Chiaramonti, D. 2019. Mass and energy balances of an autothermal pilot carbonization unit. *Biomass and Bioenergy*, 120: 144-145.

Roddy, D.J. 2012. Biomass in a petrochemical world. *Interface focus*, 3: 20120038.

Ronsse, F., Dickinson, D., Nachenius, R. & Prins, W. 2013. Biomass pyrolysis and biochar characterization. *In forebiom workshop*, :1–24.

Russell, S.H., Turrion-Gomez, J.L., Meredith, W., Langston, P. & Snape, C.E. 2017. Increased charcoal yield and production of lighter oils from the slow pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*, 124: 536–541.

Sahoo, K., Bilek, E., Bergman, R. & Mani, S. 2019. Techno-economic analysis of producing solid biofuels and biochar from forest residues using portable systems. *Applied Energy*. 235: 578–590.

Said, K.A.M., Yakub, I. & Amin, M.A.M. 2015a. Overview of Response Surface Methodology (RSM) in Extraction Process. *Advances in Process Engineering*, 2(1): 279–287.

Said, N., Abdel Daiem, M.M., García-Maraver, A. & Zamorano, M. 2015b. Influence of densification parameters on quality properties of rice straw pellets. *Fuel Processing Technology*, 138: 56–64.

Salema, A.A., Afzal, M.T. & Bennamoun, L. 2017. Pyrolysis of corn stalk biomass briquettes in a scaled-up microwave technology. *Bioresource Technology*, 233: 353–362.

Sánchez, E.A., Pasache, M.B. & Garća, M.E. 2014. Development of briquettes from waste wood (sawdust) for use in low-income households in Piura, Peru. *Lecture Notes in Engineering and Computer Science*, 2: 986–991.

Sani, B.Y. & Fidelis, I. 2008. Design , Construction and Experimental Evaluation of the Products of a Low Cost Briquette Machine for Rural Communities in Nigeria.Msc thesis. Ahmadu Bello Uniersity, Nigeria.

Sani, I. F. 2008. Design, Construction and Experimental Evaluation of the Product a low-cost briquette machine for rural communities in Nigeria. MSc thesis. Ahmadu Bello University, Nigeria.

Sapariya, D.D., Sheth, P.N.R. & Patel, P.V.K. 2010. Biomass As an Alternative Source of Energy in India. *International Journal of Engineering Science and Technology*, 2(10): 5457–5461.

Sarkar, J.K. & Wang, Q. 2020. Different pyrolysis process conditions of south asian waste coconut shell and characterization of gas, bio-char, and bio-oil. *Energies*, 13: 1970.

Seider, W.D., Seader, J.D. and Lewin, D.R. 2004. Product and process design principles: synthesis, analysis, and evaluation. New York: Wiley and Sons.

Sengar, S.H., Patil, S.S.A. & Chendake, D. 2013. Economic Feasibility of Briquetted Fuel. *Global Journal Of Researches in Engineering, Chemical Engineering*, 13(1): 21–26.

Severy, M.A., Carter, D.J., Palmer, K.D., Eggink, A.J., Chamberlin, C.E. & Jacobson, A.E. 2018. P e c c -s b p u. , 34(1): 73–84.

Shariff, A., Aziz, N.S.M., Ismail, N.I. & Abdullah, N. 2016. Corn cob as a potential feedstock for slow pyrolysis of biomass. *Journal of Physical Science*, 27(2): 123–137.

Sharma, A., Pareek, V. & Zhang, D. 2015. Biomass pyrolysis — A review of modelling , process parameters and catalytic studies. *Renewable and Sustainable Energy Reviews*, 50: 1081–1096.

Shen, Y., Jarboe, L., Brown, R. & Wen, Z. 2015. A thermochemical-biochemical hybrid processing of lignocellulosic biomass for producing fuels and chemicals. *Biotechnology Advances*, 33(8): 1799–1813.

Shuma, R & Madyira, D.M. 2017. Production of Loose Biomass Briquettes from Agricultural and Forestry Residues. *Procedia Manufacturing*, 7: 98–105.

Si, Y., Hu, J., Wang, X., Yang, H., Chen, Y., Shao, J. & Chen, H. 2016. Effect of Carboxymethyl Cellulose Binder on the Quality of Biomass Pellets. *Energy and Fuels*, 30(7): 5799–5808.

Sibalija, T. & Majstorovic, V. 2016.2015. *Advanced multiresponse process optimisation: An intelligent and integrated approach*. AG Switzerland: Springer.

Silva, G.F., Camargo, F.L. & Ferreira, A.L.O. 2011. Application of response surface methodology for optimization of biodiesel production by transesterification of soybean oil with ethanol. *Fuel Processing Technology*, 92(3): 407–413.

Singh, R.K. & Shadangi, K.P. 2011. Liquid fuel from castor seeds by pyrolysis. *Fuel*, 90(7): 2538–2544.

Sinnott, R.K. 2005. *Coulson and Richardson's Chemical Engineering: Chemical Engineering Design*, 4th edition, Volume 6. Oxford: Elsevier Butterworth-Heinemann.

Song, W. & Guo, M. 2012. Quality variations of poultry litter biochar generated at different pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis*, 94: 138–145.

Sotannde, O.A., Oluyege, A.O. & Abah, G.B. 2010. Physical and combustion properties of charcoal briquettes from neem wood residues. *International Agrophysics*, 24(2): 189–194.

Stephanopoulos, G. 2007. Challenges in engineering microbes for biofuel production. *Science*, 315 (5813): 801-804.

Steyn, M. & Minnitt, R.C.A. 2010. Thermal coal products in South Africa. *Journal of the Southern African Institute of Mining and Metallurgy*, 110(10): 593–599.

Stillwell, A.S. & Webber, M.E. 2016. Predicting the specific energy consumption of reverse osmosis desalination. *Water*, 8(12): 1–18.

Tabakaev, R., Shanenkov, I., Kazakov, A. & Zavorin, A. 2017. Thermal processing of biomass into high-calorific solid composite fuel. *Journal of Analytical and Applied Pyrolysis*, 124: 94–102.

Tamilvanan, A. 2013. Preparation of Biomass Briquettes using Various Agro- Residues and Waste Papers. *Journal of Biofuels*, 4(2): 47.

Tanui, J.K., Kioni, P.N., Kariuki, P.N. & Ngugi, J.M. 2018b. Influence of processing conditions on the quality of briquettes produced by recycling charcoal dust. *International Journal of Energy and Environmental Engineering*, 9(3): 341–350.

Tarasov, D., Shahi, C. & Leitch, M. 2013. Effect of Additives on Wood Pellet Physical and Thermal Characteristics : A Effect of Additives on Wood Pellet Physical and Thermal Characteristics : A Review. *ISRN Forestry*,: 1-6.

Tarasov, L., Dyke, A., Neal, R.M. Peltier, W.R. 2012. A data-calibrated distribution of deglacial chronologies for the North American ice complex from glaciological modelling. *Earth and Planetary letters,* 315-316: 30-40.

Thabuot, M., Pagketanang, T., Panyacharoen, K., Mongkut, P. & Wongwicha, P. 2015. *Effect of Applied Pressure and Binder Proportion on the Fuel Properties of Holey Bio-Briquettes*. Energy Procedia, 79: 890–895.

Thoreson, C., Darr, M. & Webster, K. 2010. Corn stover densification methods and their large-scale logistical impacts - Preliminary analysis. *American Society of Agricultural and Biological Engineers Annual International Meeting 2010, ASABE 2010*, 4: 3255–3270.

Tripathi, A. K., Iyer, P. V. R & Kandpal, T. C. 1998. A technoeconomic evaluation of biomass briquetting in India. *Biomass and Bioenergy*, 14: 479–488.

Tripathi, M., Sahu, J.N. & Ganesan, P. 2016. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. *Renewable and Sustainable Energy Reviews*, 55: 467–481.

Trubetskaya, A., Leahy, J.J., Yazhenskikh, E., Müller, M., Layden, P., Johnson, R., Ståhl, K. & Monaghan, R.F.D. 2019. Characterization of woodstove briquettes from torrefied biomass and coal. *Energy*, 171: 853–865.

Tumuluru, J.S., Sokhansanj, S., Hess, J.R., Wright, C.T. & Boardman, R.D. 2011a. A review on biomass torrefaction process and product properties for energy applications. *Industrial Biotechnology*, : 384–401.

Tumuluru, J.S., Tabil, L.G., Song, Y., Iroba, K.L. & Meda, V. 2011b. Effect of process variables on the quality attributes of briquettes from wheat, oat, canola and barley. *American Society of Agricultural and Biological Engineers Annual International Meeting 2011, ASABE 2011*, 2: 1019–1040.

Turton, R., Bailie, R. C., Whiting, W. B., Shaeiwitz, J. A. & Bhattacharyya, D. 2013. *Analysis, Synthesis, and Design of Chemical Processes* 4th Ed. Upper Saddle River: Pearson Education International.

Ubando, A.T., Rivera, D.R.T., Chen, W.H. & Culaba, A.B. 2019. A comprehensive review of life cycle assessment (LCA) of microalgal and lignocellulosic bioenergy products from thermochemical processes. *Bioresource Technology*, 291: 121837.

Ugwu, K. & Agbo, K. 2013. Evaluation of Binders in the Production of Briquettes from Empty Fruit Bunches of Elais Guinensis. *International Journal of Renewable and Sustainable Energy*, 2(4): 176-179.

Ujjinappa, S. & Sreepathi, L.K. 2018. Production and quality testing of fuel briquettes made from pongamia and tamarind shell. *Sadhana - Academy Proceedings in Engineering Sciences*, 43(4): 1–7.

van de Kaa, G., Kamp, L., Rezaei, J., 2017. Selection of biomass thermochemical conversion technology in The Netherlands: a best worst method approach. *Journal of Cleaner Production*. 166, 32–39.

Vassilev, S. V., Vassileva, C.G. & Vassilev, V.S. 2015. Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview. *Fuel*, 158:

330–350.

Viikari, L., Vehmaanpera, J. & Koivula, A. 2020. Lignocellulosic ethanol: From science to industry. *Biomass and Energy*, 46: 13-24.

Waghmare, V.S., Kale, G.R., Deshmukh, G.M. & Doke, S.D .2016. Experimental study of effect of pressure on pyrolysis of biomass. *International Journal of Research in Engineering and Technology*, 7 (5): 2319-1163.

Wang, L., Shahbazi, A. & Hanna, M.A. 2011. Characterization of corn stover, distiller grains and cattle manure for thermochemical conversion. *Biomass and Bioenergy*, 35(1): 171–178.

Wang, T., Li, Y., Zhi, D., Lin, Y., He, K., Liu, B. & Mao, H. 2019. Assessment of combustion and emission behavior of corn straw biochar briquette fuels under different temperatures. *Journal of Environmental Management*, 250: 109399.

Wang, W.C. & Jan, J.J. 2018. From laboratory to pilot: Design concept and techno-economic analyses of the fluidized bed fast pyrolysis of biomass. *Energy*, 155: 139–151.

Wang, Z., Lei, T., Yang, M., Li, Z., Qi, T., Xin, X., He, X., Ajayebi, A. & Yan, X. 2017. Life cycle environmental impacts of cornstalk briquette fuel in China. *Applied Energy*, 192: 83–94.

Ward, B. J. 2009. Human Fecal Biochar Briquettes from the Sol-Char Toilet for Use as a Solid Fuel in the Developing World. Msc thesis. North Carolina State University. United states

Ward, B.J., Yacob, T.W., & Montoya, L.D. 2014. Evaluation of solid fuel char briquettes from human waste. *Environmental Science of Technology*. 48(16):9852-8.

Waweru J and Chirchir DK (2017) Effect of the briquette sizes and moisture contents on combustion characteristics of composite briquettes. *International Journal of Innovative Science, Engineering & Technology* 4: 102–111.

Wilson, M. 2016. Optimal Compaction Pressure , Particle Size and Binder Ratio for Quality Briquettes Made From Maize Cobs. Msc thesis. Jomo Kenyatta University of Agriculture and Technology, Kenya.

Wright, M.M., Daugaard, D. E., Satrio, J. A. & Brown, R. C. 2010. Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *Fuel*, 89: 2–10.

Xu, J., Chang, S., Yuan, Z., Jiang, Y., Liu, S., Li, W. & Ma, L. 2015. Regionalized techno-economic assessment and policy analysis for biomass molded fuel in China. *Energies*, 8(12): 13846–13863.

Yang, C., Li, R., Zhang, B., Qiu, Q., Wang, B., Yang, H., Ding, Y. & Wang, C. 2019. Pyrolysis of microalgae: A critical review. *Fuel Processing Technology*, 186: 53–72.

Yorgun, S. & Yildiz, D. 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. *Journal of Analytical and Applied Pyrolysis*, 114: 68–78.

Zabed, H., Sahu, J.N., Boyce, A.N. & Faruq, G. 2016. Fuel ethanol production from lignocellulosic biomass: An overview on feedstocks and technological approaches. *Renewable and Sustainable Energy Reviews*, 66: 751–774.

Zaker, A., Chen, Z., Wang, X. & Zhang, Q. 2019. Microwave-assisted pyrolysis of sewage sludge: A review. *Fuel Processing Technology*, 187: 84–104.

Zanella, K., Concentino, V.O. & Taranto, O.P. 2017. Influence of the type of mixture and concentration of different binders on the mechanical properties of ‘green’ charcoal briquettes. *Chemical Engineering Transactions*, 57: 199–204.

Zanella, K., Gonçalves, J.L. & Taranto, O.P. 2016. Charcoal briquette production using orange bagasse and corn starch. *Chemical Engineering Transactions*, 49: 313–318.

Zhang, G., Sun, Y. & Xu, Y. 2018. Review of briquette binders and briquetting mechanism. *Renewable and Sustainable Energy Reviews*, 82: 477–487.

Zubairu, A. & Gana, S.A. 2014. Production and Characterization of Briquette Charcoal by Carbonization of Agro-Waste. *Energy and Power*, 4(2): 41–47.

8. APPENDICES

Appendix A: Experimental set-up, feedstock, and product

Figure A.1: Corn-stover

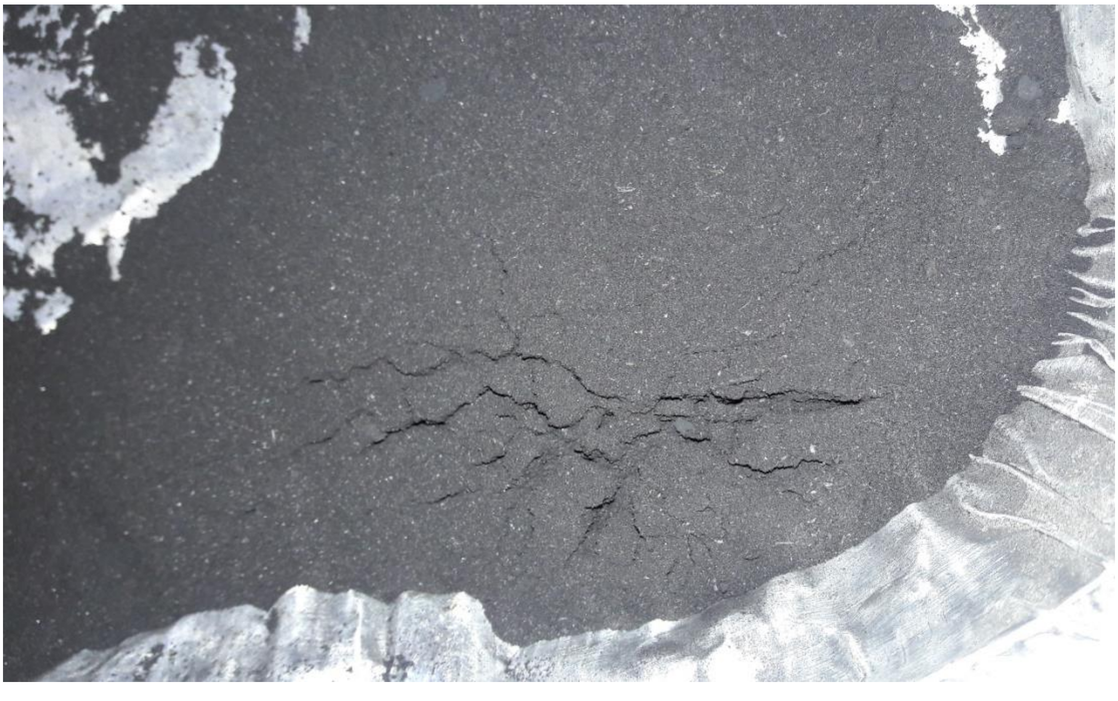


Figure A.2: Picture of biochar produced

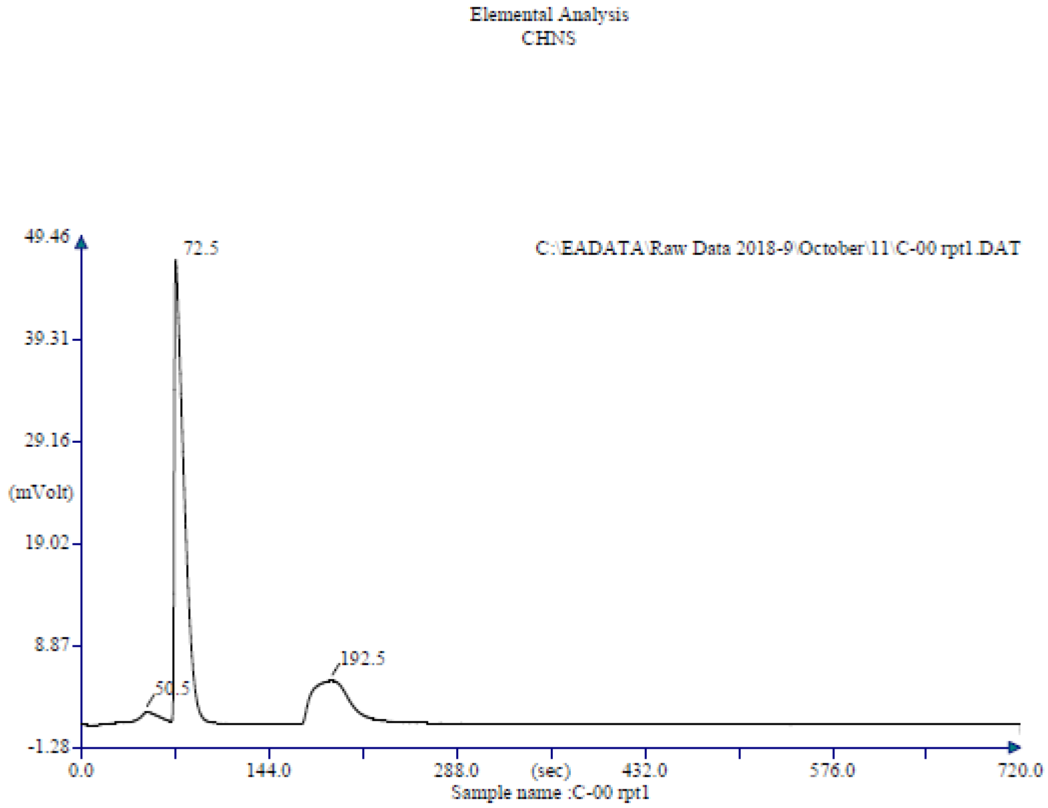
Figure A.3: Picture of corn-starch

Figure A.4: Briquettes

Figure A.5: Burning briquettes with a flame

Figure A.6: Burning briquettes

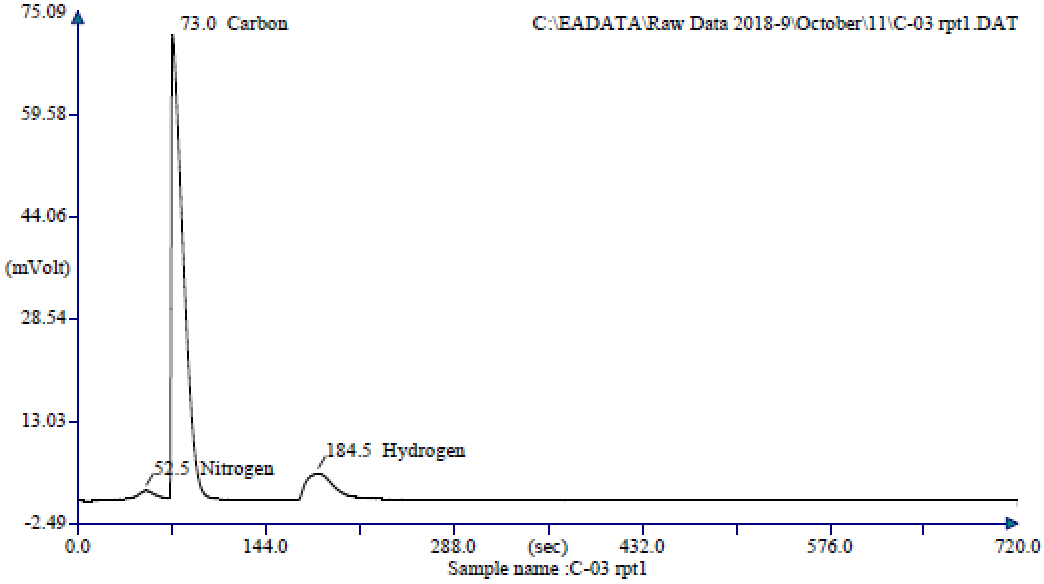
Appendix B: Analytical instrumentation of proximate and elemental analysis for feedstock and biochar



```
Retention Time    Element Name      Element %
(min)
---------------   ---------------   ---------------
0.842             Nitrogen          0.610
1.208             Carbon            38.516
3.208             Hydrogen          4.836
                                    ------
                                    43.962
```

Figure B.1: Elemental analysis results for feedstock sample

Elemental Analysis
CHNS



```
Retention Time    Element Name     Element %
(min)
---------------   ---------------  ---------------
0.875             Nitrogen         1.053
1.217             Carbon           71.404
3.075             Hydrogen         3.608
                                   ------
                                   76.065
```

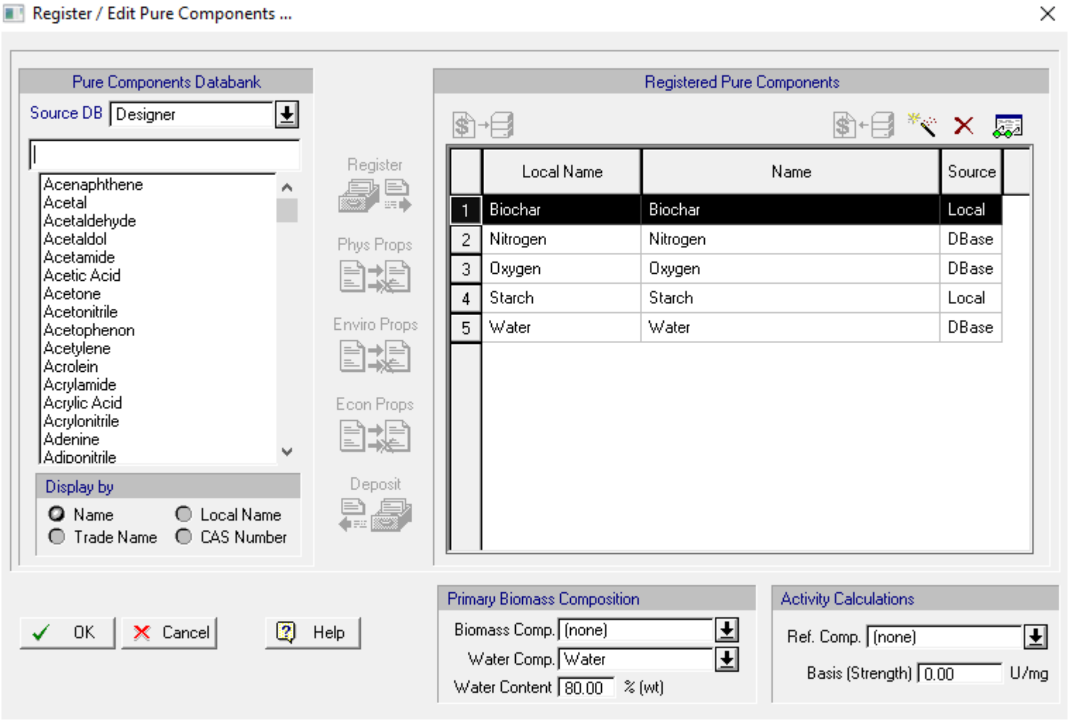
Figure B.2: Elemental analysis results for biochar sample

Appendix C: Statistical and optimization studies

Table C.1: ANOVA for all quadratic model responses

Source	**Response: HHV**					**Response: Compressevie strength**					**Response: Density**					**Response: Durability**				
Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	11,11	9	1,23	48,46	< 0.0001	11,11	9	1,23	48,46	< 0.0001	17,00	9	1,89	64,47	< 0.0001	2,089E+05	9	23211,11	112,40	< 0.0001
A-Compression pressure	8,95	1	8,95	351,04	< 0.0001	8,95	1	8,95	351,04	< 0.0001	11,34	1	11,34	387,19	< 0.0001	1,938E+05	1	1,938E+05	938,53	< 0.0001
B-Binder concentration	1,29	1	1,29	50,61	< 0.0001	1,29	1	1,29	50,61	< 0.0001	2,87	1	2,87	97,93	< 0.0001	8534,77	1	8534,77	41,33	< 0.0001
C-Drying temperature	0,0133	1	0,0133	0,5201	0,4873	0,0133	1	0,0133	0,5201	0,4873	0,3782	1	0,3782	12,91	0,0049	586,53	1	586,53	2,84	0,1228
AB	0,2485	1	0,2485	9,75	0,0108	0,2485	1	0,2485	9,75	0,0108	0,8450	1	0,8450	28,85	0,0003	1058,00	1	1058,00	5,12	0,0471
AC	0,0055	1	0,0055	0,2163	0,6518	0,0055	1	0,0055	0,2163	0,6518	0,0200	1	0,0200	0,6828	0,4279	60,50	1	60,50	0,2930	0,6002
BC	0,0300	1	0,0300	1,18	0,3033	0,0300	1	0,0300	1,18	0,3033	0,1800	1	0,1800	6,15	0,0326	60,50	1	60,50	0,2930	0,6002
A^2	0,3991	1	0,3991	15,66	0,0027	0,3991	1	0,3991	15,66	0,0027	0,0334	1	0,0334	1,14	0,3109	4430,84	1	4430,84	21,46	0,0009
B^2	0,0160	1	0,0160	0,6291	0,4461	0,0160	1	0,0160	0,6291	0,4461	0,4757	1	0,4757	16,24	0,0024	308,90	1	308,90	1,50	0,2493
C^2	0,1120	1	0,1120	4,39	0,0625	0,1120	1	0,1120	4,39	0,0625	0,7289	1	0,7289	24,88	0,0005	526,43	1	526,43	2,55	0,1414
Residual	0,2548	10	0,0255			0,2548	10	0,0255			0,2929	10	0,0293			2065,02	10	206,50		
Lack of Fit	0,2548	5	0,0510			0,2548	5	0,0510			0,2929	5	0,0586			2065,02	5	413,00		
Pure Error	0,0000	5	0,0000			0,0000	5	0,0000			0,0000	5	0,0000			0,0000	5	0,0000		
Cor Total	11,37	19				11,37	19				17,29	19				2,110E+05	19			

Appendix D: Development of SuperPro



Source DB: Designer

Display by: ● Name ○ Local Name ○ Trade Name ○ CAS Number

	Local Name	Name	Source
1	Biochar	Biochar	Local
2	Nitrogen	Nitrogen	DBase
3	Oxygen	Oxygen	DBase
4	Starch	Starch	Local
5	Water	Water	DBase

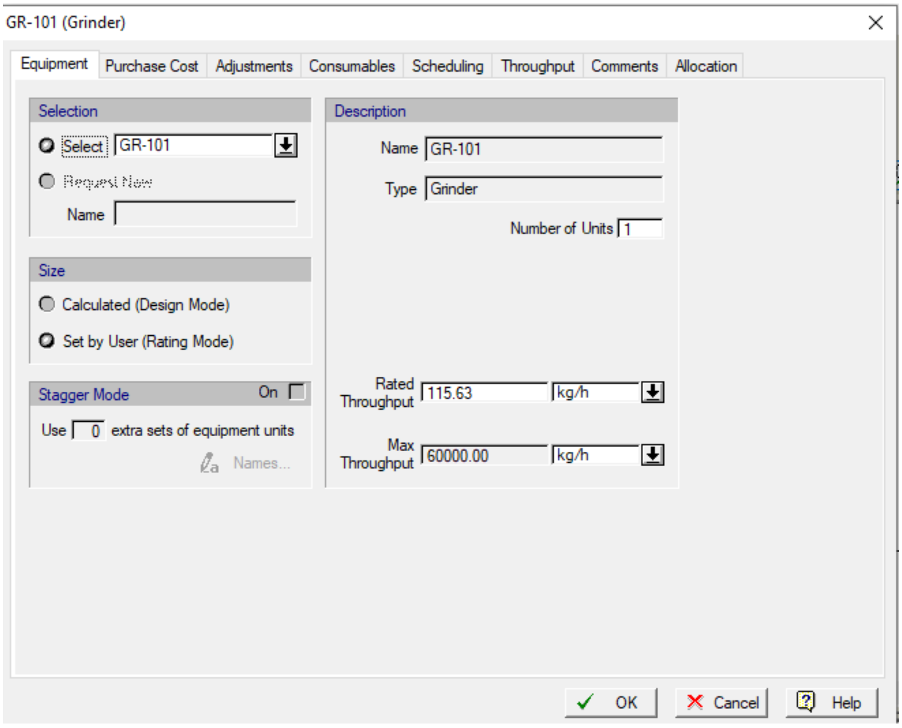
Primary Biomass Composition

Biomass Comp. (none)
Water Comp. Water
Water Content 80.00 % (wt)

Activity Calculations

Ref. Comp. (none)
Basis (Strength) 0.00 U/mg

Figure D.1: Selection of components



Selection

● Select GR-101
○ Request New
Name

Size

○ Calculated (Design Mode)
● Set by User (Rating Mode)

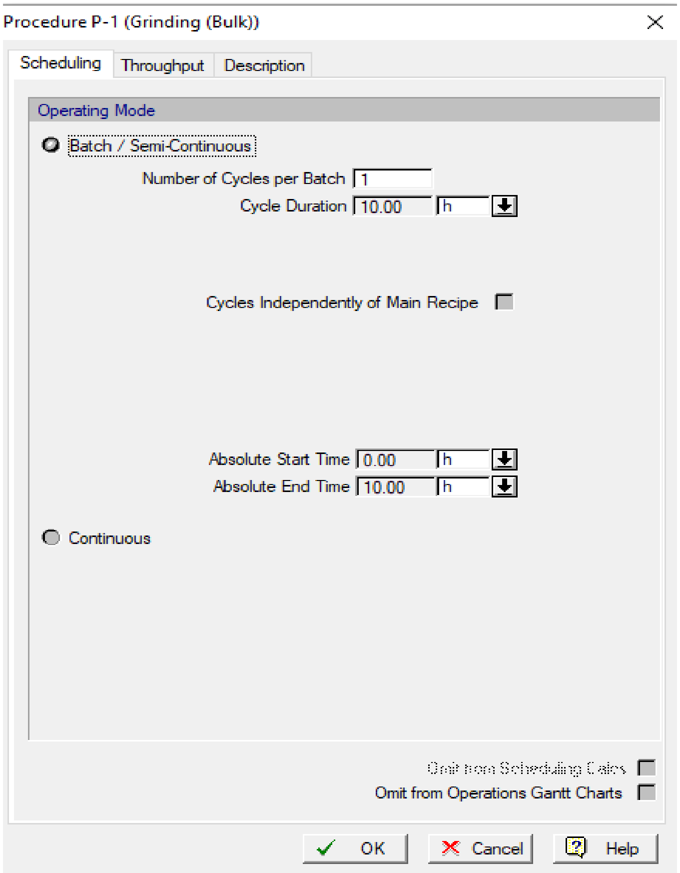
Stagger Mode On ☐

Use 0 extra sets of equipment units

Description

Name GR-101
Type Grinder
Number of Units 1
Rated Throughput 115.63 kg/h
Max Throughput 60000.00 kg/h

Figure D.2: Equipment data


Procedure P-1 (Grinding (Bulk))

Operating Mode

● Batch / Semi-Continuous

Number of Cycles per Batch: 1

Cycle Duration: 10.00 h

Cycles Independently of Main Recipe ☐

Absolute Start Time: 0.00 h

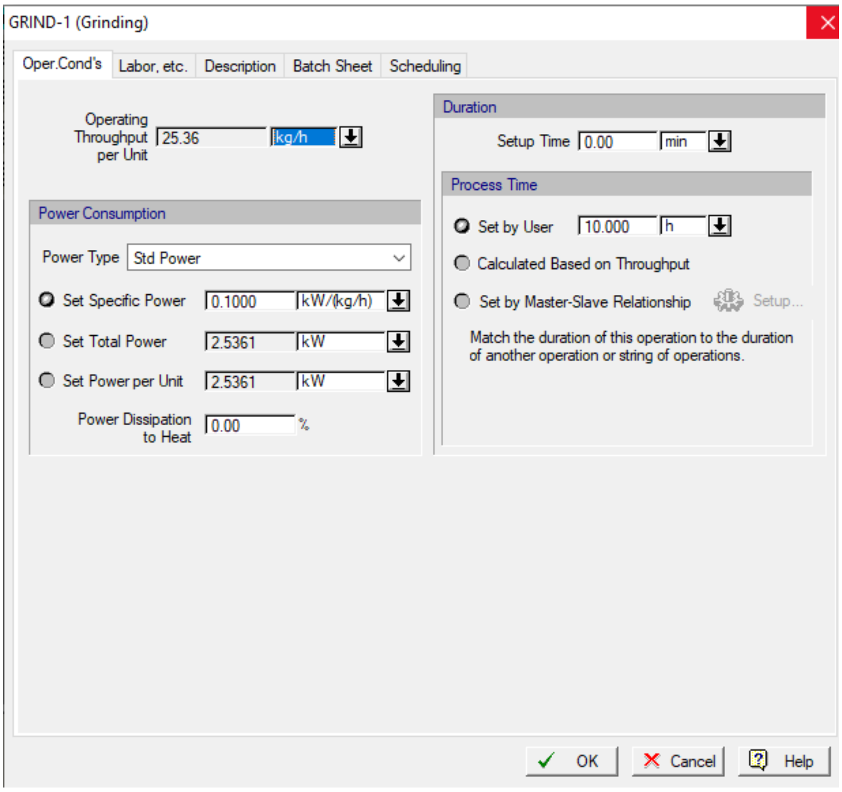
Absolute End Time: 10.00 h

○ Continuous

Omit from Scheduling Calcs ☐

Omit from Operations Gantt Charts ☐

Figure D.3: Procedure data


GRIND-1 (Grinding)

Operating Throughput per Unit: 25.36 kg/h

Power Consumption

Power Type: Std Power

● Set Specific Power: 0.1000 kW/(kg/h)

○ Set Total Power: 2.5361 kW

○ Set Power per Unit: 2.5361 kW

Power Dissipation to Heat: 0.00 %

Duration

Setup Time: 0.00 min

Process Time

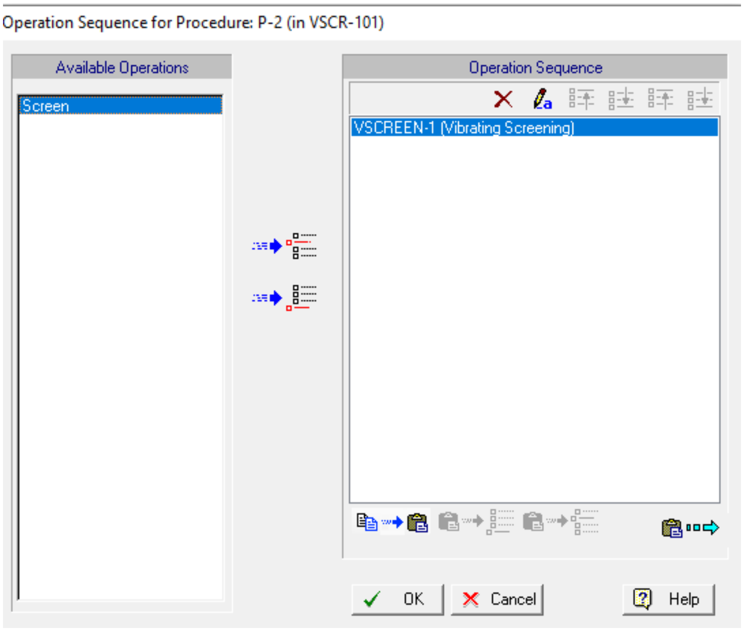
● Set by User: 10.000 h

○ Calculated Based on Throughput

○ Set by Master-Slave Relationship

Match the duration of this operation to the duration of another operation or string of operations.

Figure D.4: Operation data



Operation Sequence for Procedure: P-2 (in VSCR-101)

Figure D.5: Operation sequence for the procedure