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SCHOOL OF CHEMICAL AND BIO ENGINEERING

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PRODUCTION AND OPTIMIZATION OF BRIQUETTE FUEL FROM BREWERY WASTEWATER SLUDGE MIXED WITH SPENT GRAINS

M.Sc. Thesis

By Bontu Teshome

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A Thesis

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Investigation of Quality Briquette Fuel from Brewery Wastewater Sludge and Spent Grains

Bontu Teshome

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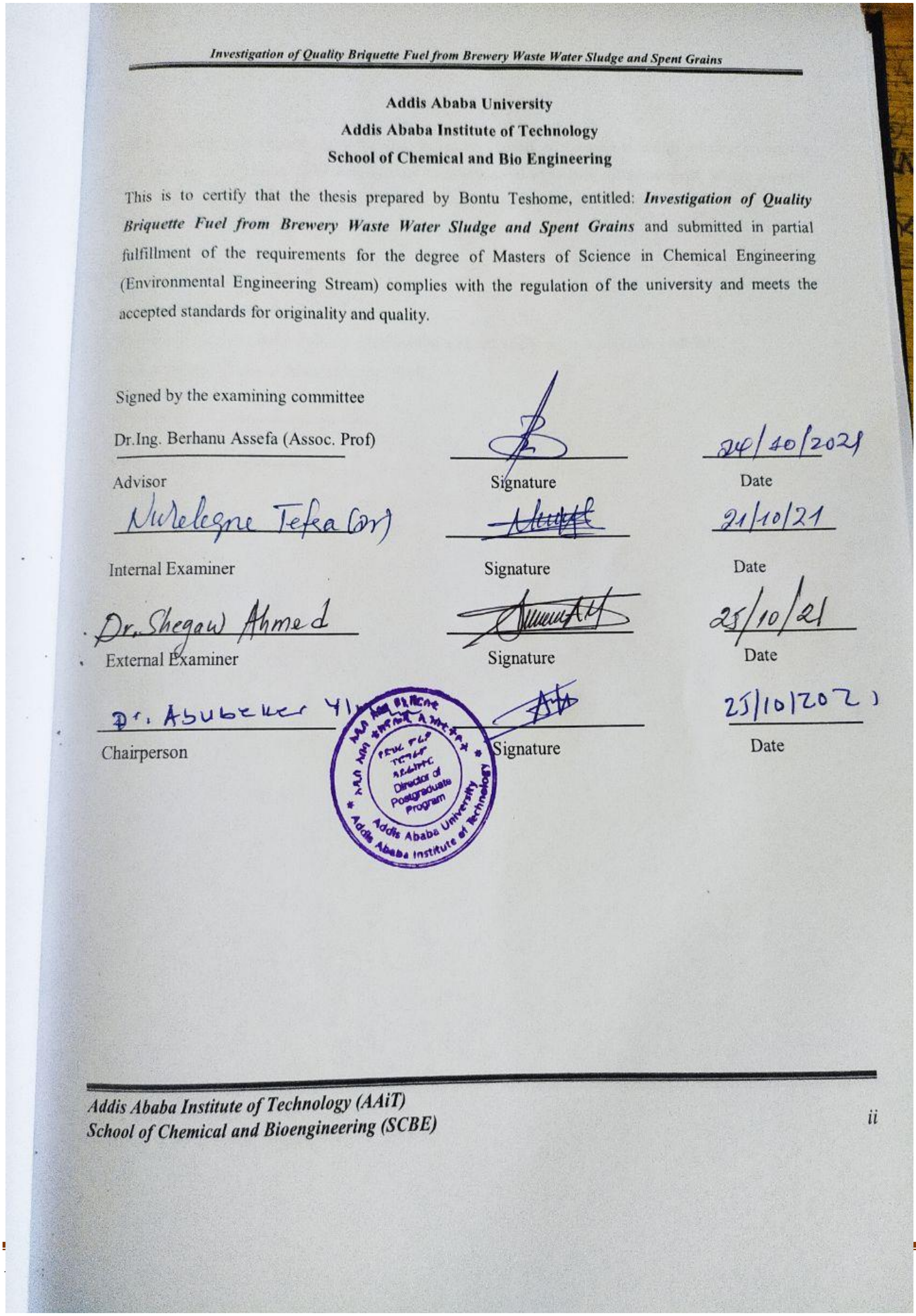

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Advisor	Signature	Date
Nurelegne Tefera (Dr)		21/10/21
Internal Examiner	Signature	Date
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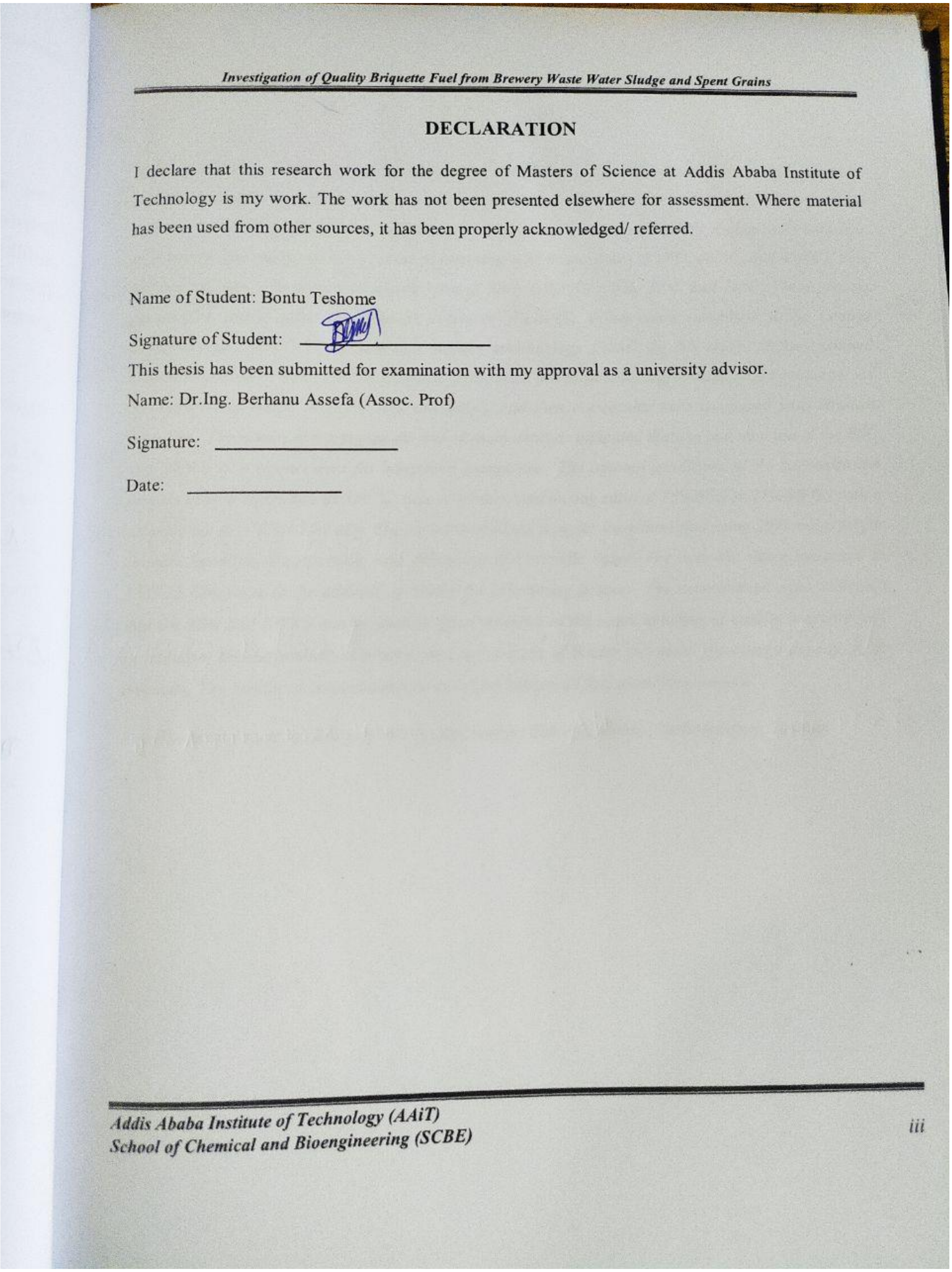

DECLARATION

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Name of Student: Bontu Teshome

Signature of Student: ______________________

This thesis has been submitted for examination with my approval as a university advisor.

Name: Dr.Ing. Berhanu Assefa (Assoc. Prof)

Signature: ______________________

Date: __________________

Abstract

Brewery wastes such as spent grain and brewery wastewater sludge are abundant brewing byproducts and have energy potential due to their high carbon contents. The objective of this study was to produce and evaluate solid fuel/briquette fuel from spent grains and brewery wastewater sludge using molasses as a binder. The carbonization process parameters were temperature (350℃, 400℃, and 450℃), time (60 min, 90 min, 120 min), and mixing ratio of BSG to BWWS (25%, 50%, and 75%). These process parameters which affect the process response (Calorific value) were optimized using Central Composite Design (CCD) of Response surface methodology (RSM). In this study, physicochemical characterizations of BSG, BWWS, Sawdust, carbonized mixed samples, carbonized mixed briquette, the non-carbonized mixed briquette was conducted, and then the results were compared with Sawdust briquette. The results of the proximate and ultimate analysis indicated that the potential use of the BSG and BWWS as a replacement for household energy use. The optimal conditions of the carbonization process were temperature at 350 ℃, time at 60 min, and mixing ratio of 75%BSG to 25%BWWS with a calorific value of 4761.10 Cal/g. The carbonized mixed samples were densified using 20% molasses for suitable handling, transporting, and enhancing the calorific value. The calorific value increased to 5385.72 Cal/g due to the addition of binder for briquetting process. The experimental work indicated that the BSG and BWWS can be used as good resource in the manufacturing of quality briquette fuel. In addition, the carbonization process and application of binder increases the energy density of the briquette. The produced briquette can be excellent household fuel alternative source.

Key Words: *Briquetting, Brewery wastewater sludge, Calorific Value. Carbonization, Sawdust*

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Abbreviations

AACNS	Addis Ababa College of Natural Science
AAiT	Addis Ababa Institute of Technology
ASTM	American Society for Testing Materials
BSG	Brewery Spent Grains
BWWS	Brewery wastewater sludge
CCD	Central Composite Design
CDM	Clean Development Mechanism
EC	Electrical conductivity
EPA	Environmental protection agency
GHG	Green House Gases
HTC	Hydrothermal carbonization
OC	Organic carbon
OM	Organic matter
RSM	Response Surface Methodology
TFC	Total fecal coliform
UASB	Up-flow anaerobic sludge blanket
WHC	Water holding capacity

Chapter One

1. Introduction

1.1 Background

Industrial solid waste pollution has becoming an increasingly severe problem throughout the globe due to the rapidly increasing Industrialization and urbanization; which has continuously extracting resources and releasing that caused a significantly increased volume of wastes (Engida et al. 2020). Especially the developing countries have been facing the problems because every year large quantities of industrial solid wastes are generated from emerging industries. There are no adequate treatment, recycling, and disposal technologies in these developing countries (Jinhui 2009). As a result of this inadequate technology of treatment, recycling, and disposal of industrial solid wastes, environmental pollution is the main problem related to the rapid industrialization, urbanization, and improvement of the living standards of people. Industrialization was mandatory for developing countries and it enables a nation to be self-reliant and consequently uplifts the nation's economy. However, as mentioned above industrialization and urbanization have also caused serious problems on environmental pollution and human health. As a result, waste appears to be an unintended consequence of industrialization and urbanization (Kunz 2010).

Industrial wastes are wastes generated during production processes such as industry, traffic, and resource development. We can classify wastes based on their components into Organic and inorganic wastes; based on their species into solid, semisolid, liquid, and gaseous wastes, and based on their pollution characteristics into hazardous wastes and common wastes. Brewing industries generate a large amount of wastes and they are among the strategic industries in the economic development of a nation. By increasing their production capacity from time to time these industries hold their significant economic position. However brewing industries are also one of the industries which produce a large amount of wastes such as effluents, brewery spent grain (BSG), excess yeast, and brewery wastewater sludge (BWWS) (Fillaudeau et al. 2006).

Brewing industries discharge large amounts of effluents because of their usage of a high quantity of water down the process. The effluents contain high-strength organic materials (Kanagachandran and Jayaratne 2006). The treatment effluents at the wastewater treatment facility produce a large amount of brewery wastewater sludge (BWWS) which must be discharged carefully. Some of the discharging methods of sludge are: landfilling, deep well injection, incineration, lagooining, solidification, and farmland application (Dolgen et al. 2004). Among all these methods the most common disposal method of brewery wastewater sludge is landfilling. The major problems of BWWS disposal are the high cost of landfilling, land space unavailability, public health problems due to offensive odor (Engida et al. 2020).

The other byproduct of concern is brewery spent grain (BSG); it is an abundant byproduct obtained in the brewing process after the ground barley is leached, and the wort is filtered. BSG is usually used as dairy cattle feed. However, in many countries where a cattle breeding on large scale is not very popular, BSG becomes a problematic byproduct regarding its storage and disposal. The quantity of this abundant by-product keeps on increasing Along with the increasing brewing capacity, Large interests are emerging in BSG, not only using as an animal feed and food additive as recent studies show (Kitryte et al. 2015) but also for briquette fuel, biogas production, substrates for microorganism cultivation, enzyme production (Mussatto et al. 2007) or as the matrix for immobilization of microorganisms (Da Silva et al. 2012). Controlling these brewery solid wastes is a critical task to minimize environmental pollution by treating, reusing, recycling, and discharging properly. Following a sustainable development strategy, waste reduction, recycling waste, and reusing are practical solutions to these wastes (Jinhui 2009).

In Ethiopia, there are about twelve brewing industries owned by six companies (Heineken, Habesha, Meta, Dashen, BGI, and Zebider). These industries produce different brands of beer products. Among these Heineken Kilinto Brewery is one of the Breweries found in Ethiopia which has a beer production capacity of 16,400hl/day. It generates a significant amount of wastewater sludge and about 3mil. Kg/month spent grains. Brewery wastewater sludge and spent grains are organic wastes that are rich in carbon content. It can be used as a source of bioenergy like biofuel, biogas, and dry fuel; whereas the potential is not known (Omer 2007). Producing fuel briquettes can be an option for the treatment and recycling of these brewery solid wastes and energy recovery from these wastes (Asamoah et al. 2016).

For briquette fuel production, various types of sludge can be used. Among these sewage sludge, which is an organic by-product of domestic, municipal, or industrial wastewater treatment plants applying biological treatment methods (Supatata et al. 2013). Sludge-based briquette fuels have a calorific value between (17-25 MJ/Kg) if their moisture content is kept below 14% which is comparable with fuel coal. This makes it suitable as a source of household energy in the form of fuel briquette (Asamoah et al. 2016). Therefore this study aims at inventing solid fuel/briquette fuel from spent grains and brewery wastewater sludge using molasses as a binder.

1.2 Statement of the problem

Most Breweries treat their wastewater using biological treatment methods which generate a large amount of Brewery wastewater sludge (BWWS). (BWWS) is produced as the result of biological treatment of brewery effluent. Heineken Kilinto Brewery also treats its wastewater generated at different places in the production process by Up Flow Anaerobic Sludge Blanket (UASB) which is a biological treating method (Zegeye 2019). Studies show Approximately 3 to 10 liters of waste effluent is generated per liter of beer produced (Kanagachandran and Jayaratne 2006). Therefore Generation of BWWS of the brewery is increasing with the rapidly increasing production of beer each year. Currently, the brewery is disposing of the BWWS by Landfilling and by applying it to the agricultural lands which are resulting in environmental impacts on surface and groundwater and severely impacting the environment. On the other hand, the High cost of landfilling and unavailability of land space as well as public health problems due to the offensive odor are major problems for the Brewery and the environment.

Brewery Spent grain (BSG) is also the other by-product of the brewery which is mainly have been used for dairy cattle feed. It corresponds to about 85% of the total solid wastes generated in the beer production process. For each hectoliter of beer produced, 14 to 20 Kg of BSG is generated (Thiago et al. 2014a). 75-80 percent BSG contains water and due to this moisture content, it deteriorates rapidly because of the growth of bacteria, yeasts, and fungi (Mohammed et al.). Storing for a long time is impossible because it is a very unstable byproduct due to its high moisture content.

Moreover, the quantities of this byproduct are keeping growing along with increasing beer production with different brands. For developing countries like Ethiopia where a cattle breeding on large scale is not very popular handling the growing amount of BSG can be a challenge. However, BSG can be used not only as an additive to animal feed but also for fuel briquettes as recent studies shows.

The production of these brewery wastes is increasing each year and current solutions of waste disposal are hardly impacting the environment. On the other hand, using brewery wastes as a raw material for the production of alternative fuel energy sources is gaining interest due to its environmental friendliness. Brewery wastewater sludge and brewery spent grains can be served as a potential resource for renewable fuel briquette production, due to having a high amount of organic matter of adequately high heating value (Nusong and Puajindanetr 2018).

This solution aims to reduce waste transportation costs, reduce the cost of landfilling, enhance the lifetime of landfills, recovers energy from waste, and minimizes human health and environmental impacts (Asamoah et al. 2016). Various investigations have been done to use industrial wastewater sludge and biomass to produce refuse-derived fuel briquettes for different applications (Chiou and Wu 2016). On the other hand, Ethiopia does not enjoy self-reliance in energy, and hence the investigation of alternative energy sources is critical to sound economic development. Therefore Recycling organic wastes like brewery wastewater sludge and spent grains for fuel briquettes is a promising alternative source of cheaper and cleaner household energy source while contributing to a sustainable environment, creating job opportunities, and generating income (Njenga and Mendum 2017).

Thus, the objective of this research was to investigate clean, environmentally friendly, alternative, renewable fuel briquettes and study the optimum conditions for fuel briquettes produced from Brewery wastewater sludge and spent grains of the beer industry using molasses as a binder. Finally, the results were analyzed and the optimum value was compared with the control briquettes produced from sawdust and Non-carbonized fuel briquette.

1.3 Objectives

1.3.1 General objective

The general objective of the research was investigating a quality briquette fuel from brewery wastewater sludge mixed with spent grains using molasses as a binder for the use as an alternative renewable energy source.

1.3.2 Specific objectives

The specific objectives of this study were:

- To characterize spent grains, brewery wastewater sludge, and sawdust
- To produce briquette fuel from carbonized spent grains and brewery wastewater sludge using molasses as a binder and analyze physicochemical properties of the briquette
- To optimize the carbonization parameters and compare the optimum fuel briquette with sawdust briquette and with the non-carbonized briquette

1.4 Significance of the study

The study should be significant in the case that it will

- Substitutes wood charcoal that has been the primary fuel for household use in Ethiopia and which has a negative impact on human health and environmental pollution due to smoking
- As concerns are increasing with the negative environmental impact of fossil fuel, using fuel briquettes produced from brewery solid wastes will have the capacity to decrease the greenhouse gas emissions
- It can also play a role in energy security and mitigation of environmental problems
- This solution reduces waste transportation costs, prolongs the lifetime of landfills, and minimizes human health and environmental impacts.
- As compared to wood charcoal fuel briquette produced from spent grain and brewery wastewater sludge is environmentally friendly, healthy (no smoke), economical, and reduces the impact of deforestation.

1.5 Scope of the study

The scope of the study was the collection of brewery wastewater sludge and spent grains from Heineken brewery, kilinto brewing factory and molasses from National Alcohol and Liquor Factory found at Mekanisa, Addis Ababa; laboratory setup, sample preparation, characterization of the samples, carbonization of samples, pulverizing of samples, mixing of the samples, molding (pressing) of the sample, characterization of the briquette fuel produced, result in analysis and finally comparing the product with the control samples (sawdust briquette and non-carbonized briquette).

Chapter Two

2. Literature review

2.1 General overview of wastes generated from breweries

The brewing sector is taking the strategic economic place in the food industry development (FAO 2009). This sector has shown new developments dynamically starting from ancient tradition till recent technologies and scientific progress (Fillaudeau et al. 2006). Despite the brewing industries are discharging large quantities of environmentally polluting wastes throughout the year (Braeken et al. 2004; Parawira et al. 2005) this industry holds an important economic portion of all countries (Fillaudeau et al. 2006, 2007). Following Tea, Carbonates, Milk, and Coffee, Beer is the fifth most consumed beverage universally (Fillaudeau et al. 2006). The brewing process constitutes two main steps, i.e., the brewing process and packaging of the finished products. The byproducts (e.g., spent grains, excess yeast, etc.) generated from these steps are responsible for environmental pollution when disposed of untreated.

On the other hand, high volumes of wastewater /effluents will be generated in the process of cleaning bottles, tanks, machines (Doubla et al. 2007). These wastes are large in volume and have high moisture contents and they contain water, spent grains, excess yeast, trub, spent hops, waste beer, caustic and acid cleaners. They have high organic matter contents and can be easily biodegradable as they consisted of volatile fatty acids, ethanol, starch sugars, kieselguhr, yeast, etc. The effluents will then be the route for wastewater treatment after separating the solids and finally being concentrated as sludge.

The other outlet stream is the solid waste disposal stream which contains spent grains, Trub, and hops. Both distinct waste streams from the brewing process have different processing implications even though they both have high BOD levels (Thomas and Rahman 2006). For the fact that different processes take place in the brewery, the quality and quantity of brewery effluent can vary significantly. The different processes are raw material handling, wort preparation, fermentation, filtration, CIP, and packaging (Driessen and Vereijken 2003).

2.2 The volume of BWWS and BSG generated from the brewery

In modern and efficient brewing industries, to produce 1 liter of beer it needs from 4 liters to 10 liters of water which 2/3 of it is used in the brewing process, and 1/3 of it is used in the cleaning activities (DEVOLLI, ARIOLA et al. 2019). Various technological improvements have been done to improve the volume of effluent generated. However, it has been studied that approximately between 3 to 10 liters of waste effluent are generated for 1 liter of beer production (Kanagachandran and Jayaratne 2006). Spent grain is also the other most abundant brewing by-product which corresponds to around 85% of total by-products generated. This amount corresponds to around 14 to 20 kg of brewery spent grain (BSG) for each hectoliter of beer produced (Thiago et al. 2014b).

2.3 Environmental challenges of brewery waste disposal

Brewing industries generate a large amount of solid waste during processing and packaging and this waste has the potential to be an environmental problem if not properly managed. The volumes of biomass wastes generated by Food and Beverage industries are considered to be one of the most severe environmental pollution issues (Siqueiros et al. 2019). These issues must be handled in the least costly manner and some cases profitably to save storage space, minimize the risk of microbial growth activity, and cost reduction.

The brewing process affects the environment negatively both during production and in the waste management phase. BSG is the largest brewery waste by volume followed by excess brewers' yeast. As the BSG deteriorates rapidly, it must be removed quickly from the brewery to avoid undesirable bacterial growth. 70% of BSG is used as animal feed, but due to its high moisture content and microbial activities, it cannot be stored for more than 48 hours. The remaining 10% of BSG goes to produce biogas, and the 20% is landfilled. Each ton of BSG in landfills releases 513 kg CO_2 equivalent greenhouse gases. Landfilling brewery wastewater sludge (BWWS) and applying it to agricultural lands also results in environmental impacts on groundwater and surface water which is severely affecting the environment (Briggs et al. 2004).

2.4 Energy potential of brewery wastes

Energy can be broadly classified into renewable energy and nonrenewable energy. It is very important in providing basic services such as heating, cooking, lighting for human beings. In developing countries demand renewable energy which includes solar, wind, biomass, hydropower, geothermal and tidal energy, has been increasing over the years where people in rural and urban centers lack access to adequate commercial energy (Onchieku et al. 2012). Energy derived from biomass feedstock appears to be attractive because of its abundance, renewability, and positively affecting the environment. It releases no net CO_2 to the environment and releases very low sulfur content (Onchieku et al. 2012). Brewery solid wastes are mostly classified as biomass feedstock. Biomass is an abundant, renewable, and sustainable fuel that can reduce greenhouse gas emissions compared with fossil fuels. Consequently, using these clean, renewable, and sustainable sources of energy is likely to be an attractive clean development mechanism (CDM) option for minimizing greenhouse gas (GHG) emissions (Li and Hu 2003; Chen et al. 2009).

The energy from biomass (agricultural residues) can be harnessed through the process of carbonization by allowing feedstock combustion in an oxygen-free environment. The carbonization process occurs when the material is subjected to high temperatures in the absence of oxygen (Bogale 2010). BSG is a lignocellulose material and is a typical biomass feedstock obtained from the brewing process. It consists of 17% cellulose, 28% lignin, and 2% non-cellulosic materials (Manyuchi et al. 2017). BWWS is also organic solid waste generated in breweries as a result of biological wastewater treatment where a large amount of biomass has resulted which finally settle as sludge (Kanagachandran and Jayaratne 2006).

The brewery industry is generating brewers' spent grain (BSG) and BWWS that have the potential for conversion into energy. Huge volumes of BSG and BWWS are generated daily (Manyuchi et al. 2017). Therefore energy can be harnessed from these Brewery wastes through combustion, carbonization, anaerobic digestion, and gasification. Various types of renewable energy including bioethanol, biogas, syngas, and biomass briquettes can be obtained from these BSG and BWWS (Mussatto et al. 2006).

2.5 International experiences to use brewery wastes as energy potential

Nowadays the focus of solid waste management is on the waste amount reduction mechanisms. Solid waste management methods include methods such as landfilling, incineration, composting, etc. However, incineration and sanitary landfills are adversely affecting the environment. Composting is a widely used waste handling method but it needs a subsequent removal of non-bio digestible materials that cannot be converted in the composting process. The resistant non-biodegradable organic materials need to be either disposed of or can be utilized as energy sources such as solid fuel briquettes and this solution will radically reduce the volumes of wastes to be disposed of unnecessary cost of landfilling (Chaiklangmuang et al. 2008).

The utilization of huge-volume brewery solid wastes and by-products as an essential raw material for energy products has been well-researched and has come to an application to regulate environmental and economic sustainability. Large breweries mostly supply their spent grain to animal feed processing industries that use the spent grain as a base material for animal feed production, rather than delivering directly to farmers. Spent grain is a low-cost alternative to expensive materials such as soybean therefore it has an economic advantage to the animal feed market (2017). The other method used for the utilization of BSG is composting, however, is difficult because of its high moisture content (Thomas and Rahman 2006).

In addition to the use of BSG as animal feed and composting, energy production is another viable use for BSG. Energy generation can be conducted through direct combustion, or the production of biogas (methane) or bioethanol through fermentation (Mada 2020). Therefore various studies done internationally have shown that renewable energy can be harnessed from brewery solid wastes.

2.6 Ethiopian context of using brewery wastes for energy

Energy is a critical input for growth and an important component for the survival of human beings. Energy security, the environmental impact of fossil fuels, and deforestation problems are the major energy concerns. Biomass energy is one of the clean alternative renewable energy which recovers energy from wastes. However, the use of biomass energy sources in most developing countries including Ethiopia is by direct burning the biomass and it is more traditional that leads to indoor air pollution as a result cause health and environmental problems.

Ethiopia depends mainly on traditional biomass burning mechanisms and it corresponds to more than 85% of the energy consumption of the nation; as more than 90% of the population live in rural areas. This has been causing different environmental, social, and economic impacts. For countries like Ethiopia not having fossil fuel resources; it may be a critical energy supply challenge soon because of depending on oil import. Therefore, there is high demand for the development of alternative renewable, clean, sustainable, biomass energy technologies in Ethiopia for utilization of biomass wastes to energy through familiarizing the briquetting technology (Rorisa et al. 2019).

2.7 Investigation of briquette fuel from BWWS and BSG

In addition to many applications cited, energy can be harnessed from brewery wastes like BWWS and BSG through biogas production by anaerobic digestion and briquetting (Thiago et al. 2014b). Briquetting this type of wastes for use as a fuel is an option for the treatment, recycling, and handling of these wastes next to biogas production which is a common use of energy produced from these types of sludge based wastes (Diener et al. 2014).

2.7.1 Brewery wastewater sludge

Brewing industries mostly use biological treatment methods for their effluent treatment; therefore huge amounts of bacterial load are produced in the effluent which eventually settles as sludge. Brewery effluent is a waste product that is dumped into the draining system. This brewery effluent has a high organic content, making it a very high strength in terms of chemical oxygen demand (ranging from 1000 mg/L to 4000 mg/L) and biochemical oxygen demand (up to 1500 mg/L) (Kanagachandran and Jayaratne 2006).

Sludge is defined by the US Environmental Protection Agency (EPA) as the semi-liquid residue or slurry left over after industrial water and wastewater treatment. It is a collection of materials extracted from sewage during the waste treatment process. Industrial wastewater solids, whether produced by biological or physical-chemical processes, are referred to as sludge (Gebrehiwet 2019). Disposal of Sludge disposal has been extremely expensive, typically accounting for more than half of the wastewater treatment facility operator's budget, in addition to causing environmental issues (Alayu et al. 2018). The physical and biochemical characteristics of brewery wastewater sludge for the typical brewery industry is presented in Table 2.1.

Table 2.1: Physical and biochemical characteristics of BWWS (Alayu and Leta 2020)

Parameters	BWWS
	Mean ± SD
PH	7.85 ± 0.01
EC(µs/cm)	2352.67 ± 2.52
WHC (%)	54.0 ± 1.00
OC (%)	49.10 ± 0.10
OM (%)	84.65 ± 0.17
TN (%)	3.84 ± 0.04
P_2O_5 (%)	5.92 ± 0.01
K (mg/kg)	1.61 ± 0.38
Na (mg/kg)	0.37 ± 0.02
Ca (mg/kg)	3.19 ± 0.34
Mg (mg/kg)	1.19 ± 0.26
TFC (MPN/ml,as FW)	$5.46\times10^6 \pm 0.02$
TFC(MPN/ml,as DW)	$3.06\times10^4 \pm 0.01$

FW (fresh weight) and DW (dry weight) pathogen content of the sludge

2.7.2 Brewery spent grains

The first solid waste formed throughout the process is brewer spent grain (BSG), also known as malt bagasse, which takes into account the present model of breweries that acquire malt from malting industries (Figure 2.1). The mashing process is one of the first steps in the brewing process, and it involves making the malt and cereal grains soluble in water. There is an exhaustion of malted grains milled during the mashing process as all of the key soluble components that make up the sweet wort is extracted. The spent grains and wort (water containing the extracted materials) must be separated after extraction. The solid content of the mash is normally 25-30% (Fillaudeau et al. 2006). This residue (BSG) has a high nutritional content and is the largest solid residue produced, resulting in a significant amount of residue throughout the year at little or no expense (Salihu Aliyu and Muntari Bala 2010). This residue accounts for around 85% of the overall waste produced throughout the brewing process.

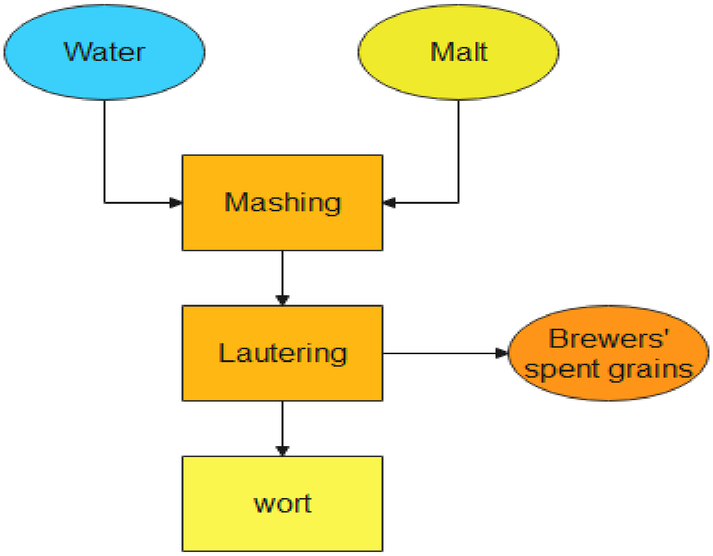


Figure 2.1: Production process of beer wort with solid byproduct (spent grain)

Normally, for every 100 kg of processed grains, 125 kg to 130 kg of wet bagasse is produced, with an average content of 80-85% when filtered via a press. For each hectoliter of beer produced, this amount corresponds to 14 to 20 kg of bagasse (Thiago et al. 2014b). Approximately 80% of the malt mass is solubilized during the mashing process, leaving the insoluble fractions in the bagasse. The brewery provided us with spent grains as a byproduct. Following the mashing process, waste grains were separated, and a sample was taken for hydrothermal carbonization (HTC) to reduce the impact of biological activity. Hydrothermal carbonization (HTC) is a thermal valorization process that takes place at high temperatures (200 to 260 °C) and high pressures in subcritical water (Jackowski et al. 2019).

As a precaution, storage in the fridge was avoided, and rapid usage was implemented as a precaution to minimize any potential bias associated with the storage of spent grain (Pearce et al. 2016). Brewer spent grain is often sold for animal feed production, although it can also be mixed along with other process leftovers. Even if they are useful destinations, it is possible to investigate the application of this by-product to attain its rich nature in some components (Thiago et al. 2014b) and the composition and nutrition value of wet spent grain is presented in Table 2.2.

Table 2.2: The composition and Nutrition value of wet spent grain (Hotta et al. 1996)

Parameters	Mean	Range
Dry matter (%)	23.6	24.2-30
Crude protein (%)	23.4(18.5)	18.4-26.2 (13.9-21.3)
Crude fibre (%)	17.6(7.9)	15.5-20.4 (6.6-10.2)
Ether extract (%)	7.7(7.7)	6.1-9.9 (5.6-9.2)
Total ash (%)	4.1	3.6-4.5
Digestible energy (MJ/Kg dry wt.)	13.8	13.0-14.8
Gross energy (MJ/Kg dry wt.)	21.4	21.1-21.8
DOMD* in vivo (%)	59.4	55.2-64.3
DOMD* in vitro (%)	48.6	44.8-51.5

DOMD* = Digestibility of organic matter (dry)

2.8 Briquette Fuel Manufacturing

Briquetting is one of the various procedures that are classified as densification technologies in general. Briquetting is a technique similar to pelletizing in which the raw material is compressed under high pressure, causing the lignin in the wood or biomass to be freed, allowing the material to bind into a hard briquette. Agglomerating and densifying residues can increase their usage in energy production by increasing the calorific value of the fuel, lowering the cost of transportation to metropolitan regions, and possibly improving the fuel situation in rural areas (Nikolaisen and Jensen 2013).

Traditionally, briquettes are created by combining briquette filler and a binder. Stock fines, such as metal fines and coal fines, minerals, fly ash, and other finely separated materials that can be used as briquette fillers are examples of briquette fillers. Briquette filler has also been made from recyclable materials such as metal scrap and organic waste such as municipal sewage sludge, waste paper, and so on. Asphalt, tar-pitch, cement, Starch, Starch molasses, molasses, lime molasses, latex, and lignosulfonates have been used as binders in traditional briquette formulations (Kong et al. 2012).

Briquettes are formed by compressing biomass material into a solid unit, either with or without a binder, using human or automated presses/machines or other ways. Binders are added to raw materials that can't densify enough to make robust briquettes on their own. When making briquettes from raw materials with low agglomeration capacity, a binding agent is necessary (Njenga and Mendum 2017). The addition of a binder to the briquettes results in improved bonding and more stable characteristics (Wamukonya and Jenkins 1995; Bhattacharya et al. 2002). Briquettes' physical properties, such as density, compressive strength, and impact resistance index, have all improved significantly as a result of the binders (Dolgen et al. 2004; Sen et al. 2016)

The amount of binder to use is determined by the raw material's and binding agent's binding characteristics. In addition, the briquette machine's ability to densify and bind decides whether or not a binding agent is required. That is, using a high-pressure briquette machine would eliminate the requirement for a binding agent. To facilitate processing, the feedstock must have an optimal amount of material with good binding ability. According to some recent experiments, 6% to 25% of such material should be present in the feedstock for efficient briquetting (Asamoah et al. 2016).

2.8.1 Raw materials for briquette fuel manufacturing

Non-carbonized (fresh) raw materials such as banana peelings and leaves, maize cobs, coffee husks and rice husks can be used to make fuel briquettes. However, before being compacted into briquettes, biomass materials can be carbonized (burned under controlled oxygen to eliminate volatile gases and liquid) before the briquette. The qualities of the briquettes produced are influenced by the raw materials used in briquetting (Asamoah et al. 2016). Sludge of various sorts can be utilized to make briquettes. Sewage sludge, for example, is an organic by-product of wastewater treatment plants that uses biological methods to treat home, municipal, or industrial wastewater (Supatata et al. 2013). Sludge-based fuel briquettes have a calorific value of 17-25 MJ/kg equivalent to fuel coal when the moisture level is less than 14 %, making them an excellent source of fuel briquettes. The high moisture level of sludge makes it a technical challenge to recycle into briquettes. Sludge is also known to contain pathogens that are potentially dangerous to people. As a result, caution must be exercised when handling sludge. The good news is that the carbonization of dried sludge in a kiln is an effective pathogen-killing technique (Wang et al. 2013).

Lower moisture, volatile matter, and ash level, together with higher fixed carbon content, are required for a high-quality, efficient fuel briquette. To achieve the appropriate briquette quality, the raw materials and briquetting methods should ensure that this is achieved (Asamoah et al. 2016). Due to its high organic content, brewer spent grain (BSG) or malt bagasse can also be used as a briquette fuel raw material. It is highly unstable as a product due to its high moisture content and is prone to microbial contamination, particularly by filamentous fungi, thus it should be removed from the brewery as soon as possible. When it comes to conservation strategies, drying is the most effective. Because excessive moisture content can easily lead to microbial infection and increase storage and transit weight and volume (Thiago et al. 2014b).

2.8.2 Physical and chemical characteristics of biomass for briquette manufacturing

To make good quality briquette the raw materials selected should be characterized for the proximate and ultimate analysis as shown in Table 2.3.

Table 2.3: Physicochemical characteristics of biomass for briquette (Asamoah et al.2016)

	Properties	Unit	Requirement
Proximate analysis	Moisture content	%	6-14
	Ash content	%	Less than 4 to avoid slagging
	Particle size	Mm	1-10mm with 10-20% powdery
	Fixed carbon	%	9-25
	Calorific value	MJ/kg	10-35
	Heating value	MJ/kg	12-20
	Bulk density	kg/m^3	More than 50
	Volatile matter	%	50-90
Ultimate analysis	Carbon(C)	%	40-55
	Hydrogen(H)	%	5-8
	Oxygen(O)	%	35-48
	Nitrogen(N)	%	0-1
	Sulfur(S)	%	0-2
	Chloride(Cl)	%	0-1

2.8.3 Production of briquette from carbonized waste

The manufacturing process flow of briquette fuel from carbonized raw material is shown in Figure 2.2.

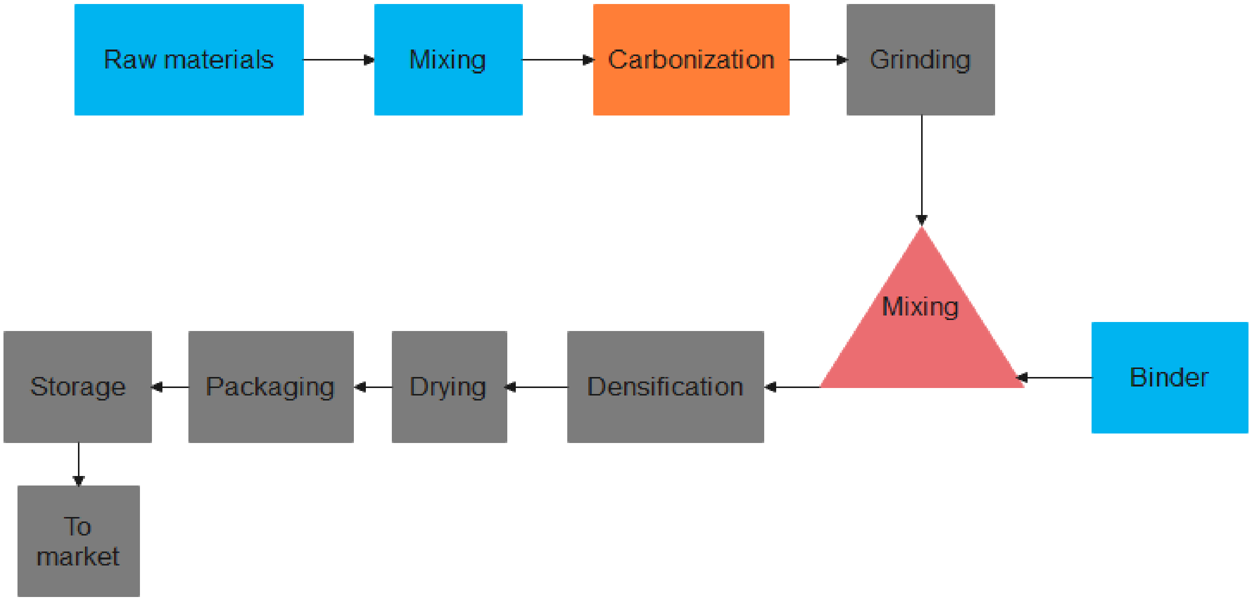


Figure 2.2: Manufacturing process of briquette Fuel from carbonized raw material

Carbonization (also known as pyrolysis) is a high-temperature anaerobic decomposition process in which biomass is "burned" in the absence of, or with restricted, oxygen (Haykiri-Acma et al. 2013). This decreases the volatile matter and moisture content of the raw material but results in the high carbon content of the carbonized material. As a result, the briquettes may persist for a long time, emit fewer hazardous gases, and have high mechanical strength (Onchieku et al. 2012). Carbonization can be used on non-carbonized briquettes or raw waste. The shape of the briquette may be distorted in the latter case. Carbonization is commonly done in batch reactors and is influenced mostly by temperature and reaction time. Raw materials must be dry, with a moisture content of less than 15%, to reduce energy demand during carbonization. In addition, because binding components in raw materials are lost during carbonization, a binder with a strong binding property must be utilized (Asamoah et al. 2016).

Because of the carbonization that occurs during the preprocessing of the sludge, the briquettes generated have no odor and are bacteria-free. Carbonized briquettes can be made using a screw press or a hydraulic press. A hydraulic press transfers energy from an electric motor to the piston via a high-pressure hydraulic oil system. It has the advantage of being simple to operate, low maintenance, and energy-efficient. The disadvantages of employing a hydraulic press to make carbonized briquettes are the slower press cylinder, as well as the lesser density and abrasion resistance of the briquettes produced.

Brewery wastewater sludge and spent grains are often dewatered and dried (for example, in a rotary kiln or in drying beds) to reduce moisture content below 15%. The sludge is subsequently carbonized for 1 to 2 hours at temperatures between 350 and 450°C. After that, the mixture of carbonized sludge and spent grains will be crushed, sieved, and combined with a 20% binder (molasses). As a result, the carbonized briquettes will be densified using a hydraulic press (Supatata et al. 2013).

2.8.4 Binders used for briquette manufacturing

The fact that charcoal is a material that is devoid of plasticity and hence needs a sticking material or an agglomerating material to enable a briquette to be formed. Therefore briquetting requires the binder to be mixed with the charcoal fines, a press to form the combination into a cake or briquette, and then a drying oven to cure or set the briquette by drying out the water so that it is strong enough to be used in the same burning equipment as regular lump charcoal. The binder substance aids in holding the charcoal particles firmly in place, resulting in a briquette that is sufficiently hard to hold up in the fire (Zubairu and Gana 2014).

As a result, the binder material is employed to reinforce the briquettes. Binding can include water-soluble organic binders like paper, lime, molasses, or starch. Lime is added to prevent slagging, which can occur sometimes. Following the mixing of the raw materials with the binders, the feedstock can be densified at a pressure of 5.5-34.5 MPa (55 bar to 345 bar) to make briquettes using a hydraulic press, for example (Supatata et al. 2013).

2.8.5 Key physical and chemical characteristics of briquette fuel

The following are key physical and chemical characteristics of briquette fuel. *Total carbon content* represents the amount of carbon available in the waste material which could eventually be burned for heat to be released. *Volatile matter* is the part of biomass that may be released when the biomass is heated up, for example, during carbonization. On the other hand, the high volatile matter may result in the high release of emissions during burning. Therefore, the low volatile matter is of importance.

Fixed carbon is useful because it determines the amount of solids remaining once the carbonization process has been completed, i.e., used subsequently to produce briquettes. In this case, the higher carbon content in the feedstock is likely to result in long-lasting and mechanically strong carbonized briquettes. *Ash content* is a powdery residue that remains after the burning of a material. It is comprised of non-combustible materials (e.g., minerals). A higher ash content will result in ash slagging. This inhibits the combustion process by supporting overheating of the burning device and subsequently its corrosion. Therefore, the optimum ash content in the feedstock is needed to control the burning process and to maintain the machine parts.

Moisture content in feedstock may increase the production cost in terms of energy, due to the fact that more energy is required to reduce the water content during drying and densification. Lower moisture content may cause flakiness in the raw materials. This implies that moisture is also needed in the right amount to assist the bonding process of the feedstock (Asamoah et al. 2016). *Bulk density* results in high durabilities, such as resistance to shear stress. It may increase the cost involved in transporting the raw material in terms of its weight or volume depending on the scenario - high and low density, respectively. The use of a smaller *particle size* tends to increase the bonding ability of the raw materials used for producing briquettes. On the other hand, using different particle sizes also enhances the bonding ability, because larger particles get filled with the smaller particles to form an interlocking bond. *The calorific value* determines the amount of energy released during the complete combustion of a unit mass of briquette (Asamoah et al. 2016).

Moisture content, ash content, and flow characteristics are three main physicochemical parameters to consider while making good briquettes. First, moisture content should be minimal since high moisture content will cause problems in firing and will require a lot of energy to dry, which will impact the quality of the combustion. Second, the ash content of biomass should be less than 4%, because biomass with high ash content is primarily made up of massive alkaline earth metals. The fusing temperature of these components is low, increasing the slagging potential. Third, there should be a high level of flow characterization. The briquetting process will be made more difficult by particles with low flow characteristics. Conveyors, bunkers, and storage silos designed for briquetting can easily handle more granular homogeneous materials.

Chapter Three

3. Materials and Methods

3.1 Materials

The brewery wastewater sludge and brewery spent grain collected from Heineken Kilinto Brewery were used in this study. Molasses was used as a binding material for briquette production. The molasses was collected from National Alcohol and Liquor factory located at Mekanisa, Addis Ababa. The samples were collected directly from the discharge point of the factory. The study was conducted at the School of Chemical and Bio Engineering laboratory, Addis Ababa University.

3.1.1 Laboratory Equipment and Instruments

The laboratory equipment and the instrument used for the study are presented in Table 3.1

Table 3.1: List of Lab equipment and instruments used in this study

Instrument	Model	Use
Drying Oven	202-OA Electric thermostatic heated dry box	To dry the specimen
Muffle furnace	VF2 Vecstar Ltd., U.K	To carbonize the samples and to determine the Ash content and Volatile content
PARR® Adiabatic Bomb Calorimeter	1241EF ADIABATIC CALORIMETER	To determine the calorific value of samples
Elemental analyzer	EA1112 Flash CHNS/O-analyzer	To determine the ultimate analysis of the samples
Grinder (Beater Mill)	5657 HAAN, West Germany	To pulverize the samples
Pelletizer(hydraulic press)	OMCN 158, ITALIA	To densify the carbonized samples into pellets

3.2 Methods

3.2.1 Preparation of samples

Brewery wastewater sludge and spent grains were sun-dried in drying beds for four days to reduce the moisture content. The samples were dried until the moisture content was below 15%. The moisture content of the samples was determined using standards of the American Society of Testing Materials (ASTM D3173-03, 2004) from equation 3.1. The samples were then pulverized by the Attrition mill to reduce their sizes in the range of required size according to the requirement of the characterizations.

$$\text{Moisture content } (\%) = [\frac{W_0 - W_1}{W_0}] \times 100 \quad \ldots\ldots\ldots\ldots 3.1$$

Where, W_0 = initial weight of the sample before drying

W_1 = final weight of the sample after drying

The BWWS and BSG were carbonized using a Muffle furnace at a temperature range of 350 - 450 ^{o}C for the time range of 1-2 hours. The samples were then pulverized and mixed at the ratio of 25%, 50%, and 75% of spent grain to wastewater sludge. The mixture comprising carbonized, pulverized and mixed spent grains and sludge were then mixed with 20% of the binder (molasses). Experiments and characterizations were conducted in different laboratory institutions. Proximate analysis to know the characteristics and property of the raw materials to their energy content, carbonization process, and briquetting were done at the Addis Ababa Institute of Technology, School of Chemical and Bio Engineering laboratory (AAiT) while calorific value determination was done at Ethiopian Geological Survey laboratory. Ultimate analysis (Elemental analysis) was done at Addis Ababa University College of Natural Science (AACNS) to know the elemental composition of the materials.

3.2.2 Characterization of samples

3.2.2.1 Proximate analysis

The proximate analysis of the BWWS and BSG was determined according to the American Society of Testing Materials (ASTM methods). These included determination of Moisture content, volatile matter, ash content and fixed carbon content of the BWWS and BSG. Moisture content is the amount of water contained in the material. It was determined using the method (ASTM D3173-03, 2004) and calculated from equation 3.2.

$$\text{Moisture content)} = [\frac{W_0 - W_1}{W_0}] \times 100 \text{ .... } 3.2$$

Where:

W_0 = initial weight of the sample before drying

W_1 = final weight of the sample after drying

Ash content refers to an inorganic residue left after the sample is completely burned. It was determined using the ASTM method (ASTM D3174-02, 2004) and calculated from equation 3.3.

$$Ash\ content(\%) = \left[\frac{A-B}{C}\right] \times 100 \text{ .... } 3.3$$

Where

$A = weight\ of\ crucible, cover\ and\ Ash\ residue, g,$

$B = weight\ of\ empty\ crucible\ and\ cover, g,$ And

$C = weight\ of\ sample\ used, g$

The other parameter determined was the volatile matter content of the samples. It consists of mainly combustible gases such as Carbon monoxide, hydrogen, hydrocarbons, incombustible gases, and vapor are liberated from the sample when it was heated at a high temperature. It was determined by the ASTM method (ASTM D3175-02, 2004) and calculated from equation 3.4. The Volatile matter is calculated from equation 3.5.

$$\text{Weight loss \%} = [\frac{A - B}{A}] \times 100 \text{ .... } 3.4$$

Where:

A = weight of sample used, g, and

B = weight of the sample after heating, g.

$$\text{Volatile matter \%} = \text{C} - \text{D} \ldots\ldots 3.5$$

Where:
$\text{C} = \text{Weight loss, \%}$, and
$\text{D} = \text{Moisture, \%}$

The fixed carbon is a calculated value from equation 3.6 and it is the resultant of the summation of percentage moisture, ash content, and volatile matter subtracted from 100. All contents shall be taken from the same moisture base. The details of the proximate analysis methods were described in Appendix A.

Fixed Carbon% = 100 – (moisture%+Ash%+volatile matter %)……………………………….……..3.6

3.2.2.2 Ultimate analysis (Elemental Analysis)

The chemical compositions of the biomass were done through ultimate analysis to know the contents of important chemical elements contained in the biomass. It was determined following the ASTM methods using an elemental analyzer (EA 1112 Flash CHNS/O- analyzer). A device was loaded with an average sample weight of 1.5 to 2 mg weighted in a tin capsule. Then the tin was dropped into a combustion tube with a high heat oxygen environment. An exothermic reaction was created with a carrier gas flow rate of 120 ml/min, the reference flow rate of 100 ml/min, the oxygen flow rate of 250 ml/min, furnace temperature of 900 ℃, and an oven temperature of 75 ℃.

First, the samples were oxidized in a combustion zone with a pure oxygen environment. In the combustion zone, CO_2, H_2O, N_2, and S were produced. In this zone, elements like halogens were removed by scrubbing reagents. The remaining gases were then homogenized and the temperature, pressure, and volume were controlled. N_2, S_2, CO_2, and H_2O were moved by helium into the column, separated by frontal chromatography, and detected by a thermal conductivity detector. The whole procedure was controlled by a microprocessor taking into account data from analysis of blanks, internal and external standards. The experimental run was done in duplicate by taking six calibration points for every component and the average values were to be taken in determining oxygen, there is no satisfactory direct ASTM test method; it shall be calculated by subtracting from 100 the resultant of the other components of the ultimate analysis.

3.2.2.3 Calorific value determination of BSG and BWWS

The calorific values of all samples were determined by using an adiabatic bomb calorimeter at the Geological Survey of Ethiopia. First, dried, carbonized, grinded and mixed sample was determined by pelletizing 1g samples and recorded the weight of the prepared sample on screen. The decomposition vessel is fitted with a permanent ignition wire. Pair of tweezers suspended into the crucible was aligned with cotton thread to initiate the combustion. The cotton thread was attached to the ignition wire. Then 1g pelletized prepared sample was charged into the crucible and it must be well touched with the sample so that during the ignition process, the burning thread ignites the sample. When the decomposition vessel was filled with distilled water and closed, loaded on a calorimeter then finally the calorimeter would be ready to analyze the calorific value.

As soon as the experiment began and the system started in dynamic mode, the decomposition vessel was filled with oxygen. Until the jacket temperature of the calorimeter reached up to equilibrium with the vessel, the calorimeter was left running for five minutes. Then the bomb was fired and the vessel temperature was raised within 20 seconds and the temperature reading was started at about 10 minutes after firing. The display shows a graph of the change over time in the temperature of the inner vessel. When the measurement is complete, the measurement cell cover opens and pressure is released from the decomposition vessel. Simultaneously, the inner vessel was emptied after that, the cover opens up completely. As soon as the message bomb appears and the final calorific value was recorded on the bottom screen.

3.2.3 Carbonization of brewery wastewater sludge and spent grains

The carbonization experiments of brewery wastewater sludge and spent grains were carried out with a muffle furnace having a temperature and time controller. First, the dried BWWS and the BSG samples were weighted and covered with aluminum foil totally to create an Oxygen-free environment or limit the oxygen inside the furnace. The experiments were carried out with three factors (temperature, time, and mixing ratio) at three levels (minimum, center point, and maximum) were controlled to see their effect on carbonization results (calorific value). The temperature effect was maintained at three levels at 350, 400, and 450 °C with a corresponding time level for 60, 90, and 120 minutes and arranged mixing ratio levels of 25, 50, and 75%. Of BSG to BWWS. After carbonization, the solid char was removed from inside the furnace and placed into the desiccator, pulverized and sieved below 1mm size, and was prepared for the next steps.

3.2.4 Design Expert

3.2.4.1 Experimental Design

Response surface methodology (RSM) is an empirical modeling approach for determining the relationships between various operation variables and response variables. It provides a sequential experimentation strategy for building and optimizing an empirical model. The main purpose of using RSM is to optimize these variables taking into account the desired value of the response function. For this study Design-Expert version 12 software was used and the experiment was designed with Central Composite Design Method (CCD). The selected study factors were temperature, residence time, and mixing ratio, and three levels were used for each factor i.e. minimum, center point, and maximum. The experimental runs were performed as a completely randomized design with three factors at three levels and one response. The response of the experimental design was calorific value.

The design was applied to evaluate the effect of these three factors on calorific value and to optimize the factors after studying the effects of independent variables on the dependent variable. The interaction effects of independent variables and their influences on response were studied and the factors were optimized. Temperature, Time, and Mixing Ratio were designated as A, B, and C respectively. Factors and levels are shown in Table 3.2 and the number of experimental runs was computed using CCD. In this experiment by using CCD, 20 experimental runs have been carried out.

Table 3.2: Levels of independent variables based on central composite design

Code	Independent variable	Units	Minimum	Center point	Maximum
A	Temperature	^{o}C	350	400	450
B	Time	Minute	60	90	120
C	Ratio of BSG to BWWS	%	25	50	75

In the experimental run design, six runs were replicates at the center points and the other fourteen runs were random. The redundancies at the center points minimize errors. Following the design of the experimental run given by the software, the carbonization process was done according to the given data. The experimental runs design was shown in Table 3.3.

Table 3.3: The effect of operation variables on the responses

Run	Factor 1 A: Temperature (°C)	Factor 2 B: Time (min)	Factor 3 C: Mixing ratio of BSG to BWWS (%)	Response Calorific value (Cal/g)
1	400	90	50	
2	450	60	75	
3	400	90	50	
4	400	90	50	
5	350	90	50	
6	350	60	75	
7	450	60	25	
8	400	90	75	
9	350	120	75	
10	350	120	25	
11	450	120	75	
12	450	120	25	
13	400	90	50	
14	400	90	50	
15	400	90	25	
16	400	60	50	
17	450	90	50	
18	350	60	25	
19	400	120	50	
20	400	90	50	

3.2.4.2 Statistical analysis

A polynomial equation of second-order (quadratic equation) will be employed to find the relationship between the independent variables or factors (i.e. Temperature, Residence Time and Mixing Ratio) and the response (i.e. calorific value). For the three selected factors will be given as follow:

$$Y = \beta_{11}A^2 + \beta_{22}B^2 + \beta_{33}C^2 + \beta_{12}AB + \beta_{13}AC + \beta_{23}BC + \beta_1 A + \beta_2 B + \beta_3 C + \beta_0 + \varepsilon$$

Where, Y- the response, A, B, and C are the independent variables, β_i - coefficients of a linear interaction effect, β_0 - a constant, β_{ij} - coefficients for cross-product interaction effect, β_{ii} - coefficients for quadratic interaction effect, and **ε** –is the random error

The estimation of coefficients and the regression analysis will be carried out with a statistical software package Design-Expert® version 12 (Stat-Ease, Inc.). The analysis of variance (ANOVA) was employed to evaluate the adequacy of the model equation. The statistical significance and the quality of fit of the model equations were expressed using prediction coefficients of determination (Pred R^2), coefficient of determination (R^2), and adjusted coefficients of determination (adj-R), F-test, and coefficient of variation (CV), where the main comparison was conducted at 5% levels of the Least Significance Difference (LSD).

3.2.4.3 Optimization of quality briquette fuel

The optimization module in Design-Expert version 12 searches for a combination of factors and levels that simultaneously satisfy the requirements placed on each of the responses and factors. To use optimization, first, it has to analyze each response to establish the appropriate model due to the engineering aspects and cost-benefit. From experimental data generated the briquette quality with the highest calorific value was analyzed and optimized using Central Composite Design (CCD) method.

3.2.5 Briquetting

After optimization, the optimum carbonized sample was pulverized and sieved with less than 1 mm mesh size then weighted and mixed with each mixing ratio. The mixed optimum carbonized samples were then mixed with molasses of 20% as a binding agent and well homogenized. Then the measured mixture sample was put into the cylindrical shape mould with a diameter of 42 mm and with no more than 52 mm length using a press at 100bar densifier (hydraulic press). The hydraulic press was mainly used to compact carbonized briquettes according to (Supatata et al. 2013). After being compressed manually and waited for 15 min, the briquette was taken out from the cylindrical mould. Finally, the briquettes were dried under the sun for 3-4 days and then, the briquettes was kept in a closed container to minimize moisture absorption from the surrounding humidity (Nazari and Idroas 2019).

3.2.6 Analyzing the physicochemical properties of the briquettes

Finally, the optimum briquette produced was analyzed according to ASTM methods to determine its physical and chemical properties such as moisture content, volatile matter content, ash content, fixed carbon content, density, and heating value (HV). Then the carbonized briquettes were compared with Sawdust briquette and Non-carbonized briquette.

Chapter Four

4. Results and Discussions

4.1 Characterizations of Raw Samples

4.1.1 Proximate analysis

In proximate analysis Moisture content, volatile matter content, ash content, fixed carbon content, and calorific value of BSG, BWWS, and sawdust were determined and presented in Table 4.1.

Table 4.1: Proximate analysis Results of Raw BSG, BWWS, and Sawdust

Raw sample	Moisture content (%)	Volatile matter content (%)	Ash content (%)	Fixed carbon	Calorific value (Cal/g)
Spent grain	5.11	74.92	4.92	15.05	4823.75
Brewery wastewater sludge	5.83	53.03	20	3.05	3296.88
Sawdust	6.93	75.92	1.90	15.25	4842.80

4.1.1.1 Moisture content

The moisture content of BSG and BWWS were high which is 71% and 88%, respectively, at the disposal point of the factory which is difficult to store and dispose of as well. Therefore, the samples were sun-dried for four days to reduce moisture content below 15%. The moisture contents for both Brewery spent grain, brewery sludge and sawdust obtained were below 15%, which meet the requirements for briquette described by many studies (Giacomo et al. 2014; Rodrigues et al. 2014; Kpalo et al. 2020a, b). This could result in the briquettes would have high density, durability, and calorific value. Then the moisture content of the BWWS was reduced to 5.83% and moisture of BWS was reduced to 5.11%. The moisture content of the sawdust was 6.93% which was suitable for the carbonization process to have proceeded. The moisture of the biomasses needs to be dried with moisture content below 15% before carbonization to reduce the energy of carbonization (Asamoah et al. 2016).

In the biomass briquetting process, the determination of the raw material moisture content is very important (Hansted et al. 2016). Moisture content corresponds to the water contained in the biomass and the water acts as both a binding agent and a lubricant in these materials. As a binding agent, water helps in the development of Vander Waals' forces and hydrogen bonds by increasing the contact area between particles, which is essential to raise their cohesion strength. The moisture content in briquettes should be as low as possible, in the range of 12-15% (Kpalo *et al.*, 2020a). The less moisture content and higher volatile material for the samples indicated that the good combustible properties of the materials. The main parameter that determines the heating value of briquettes is the calorific values of the materials.

4.1.1.2 Volatile matter Content

It was observed that the volatile matter of the BSG, BWWS, and Sawdust were 74.9%, 53.0%, and 75.9%, respectively which were within the acceptable range. According to (Asamoah et al. 2016), recommended range for Volatile matter to produce quality briquette is 50-90%. Blending of higher volatile material with lower volatile material results in the production of optimum quality briquette (Onukak et al. 2017). Lower volatile matter is an indication that the briquettes might not be easy to ignite, but once ignited they will burn smoothly, while high volatile matter results in high combustibility at low ash content (Kathuria 2012). The moisture content and volatile matter were minimized during the carbonization process whereas fixed carbon content and calorific value were increased.

To minimize volatile matter and improve the calorific value of the briquettes together with increasing fixed carbon content, a carbonization process was carried out. The process removes most of the volatile content that is responsible for smoke emissions during the burning of raw biomass while the organic residue is converted to solid char. Carbonizing at a high temperature of around 600^oC results in lower carbon content and increases the ash value. Carbonizing at the lower temperature with increasing residence time better yields solid char (Christian et al. 2015). The carbonization of BSG and BWWS was carried out at a temperature of 350^oC for 60 minutes, which has good agreement with other experimental studies (Akowuah et al. 2012a; Mohamed et al. 2019; Tsehaye 2019).

The results of volatile matter content in this study were higher than the range of values for volatile matter 24.2% to 34.95% of briquettes reported in another study (Falemara et al. 2018); a range of 43% to 49% studied by (Emerhi 2011) for briquettes made from a mixture of tropical hardwood species' sawdust; with volatile matter range of (13.89% to 19.33%) obtained by study (Egbewole et al. 2020) for briquettes made from wood sawdust and range of(10 to 13%) reported by (Sotannde et al. 2010) for briquettes from neem-wood residues. Conversely, a higher volatile matter range from 72.33% to 77.44% for briquettes produced from sawdust of three hardwood species reported by (Emerhi 2011). The volatile matter content of 68% was reported by (Rapheal et al. 2018) and volatile matter ranging between 57.82% and 62.91% in their study on briquettes from maize cobs was reported by (Adetogun et al. 2014).

4.1.1.3 Ash Content

In this study, it is observed that the Ash content of the BSG, BWWS and the Sawdust were 4.92%, 20%, and 1.90%, respectively. The Ash content of the BSG and Sawdust was nearly at the acceptable values but the Ash content of the BWWS was higher than the acceptable value. This contradiction can be reduced considerably on the mixing of the BSG and BWWS. The Lower ash content is an indication of good quality briquette. It is acceptable around 4% tolerance level of ash content for fuel briquettes (Dhingra et al. 1996). The results of the experimental data of proximate analyses were in good agreement with others studies (Nusong and Puajindanetr 2018; Luo et al. 2020).

Furthermore, it was comparable to ash contents of many types of agricultural biomasses which varies between 2% to 6% (Nikolopoulos et al. 2013; Adrian et al. 2018; Werle et al. 2019; Bala-Litwiniak and Zajemska 2020; Jewiarz et al. 2020; Romanowska-Duda et al. 2020; Szufa et al. 2020). The low ash content implies high specific heat of combustion/heating value which is an indication that the briquette does not contain high mineral (non-combustible) matter (Sotannde et al. 2010). Higher ash content in a fuel usually leads to higher dust emissions, air pollution, and affects the combustion volume and efficiency of combustion (Katimbo et al. 2014).

4.1.1.4 Fixed Carbon Content

The Fixed Carbon content of the BSG, BWWS and the Sawdust were 15.05%, 3.05%, and 15.25% respectively. Fixed carbon value within the range of 9% -25% is acceptable according to (Asamoah et al. 2016). The Fixed Carbon Content values of the BSG and Sawdust were within the acceptable ranges and they are suitable for Briquette production while the Fixed Carbon Content value of the BWWS was low and can be increased considerably while blending with BSG. Fixed carbon indicates the proportion of char that remains after the volatile matter is distilled off. It gives a rough estimate of the heating value of fuel and acts as the main heat generator during burning (Akowuah et al. 2012b).

A good quality and efficient fuel briquette is dependent on lower volatile matter and ash content with higher fixed carbon content (Asamoah et al. 2016). The percentage of fixed carbon content in briquettes is a critical factor that influences the calorific value of fuel (Thabuot et al. 2015).

4.1.1.5 Calorific Value

As the result indicated in Table 4.1, the calorific values of the BSG, BWWS, and Sawdust were 4823.75 Cal/g, 3296.88 Cal/g, and 4842.80 Cal/g, respectively. The values are nearly close to each other except for the calorific value of the sludge which is lower than the others due to its lower content of fixed Carbon and higher Ash content. It can be enhanced upon blending with BSG and the carbonization process. This energy value is sufficient enough to produce the heat required for household cooking and small-scale industrial cottage applications according to Akowuah et al. (2012). The calorific value has a direct relation with the elemental content of the samples and the fixed carbon content of the samples.

4.1.2 Ultimate Analysis (Elemental Analysis)

In the results of the Ultimate Analysis, the chemical composition of the BSG “as received basis” was shown as 49.5% Carbon, 7.1% Hydrogen, 1.7% Nitrogen, and 41.8% Oxygen (Table 4.2). Similarly, the elemental composition of the BWWS was 16.4% Carbon, 2.7% Hydrogen, 1.9% Nitrogen, and 79.1 Oxygen and the elemental composition of Sawdust was 53.1% Carbon, 4.1% Hydrogen, 3.2% Nitrogen, and 39.6% Oxygen, respectively. From these results, it can be seen that the amount of carbon and hydrogen content in the samples examined was very satisfactory to use the samples as household heating energy sources.

Table 4.2: Ultimate Analysis Results of BWWS, BSG and Saw dust

Raw Sample	C (%)	H (%)	N (%)	O (%)	S (%)
Brewery Spent Grain(BSG)	49.5	7.1	1.7	41.8	-
Brewery Waste Water Sludge(BWWS)	16.4	2.7	1.9	79.1	-
Sawdust	53.07	4.1	3.23	39.6	-

4.2 Design Expert Results

4.2.1 Experimental design

To investigate quality fuel Briquette with good calorific value intended for alternative household energy sources, three parameters were studied. These important parameters were mixing ratio, time, and temperature. The response of the performed experiment was a Calorific value and determined by three factors at three levels. The experimental design of the three factors at three levels was indicated in Table 4.3 with respective response values.

Table 4.3: Experimental Design and Response Results

Run	Factor 1 A: Temperature (℃)	Factor 2 B: Time(min)	Factor 3 C: Mixing ratio of BSG to BWWS (%)	Response(Calorific value (Cal/g)
1	400	90	50	3570.55
2	450	60	75	3754.37
3	400	90	50	3409.17
4	400	90	50	3309.44
5	350	90	50	3782.37
6	350	60	75	4764.58
7	450	60	25	3238.04
8	400	90	75	3267.55
9	350	120	75	4291.91
10	350	120	25	4429.29
11	450	120	75	2501.33
12	450	120	25	3978.76
13	400	90	50	3760.59
14	400	90	50	3325.55
15	400	90	25	3104.68
16	400	60	50	3705.19
17	450	90	50	2844.77
18	350	60	25	3000.12
19	400	120	50	3979.29
20	400	90	50	3337.24

4.2.2 Analysis of Variance (ANOVA) of the Quadratic model

Results ANOVA of the response surface quadratic model is presented in Table 4.4. The experimental data were analyzed using design expert version 12. The effect of each factor on the calorific value and the interaction effects of each variable were analyzed using the software.

Table 4.4: Analysis of Variance (ANOVA) for Calorific Value

Response: Calorific Value						
Source	Sum of squares	Df	Mean Square	F-Value	P-Value	Remark
Model	5.546E+06	9	6.163E+05	27.15	< 0.0001	significant
A	1.561E+06	1	1.561E+06	68.76	< 0.0001	
B	51592.62	1	51592.62	2.27	0.1626	
C	68699.23	1	68699.23	3.03	0.1126	
AB	2.697E+05	1	2.697E+05	11.88	0.0063	
AC	8.373E+05	1	8.373E+05	36.88	0.0001	
BC	1.897E+06	1	1.897E+06	83.56	< 0.0001	
A^2	1984.55	1	1984.55	0.0874	0.7735	
B^2	6.925E+05	1	6.925E+05	30.50	0.0003	
C^2	65489.16	1	65489.16	2.88	0.1203	
Residual	2.270E+05	10	22701.61			
Lack of fit	66416.99	5	13283.40	0.4136	0.8226	not significant
Pure error	1.606E+05	5	32119.81			
Cor total	5.773E+06	19				

A=Temperature, B= Time, C= Mixing Ratio

The Model F-value measures the significance of the overall ANOVA model. The Model F-value of 27.15 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, AB, AC, BC, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Therefore B, C, A^2, C^2 are not significant model terms. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. To give a good approximation to the reality, it is very important to check that the model is fit otherwise the results obtained and optimization results may lead to wrong results and conclusions. The Lack of Fit F-value of 0.41 implies the Lack of Fit is not significant relative to the pure error. There is an 82.26% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good so we want the model to fit.

The quality of the fitted statistical model (Table 4.5) was explained by the R-Squared (R^2), which explains the percentage of variation in the Response (dependent variable) which is explained by variation in the explanatory (independent variable). It was very important in the validation of the statistical model. The value of R^2 for Equation 4.1 was 0.9607 and this indicated that 96.07% of the total validation in the calorific value correlation between experimental and predicted values and the independent variables can explain 96.07% variation in the dependent variable. The higher the value of R^2, the efficiency of the quadratic model in fitting the data would be higher under the conditions of the experiment.

Table 4.5: Fit Statistics

Std. Dev.	150.67	R^2	0.9607
Mean	3567.74	Adjusted R^2	0.9253
C.V. %	4.22	Predicted R^2	0.8976
PRESS	5.910E+05	Adeq Precision	21.2830

The Predicted R^2 of 0.8976 is in reasonable agreement with the Adjusted R^2 of 0.9253. This indicated that there was a good agreement between the experimental and predicted values. The difference between Adjusted R^2 and Predicted R^2 is less than 0.2 which is acceptable. “Adeq Precision” was another model fit statistics value that measures the signal to noise ratio. It shows the range of variation in the predicted dependent variable to an estimate of standard error. It was gained by subtraction of the minimum predicted value from the maximum and dividing by the average standard deviation of the predicted value. A ratio greater than 4 is desirable. The analysis ratio of 21.283 indicates an adequate signal. Therefore, the model can be used to navigate the design space.

The coefficient of variance (CV %) is the measure of the percentage of the residual variation of the experimental data relative to the size of the mean. The higher values of Coefficient of Variance imply the reliability of the experiment is low. In this experiment, it was shown that the Coefficient of Variance was 4.22, which was lower and the experiment was reliable, and has good precision. The experimental values of the independent variables and the actual values of the dependent (response) of 20 experimental runs were used for the prediction of equations of the model. According to the ANOVA, the experimental data was best fitted with quadratic equations. Using the quadratic model it was shown that the significance of each independent variable for the dependent variable.

The quadratic model (equation) for the carbonization of a BSG and BWWS expressed in terms of coded factors is given as equation 4.1. The coefficients having only one factor show the effect of only one variable and coefficients with two variables implies the interaction effect of two variables. Similarly, coefficients with second-order factors indicated the quadratic effect of the factors. The ANOVA was computed at a 95% level of confidence for the performed experiments. The quadratic model equation in terms of coded factors:

$$\text{Calorific value} = 3407.43 - 395.10\text{A} + 71.83\text{B} + 82.89\text{C} - 183.60\text{AB} - 323.52\text{AC} - 486.95\text{BC} - 26.86\text{A}^2 + 501.81\text{B}^2 - 154.32\text{C}^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4.1$$

The quadratic model equation in terms of actual factors:

$$\text{Calorific value} = -4137.84 + 24.65A - 16.54B + 189.97C - 0.12AB - 0.26AC - 0.65BC - 0.01A^2 + 0.56B^2 - 0.25C^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4.2$$

According to the model quadratic equation indicated in equation 4.1, Time (Factor B) and mixing ratio (Factor C) was affecting the response (Calorific value) positively but Temperature (Factor A) was affecting the response negatively. The temperature has a significant linear effect on calorific value (the response) with a negative regression coefficient of -395.10 and; time and mixing ratio indicated a linear effect on calorific value with a positive regression coefficient of 71.83 and 82.89, respectively.

In the model quadratic equation in terms of a coded factor the calorific value was expressed by all three linear terms (A, B, C), quadratic terms (A^2, B^2, C^2), and interaction quadratic terms (AB, AC, BC). Coefficients of linear terms of B and C and quadratic term B^2 were positive and the response (calorific value) was positively affected by these factors, but the coefficients of linear term A, interaction terms AB, AC, BC, and quadratic terms A^2, C^2 were negative so the response was negatively affected by these factors.

4.2.3 Diagnostics Plots

Model graphs and diagnostics plots indicate the graphical representation of the experimental analysis. A good normal probability graph shows a straight line and linear. The normal probability graph was given in Figure 4.1. In this study, the Normal probability versus Internally studentized residuals plot seems to befall almost on a linear straight line which indicated that the errors were normally distributed. The residual versus predicted plot was shown in Figure 4.2 and it is expected to be randomly scattered. Diagnostic plots can be obtained by selecting the Diagnostics button from the toolbar in the analysis section of Design expert software. The plots simply can show how the experimental model was satisfied the assumption of the ANOVA.

4.2.3.1 Normal Probability plot

The normal probability tells whether the residuals were normally distributed or not. In this case, the residuals were almost followed a linear line which implies the error distribution is normal. As it can be seen in Figure 4.1, only one point was escaped from the straight line however these cases are expectable.

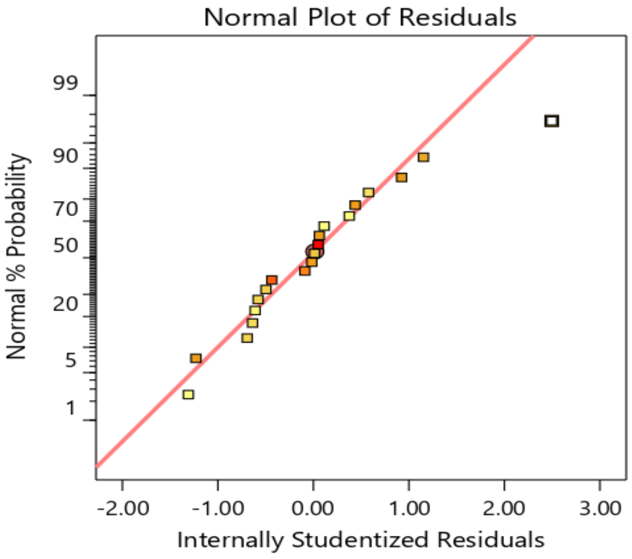


Figure 4.1: Normal probability plot

4.2.3.2 Residuals versus Predicted plot

The graph showed in Figure 4.2 was a plot of the residuals versus the increasing predicted dependent variable (response) values. It was randomly scattered and have constant variance across the graph.

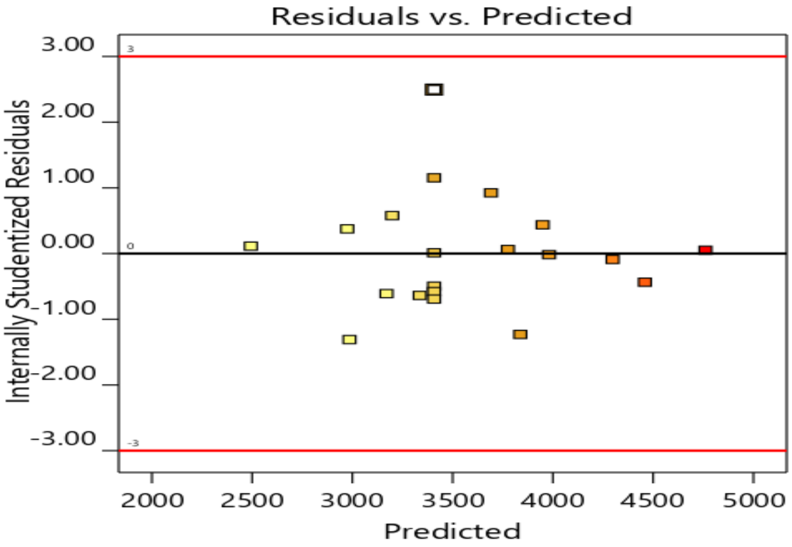


Figure 4.2: Studentized Versus Residual plots

4.2.3.3 Residuals versus Run plot

The residual versus run plot indicated how the experimental run was randomized and the plot was shown in Figure 4.3.

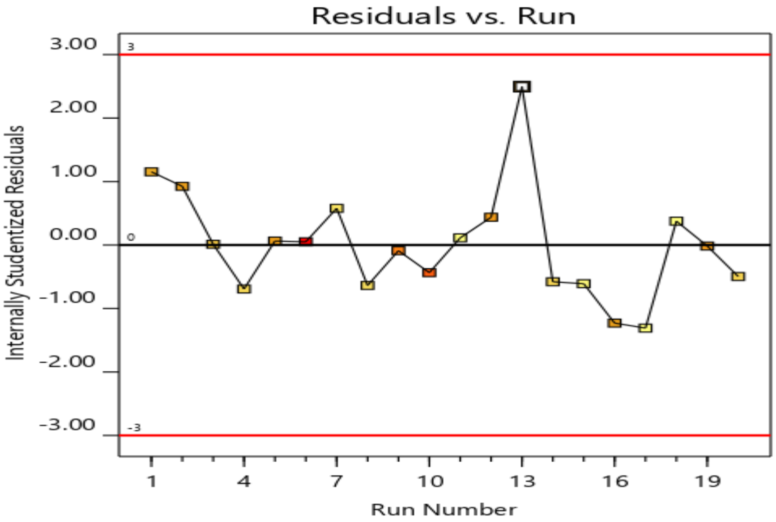


Figure 4.3: Residuals versus Run plot

4.2.3.4 Predicted versus Actual plot

A plot of the predicted values obtained versus the actual values of the dependent variable is shown in Figure 4.4. The regression equation of the quadratic model yielded a highly precise description of the experimental data. The linear straight line passes through all of the spots.

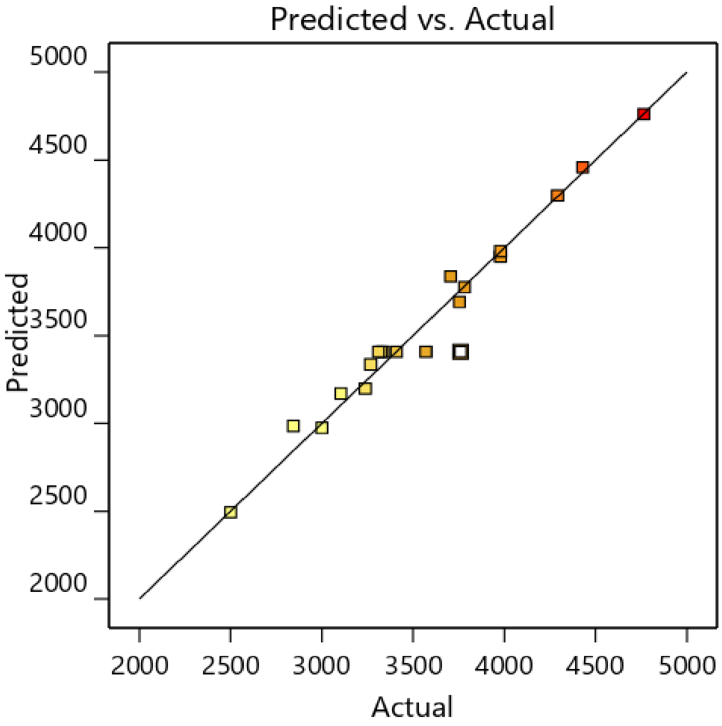


Figure 4.4: Predicted Versus Actual Plot

4.2.3.5 Residuals versus Factor

The residuals are plotted against each of the factors and shown in Figure 4.5. It determines if the variation not accounted for by the model varies depending on the level of a factor. If everything is in order, the plot should show a random scatter. The severe curvature could imply that the independent factor has a systematic contribution that the model does not account for.

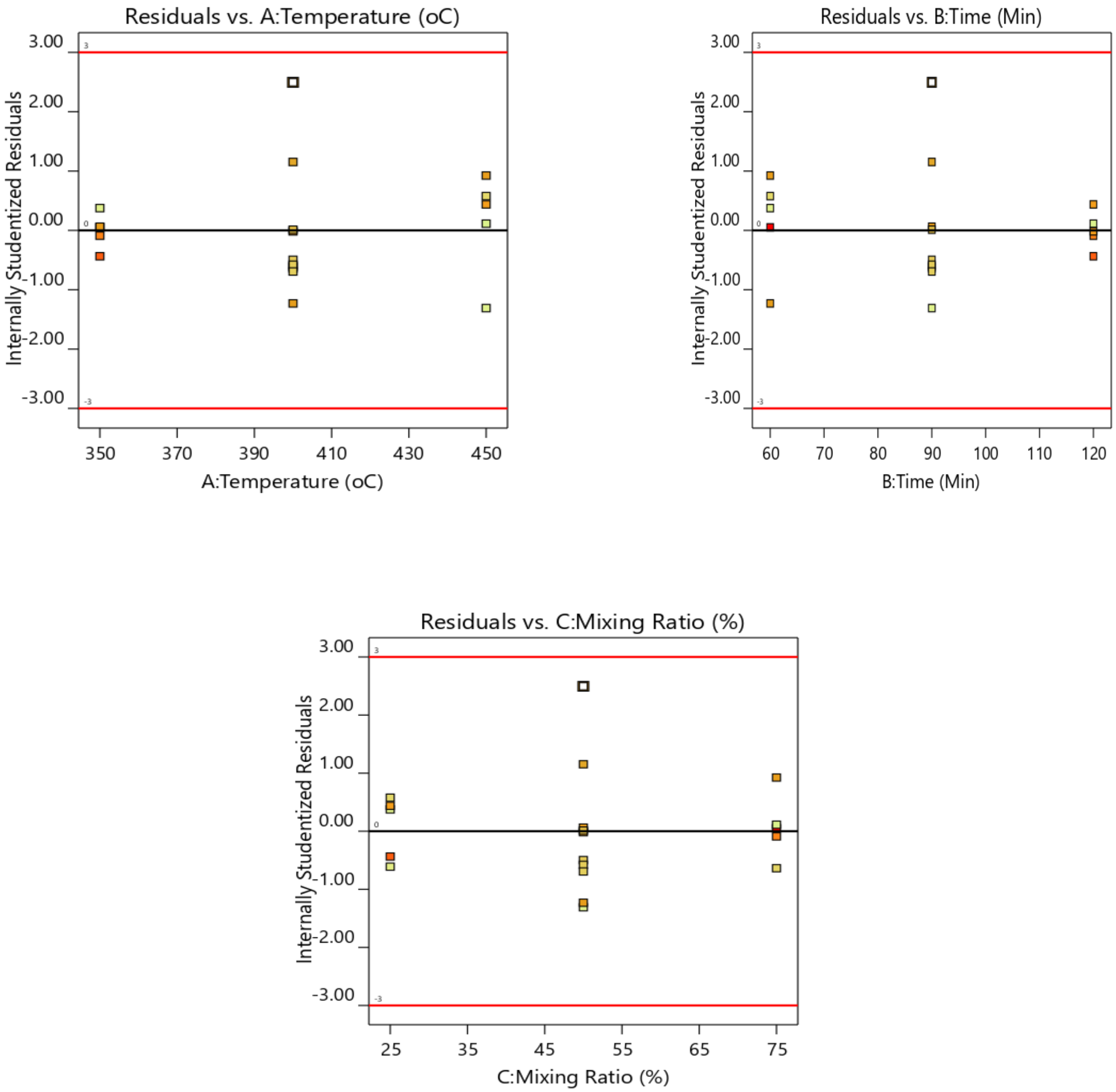


Figure 4.5: Residuals versus Factors plots

4.2.4 Effects of individual process variables on the response

The effect of each factor on calorific value was analyzed by keeping the other variables constant. As it was shown in the quadratic model equation, each independent variable has an interaction effect on the dependent variable (calorific value). Time and mixing ratio were affecting the calorific value positively but Temperature was affecting the calorific value negatively.

4.2.4.1 Effect of temperature on calorific value

The effect of temperature on the calorific value was indicated in Figure 4.6. As can be seen from the graph, the temperature affects the response. As the temperature increased at the maximum of 450 ^{o}C a minimum calorific value of 2844.77 Cal/g was obtained which implied that the amount of temperature plays a decisive role in the carbonation. Keeping on increasing the temperature would decrease the calorific value because the maximum calorific value was obtained at minimum temperature. According to(Industries 2018), range of temperature from 350℃ and 600℃ was suggested for effective bio char production but in this study optimum calorific value was attained at the lowest temperature which was 350℃ therefore further study needed at lower temperatures.

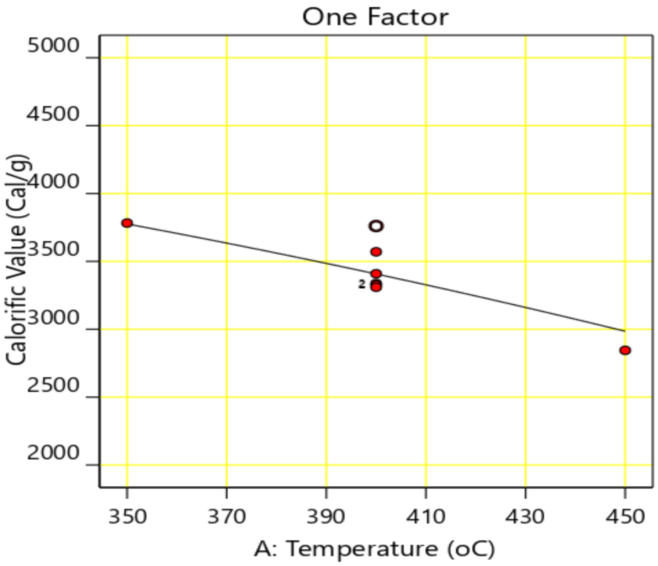


Figure 4.6: Effect of Temperature on Calorific Value

4.2.4.2 Effect of time on calorific value

The calorific value of samples was affected by the residence time (Figure 4.7). The calorific value of the sample was determined at a time interval of 60 to 120 min for different carbonization temperatures at 350^{o}C, 400 ^{o}C, and 450 ^{o}C. The maximum calorific value of the mixed sample obtained was 4764.58 Cal/g at 350 ^{0}C and 60 minutes while the minimum calorific value was 2501.33 Cal/g at 450 ^{o}C and 120 minutes. The results showed that the maximum calorific value of the char was found at the minimum time. This indicated the fact that the biomass samples were completely burned at the minimum time.

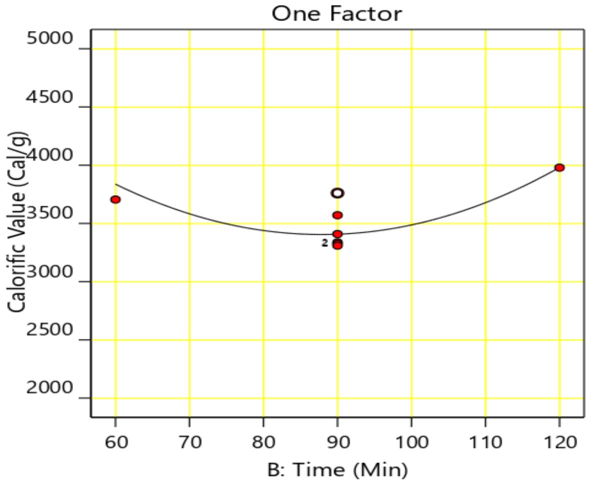


Figure 4.7: Effect of Time on Calorific Value

4.2.4.3 Effect of mixing ratio on Calorific value

The effect of the mixing ratio on the calorific value is shown in Figure 4.8. As it was indicated in the plot, the mixing ratio has a positive effect on the calorific value. As the BSG percentage increased to the maximum of 75%, a maximum calorific value of 4764.58 Cal/g was obtained and this implied that BSG plays a vital role in the mixing process. Most of the energy came from the BSG and increasing to the maximum percentage brings maximum energy content and this was due to its chemical composition (ultimate characteristics), having high fixed carbon content, low ash content, low moisture content, and good volatile matter contents (proximate characteristics). The fixed carbon content of briquette is the mass of solid combustible residue remaining after the release of volatile matter. Briquettes with higher fixed carbon content mean it is made up mostly of carbon.

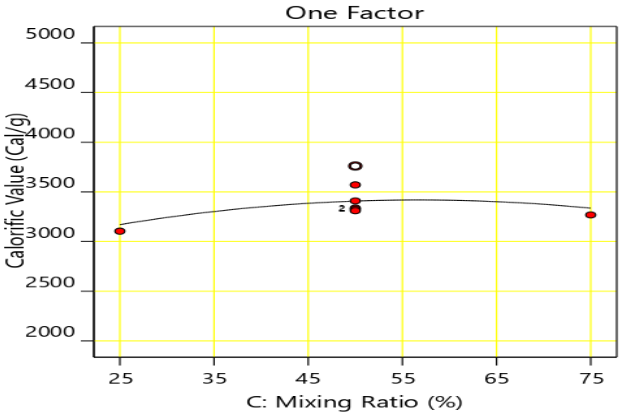


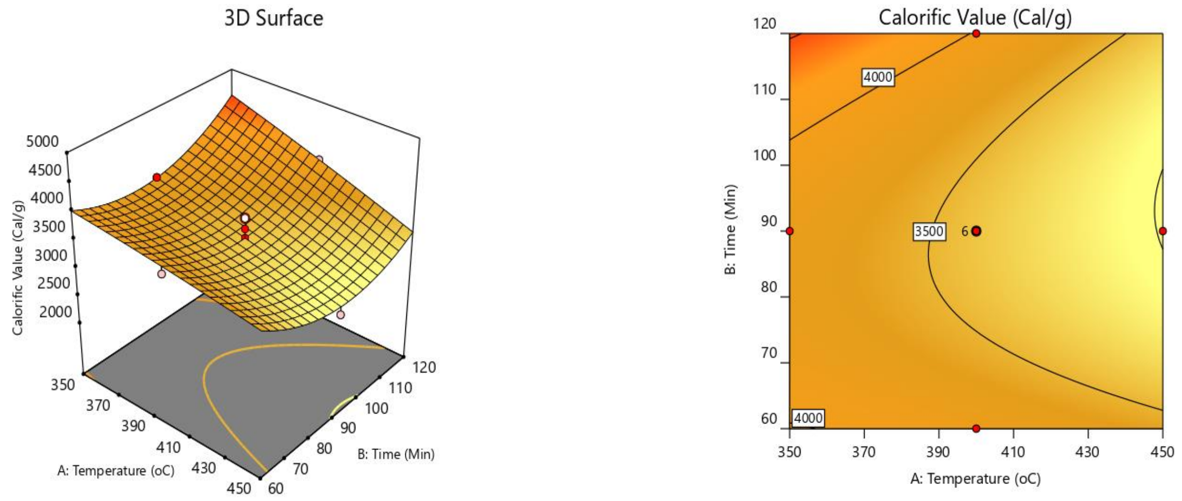
Figure 4.8: Effects of mixing ratio on calorific value

4.2.5 Effects of Interaction Variable

The interaction effect among the factors was analyzed by plotting on three-dimensional contour maps. The plot was indicated by two factors for the calorific value.

4.2.5.1 Interaction effect of temperature and time on calorific value

The interaction effect of temperature and time is shown in Figure 4.9 (a) Response surface and the contour plots (b) show calorific value variation as a function of temperature and time with the mixing ratio set constant at 50%. As the temperature increases from 350 °C to 450 °C, the calorific value decreased slightly, and when the time increased from 60 min to a certain point, the calorific value was decreasing and then started to increase slightly until it reached 120 min. This shows maximum calorific value was attained at 350 °C and 60 min. The maximum mass conversion and de-volatilization of organic matters were discovered to occur at 350 °C during the carbonization process (Nusong and Puajindanetr 2018). This indicated that it can be understood that time and temperatures have significant effects on the carbonization process. Figure 4.9 indicates that time has more interaction effect on calorific value than temperature.

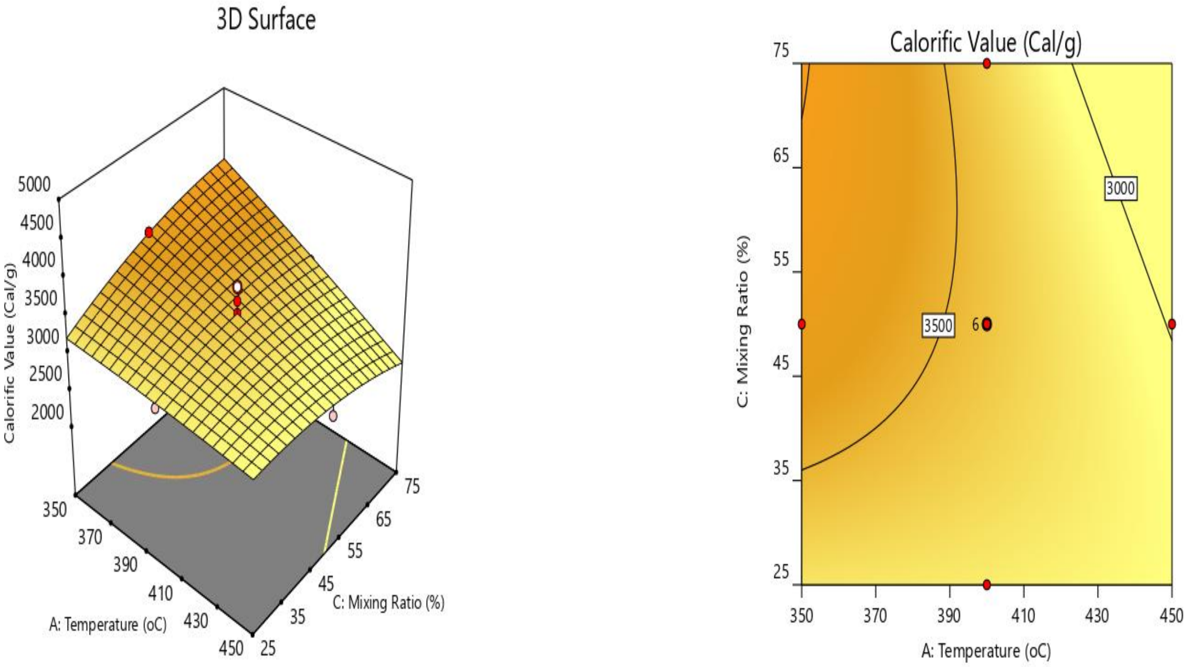

(a)

(b)

Figure 4.9: Interaction Effect of Temperature and Time: a) Response surface and b) Contour plot

4.2.5.2 Interaction effect of temperature and mixing ratio of BSG to BWWS on calorific value

The interaction between a temperature and mixing ratio is shown in Figure 4.10. While the reaction time kept constant at 90 min, as the temperature increases from 350 ^{o}C to 450 ^{o}C the calorific value slightly decreased and when the mixing ratio increased from 25 to 75%, the calorific value was increased. From the ANOVA analysis, the P-value of the interaction effect of temperature and mixing ratio was P=0.0001, which showed that the temperature and the mixing ratio has significant interaction effect. From the 3D plot, it can be observed that a high mixing ratio has favored the response and it has a more strong effect on calorific value than temperature. The calorific value of the mixture of spent grain and brewery wastewater sludge decreased as the temperature increased and the mixing ratio decreased. This is maybe due to spent grains has a higher heating value than wastewater sludge and the mixture mass conversion occurs at low temperatures.

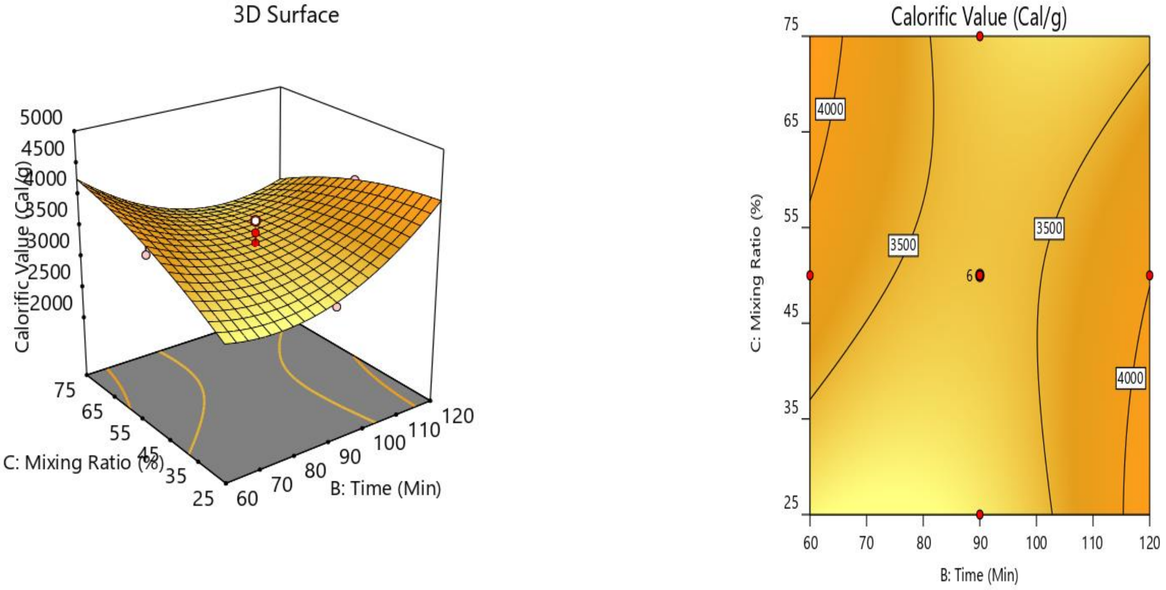


(a) **(b)**

Figure 4.10: Interaction Effect of Temperature and mixing ratio (a) Response surface (b) Contour plot

4.2.5.3 Interaction effect of time and mixing ratio on calorific value

Figure 4.11 explained that the interaction effect of time and mixing ratio on the calorific value when the temperature kept constant at 400 ℃. As it can be seen from the model regression quadratic equation, these independent variables have a negative interaction effect on the calorific value. The plot indicated when the time increases from 60 min up to approximately 83.4 min, the calorific value was decreasing and then started to increases slightly up to 120 min and the calorific value was increased while the mixing ratio was increasing from 25% to 75%. From the plot, we can conclude that calorific value was more favored with increasing mixing ratio than reaction time.



(a) (b)

Figure 4.11: Interaction effect of time and mixing ratio a) Response surface and b) Contour plot

4.2.6 Optimization of the independent variables

The optimum conditions for the three factors were determined by using the numerical optimization feature of the Design-Expert 12 software. The selection of the optimized variables was done depending on the highest desirability. The central composite design method of the RSM verifies the optimum condition selected which helps in the optimization of the variables. The targets were set either at maximum, in range, or at minimum according to the purpose of study and cost considerations. The design expert assesses the combination of parameters that can simultaneously fulfill the requirements put in the targets for each of the variables.

The optimum conditions (Goal, the Higher and Lower limits) on the response (calorific value) and the factors (temperature, time, and mixing ratio) employed during the optimization analysis (Table 4.6). Considering the minimization of energy consumption during carbonization regarding cost-benefit, the targeted criteria for temperature was minimized. To obtain the maximum calorific value, carbonization at lower temperatures produces a large quantity of char. While the time target was kept in range and the mixing ratio was maximized since the spent grain comprises the higher energy content in the blending process. The optimum conditions obtained were then evaluated by composite desirability, which has a value from 0 to 1, to determine the degree of satisfaction of the optimum conditions for the ultimate goal of response.

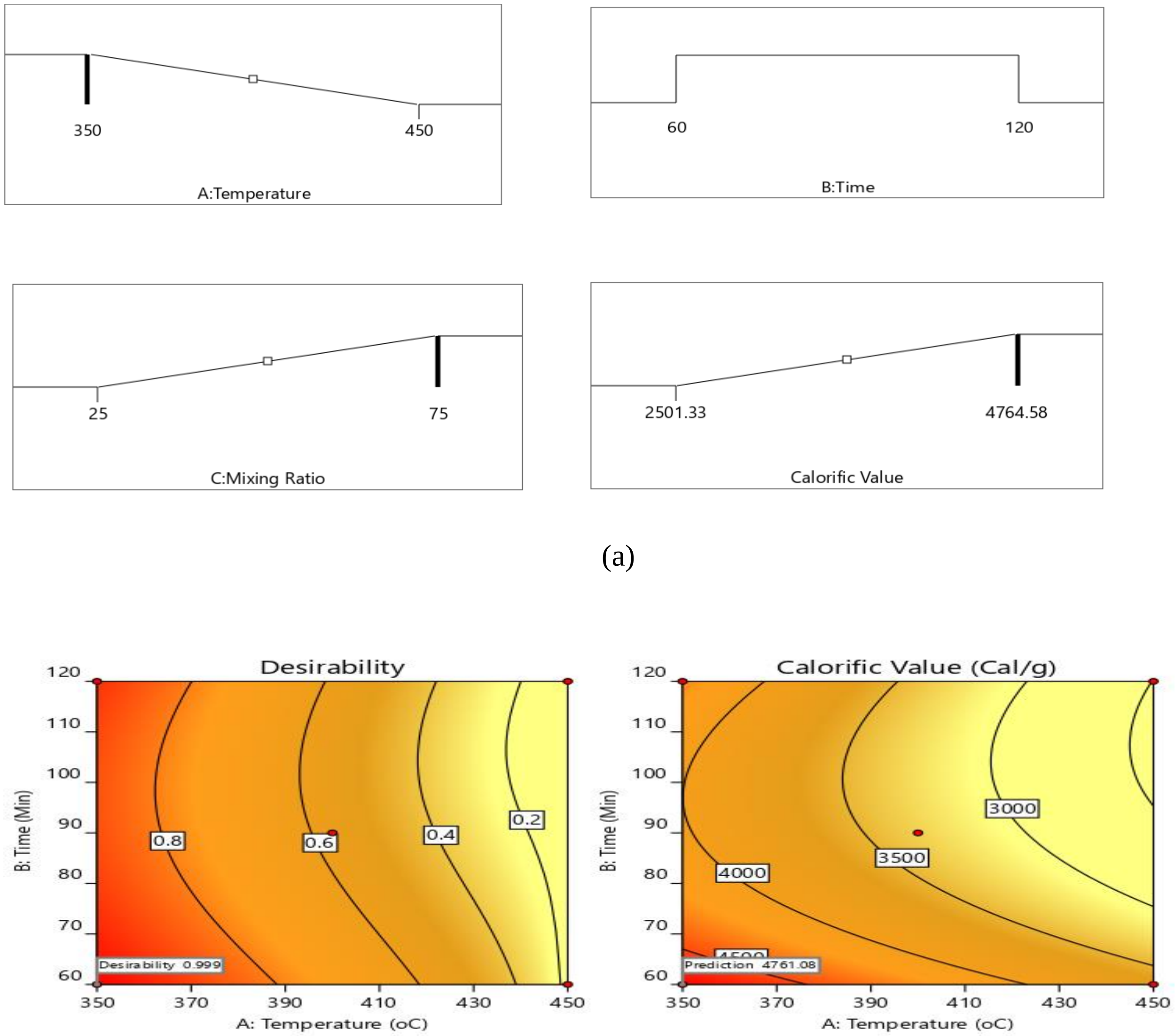
Table 4.6: Optimization conditions of all factors

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:Temperature	minimize	350	450	1	1	3
B:Time	is in range	60	120	1	1	3
C:Mixing Ratio of BSG to BWWS	maximize	25	75	1	1	3
Calorific Value	maximize	2501.33	4764.58	1	1	3

The optimum conditions of calorific value were achieved at temperature, time, and mixing ratio of 350 ^{o}C, 60 min, and 75%, respectively with cost considerations is presented in Table 4.7 and Figure 4.12. To validate the optimum condition predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized carbonization process conditions and calorific value of 4761.10 with a desirability value of 0.99.was obtained.

Table 4.7: Model Validation of Calorific Value

Response	Desirability	Temperature	Time	Mixing ratio	predicted	experimental	Error
Calorific value	0.99	350	60	75	4761.10	4764.58	0.073



(a)

(b)

Figure 4.12: Optimization result with desirability (a) 2D plot and (b) contour plot

Model desirability approaching unity and with low error, value portrays the applicability of the model towards the responses. The result actual or experimental is closely related to the data predicted obtained from optimization analysis using the desirability function. From Table 4.7, the error was obtained 0.073%, relatively small because it is less than 0.5 for the predicted and the actual values indicating that the models are suitable and sufficient to predict the responses. Therefore, this study showed that a mixture of a spent grain and wastewater sludge can be replaced with sawdust briquette as an alternative energy source for household energy sources due to their calorific value at optimum carbonation conditions.

4.3 Briquetting of Optimum Mixed Carbonized Sample

For all types of binders, the density of briquette eventually increased with the increasing amount of the binders and increase with the applied pressure during pressing. The strength and density of the briquette also increase by adding extra. This implied that the bonding of adjacent particles of pellets increased with increasing binder amount and pressure. Briquetting of biomass char was done using a hydraulic press which has a 50-ton capacity. The bulk density of Non-Carbonized briquette with a constant compression pressure of 100 bar was 1.118 g/cm³ and it was increased upon the carbonization process to 1.247 g/cm³. So it was better than Sawdust briquette. The more the bulk density would be, the calorific value gets better. The physical properties of the optimum mixed carbonized sample and briquettes are presented in Table 4.8.

Table 4.8: Physical properties of optimum mixed carbonized sample and briquettes

Raw sample	Density(g/cm³)	Calorific Value(Cal/g)
Optimum mixed carbonized sample	_	4764.01
Mixed carbonized briquette with 20% molasses binder	1.247	5385.72
Mixed non-carbonized briquette with 20% molasses binder	1.118	5286.58
Sawdust briquette with 20% molasses binder	0.888	5464.51

The calorific value of optimum mixed carbonized sample without molasses binder was 4764.01 Cal/g whereas calorific values of mixed carbonized briquette densified with pressure 100 bar by 20% of molasses resulted in 5385.72 Cal/g. The result (Table 4.8) indicated that the calorific value of the briquette increased upon the addition of a molasses binder.

In this investigation, it can be seen that the differences in the physical properties of the non-carbonized briquettes, carbonized briquettes, and sawdust briquettes. The operating variables of the briquetting process would affect the quality of the briquettes. The physical and mechanical properties of the briquettes have been enhanced by using molasses binder and being densified. The biomass briquettes pressed at piston press (hydraulic press) with the power consumption of 50 KWh/ton would have a range of density from 1-1.2 g/cm³ and therefore, the density was almost satisfied (Sharma et al. 2015). The main purpose of the densification process was suitability for handling, storage, transportation, and enhancing the calorific value. Carbonizing the mixed samples improved the calorific value to be comparable with sawdust briquettes.

4.4 Characterization of the Briquettes

4.4.1 Proximate analysis of briquettes

On the percentage weight basis, the proximate analysis provides moisture, ash, and volatile matter contents. The differences among the result of sawdust briquette, optimum mixed raw sample (75% spent grain to 25% wastewater sludge), and carbonized mixed sample values can be explained by the de-volatilization during carbonization, which produces an increase in ashes content, fixed carbon, and also decrease moisture content and volatile matter as presented in Table 4.9.

Table 4.9: Proximate analysis of briquettes

Sample	Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)
Mixed Non-carbonized briquette with 20% molasses binder	5.37	8.69	63.24	10.53
Mixed carbonized briquette with 20% molasses binder	2.92	10.86	53.49	13.38
Sawdust briquette with 20% molasses binder	6.93	1.90	75.92	15.25

The consequences of the moisture content of the briquettes are as follows. It absorbs a portion of the heat released during combustion. When the raw material's moisture content is high, the effect is a decreased heating value and fuel efficiency. The moisture content of the non-carbonized pellet sample and carbonized pellet sample, are 5.37 and 2.92, respectively. This may be due to the carbonization of the raw material decreases the content of water.

When samples are heated, volatile matter (flammable gas and smoke) is emitted. On a supply of adequate air, time, temperature, and turbulence, this burns as a visible flame. For effective combustion, a considerable amount of secondary air at high pressure must be provided at a strategic place if the volatile matter in the fuel is higher. Dark smoke, heat loss, pollution risk, and soot deposition on boiler surfaces result from the complete combustion of volatile materials. The volatile and reactive components in the non-carbonized mixed sample are higher than in the carbonized pellet sample. Biomass combustion is quick and difficult to manage due to the extremely volatile materials.

The ash content of a fuel refers to the amount of non-combustible solid mineral materials in the fuel. It mostly consists of silica (SiO_2), alumina (Al_2O_3), iron oxides (FeO, Fe_2O_3), calcium oxide (CaO), and magnesium oxide (MgO). The ash fuses/softens and produces clinker at higher temperatures, trapping combustible materials and preventing appropriate air distribution, lowering combustion efficiency.

Chapter Five

5. Conclusion and Recommendation

5.1 Conclusion

The main objective of this investigation was to maximize the calorific value of briquettes produced from mixture brewery spent grain and brewery wastewater sludge by carbonization process. Carbonation of BSG and BWWS were analyzed and optimized by using the Central Composite Design of RSM as an alternative energy source for household energy use. A design-expert-12 was used to analyze and optimize the quadratic model equations built by using sets of experimental data. The quadratic model can only compute the change of independent variables (temperature, time, and mixing ratio) on the carbonization process for the dependent variable (calorific value) but it was not able to calculate the chemical output. Up on carbonization, the fixed carbon would increase and as a result, the calorific value was also increasing. The heating results in the calorific value of carbonized mixed sample were varying from 2501.33 Cal/g to 4764.58 Cal/g. The optimum conditions of temperature, time, and mixing ratio were at 350 ℃, 60 min, and 75%, respectively. The predicted calorific value of optimum carbonized briquette by Design-Expert 12 and the experimental result were closely related which was related 4761.10 Cal/g and 4764.58 Cal/g, respectively. The binding material (20 % molasses addition) improved the calorific value to 5385.72 Cal/g.

From the study, we can conclude that briquette fuel produced from brewery wastes (BSG and BWWS) was suitable for alternative household energy sources, for the fact that the results are comparable with Sawdust briquette on which many studies have done and been commercialized. It is clean, environmentally friendly, and pollution-free fuel and is suitable for storage, handling, and transportation. So this investigation identified that a model for an alternative briquette fuel from carbonization of brewery solid wastes.

5.2 Recommendation

Investigation of fuel briquette from a mixture of brewery spent grains and brewery wastewater sludge was done. Based on the study, the following recommendations were made

- Briquettes made of brewery wastewater sludge and spent grains can be used as an alternative energy source and can be the solution of waste treatment for breweries.
- Brewing industries must be adopted the manufacturing of these briquettes made of brewery solid wastes to change their wastes into useful, user-friendly briquette fuel simultaneously minimize their cost of solid waste disposal and landfilling cost.
- The production of these alternative fuel briquettes from brewery solid wastes must be established to increase sustainable environmental impact
- The briquette manufacturing facility must be planted in proximity with the breweries to reduce the cost of transportation and easily access the brewery wastewater sludge and spent grains
- The cost-benefit analysis (feasibility study) of these alternative briquette fuels must be studied.

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APPENDICES

APPENDIX A: Proximate Analysis Experimental Method

Proximate analysis was determined as per the ASTM method. Parameters such as Moisture content, Volatile matter content, Ash content, Fixed carbon content and Calorific value of the Spent grain, Wastewater sludge, and the Sawdust were determined.

Moisture content

Moisture was determined by establishing the loss in weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample weight, and equipment specifications. The moisture content of the sample was determined by using (ASTM D3173-03, 2004). The empty crucible with cover was weighed and preheated in the oven at 105 ℃, covered and put in a desiccator for 15-30min, and cooled to room temperature. 1 g pulverized to 250μm of the sample was weighed to the nearest 0.1g and placed into the crucible and closed. After removed the cover the sample was immediately put into the preheated oven and heated for 1h. The samples were removed from the oven, covered, and allowed to cool to room temperature in a desiccator for 15 to 30 min. The samples were re-weighed to the nearest 0.1g to obtain the final (dried) weight. The moisture content was then calculated using the Equation below.

$$\boldsymbol{Moisture\ in\ analysis\ sample\ (Moisture\ content)} = \left[\frac{W_0 - W_1}{W_0}\right] \times \mathbf{100}$$

Where:

$\mathbf{W_0} = \boldsymbol{initial\ weight\ of\ the\ sample\ before\ drying}$

$W_1 = \boldsymbol{final\ weight\ of\ the\ sample\ after\ drying}$

Volatile Matter Content

The volatile matter was determined according to (ASTM D3175-02, 2004). It was determined by establishing the loss in weight resulting from heating a sample under rigidly controlled conditions. 1g of pulverized sample to pass 250µm was weighed to the nearest 0.1g and placed in a crucible of known weight and closed. The muffle furnace was maintained at the temperature of 950± 20°C and the covered sample was put in to the furnace and heated for 7 min. Then the crucible was removed out of the furnace as it was covered and allowed to cool in a desiccator. Finally the sample was weighed to the nearest 0.1g and the volatile matter was then evaluated as the percentage loss in weight of the sample using Equation below.

$$\boldsymbol{Weight\ loss}\,\%\ (\boldsymbol{volatile\ matter\ content}) = \left[\frac{\boldsymbol{A-\ B}}{\boldsymbol{A}}\right]\times \mathbf{100}$$

Where:

$\boldsymbol{A\ =\ weight\ of\ sample\ used}\ (\boldsymbol{oven\ dried\ sample}), \boldsymbol{g}$, and

$\boldsymbol{B\ =\ weight\ of\ sample\ after\ heating}, \boldsymbol{g}.$

And then, $\boldsymbol{Volatile\ matter\ in\ analysis\ sample}, \% = \boldsymbol{C - D}$

Where:

$\boldsymbol{C} = \boldsymbol{Weight\ loss}, \%$ **,** and

$\boldsymbol{D} = \boldsymbol{Moisture}\ , \%$

Ash Content

Ash content was determined following (ASTM D3174-02, 2004).Ash was determined by weighing the residue remained after burning the sample under rigidly controlled conditions of sample weight, temperature, time, atmosphere and equipment specifications. 1g dried sample from moisture determination Pulverized to pass 250µm was weighed to the nearest 0.1 and passed to weighed crucible and covered quickly. After the cover was removed the sample was put in to the muffle furnace and the temperature was maintained at 700 to 750°C, and heated for two hours. At the end of the second hour the crucible was removed from the furnace, closed and put in desiccator to cool. Finally the sample was weighed and Ash content was calculated using the following equation.

$$\boldsymbol{Ash\ content}(\%) = \left[\frac{\boldsymbol{A-B}}{\boldsymbol{C}}\right]\times\mathbf{100}$$

Where:

$\boldsymbol{A = weight\ of\ crucible, cover\ and\ Ash\ residue, g,}$

$\boldsymbol{B = weight\ of\ empty\ crucible\ and\ cover, g,}$ **And**

$\boldsymbol{C = \ weight\ of\ sample\ used, g}$

Fixed carbon content

The fixed carbon content of the samples was obtained by subtracting the summation of percentage moisture content, Volatile matter content, Ash content from 100.

$$\boldsymbol{Fixed\ Carbon\ Content}(\%) = \mathbf{100} - (\%\boldsymbol{moisture} + \%\boldsymbol{volatile} + \%\boldsymbol{Ash})$$

Bulk Density

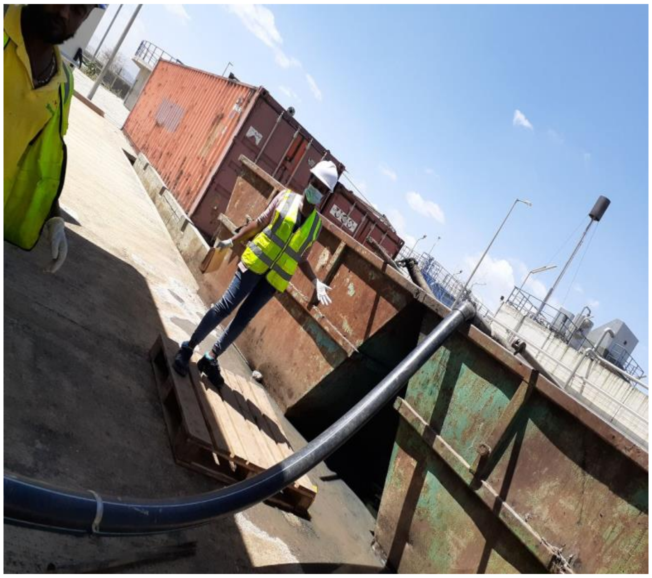
As a physical property of the briquette, density is defined as the structural packing of the material's particles in a given volume. The density of the briquettes was determined by weighing the briquettes with a laboratory weighing balance and measuring the diameter and length of the briquettes using vernier caliper. The volume was evaluated using the relation $V = \pi * r^2 * h$ and the density was calculated using the following equation.

$$\boldsymbol{Density}\left(\frac{g}{cm^3}\right) = \left(\frac{mass}{volume}\right)$$

Where: π = 3.14, r = radius of the briquette, h= length (height) of the briquette

APPENDIX B: Laboratory Experiment Photos

BWWS at the Discharge point of Heineken brewery



BSG at the Discharge point of Heineken

Raw sample of the BWWS

Raw sample of the BSG

-Sun Dried BSG

Grinded BSG

Sun dried BWWS

Grinded BWWS

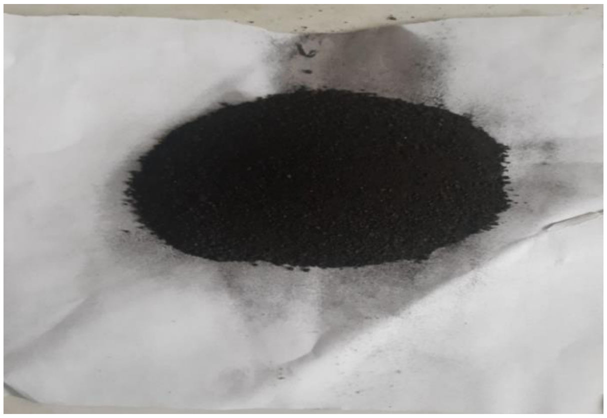
Sawdust

Grinded Sawdust

Samples prepared for carbonization

carbonizing with muffle furnace

Mixed carbonized sample



carbonized pellets

Sawdust pellet

Non-carbonized mixed pellet

Carbonized, Sawdust, Non- carbonized

Drying Oven

Attrition Mill

Adiabatic Bomb Calorimeter

Muffle Furnace

Hydraulic Press Machine

Mould

APPENDIX C: Design-Expert outputs

Table C.1: optimization possible solutions

Number	**Temperature**	**Time**	**Mixing Ratio**	**Calorific Value**	**Desirability**
1	**350.000**	**60.000**	**75.000**	**4761.079**	**0.999**
2	350.003	60.374	75.000	4745.738	0.997
3	350.000	60.000	74.767	4755.614	0.997
4	350.503	60.000	75.000	4756.232	0.997
5	351.909	60.000	75.000	4742.658	0.990
6	350.000	61.892	74.999	4685.172	0.988
7	352.480	60.000	75.000	4737.140	0.988
8	350.004	60.000	73.815	4732.969	0.987
9	350.000	62.178	75.000	4674.061	0.986
10	353.395	60.000	74.998	4728.226	0.983
11	352.200	61.377	75.000	4683.841	0.981
12	354.799	60.000	75.000	4714.635	0.976
13	350.000	64.198	74.999	4598.029	0.975
14	355.263	60.000	75.000	4710.118	0.974
15	350.001	64.458	75.000	4588.614	0.973
16	355.986	60.000	75.000	4703.066	0.971
17	350.000	60.000	72.109	4691.400	0.970
18	350.000	60.000	71.528	4676.894	0.964
19	350.000	66.782	75.000	4507.504	0.961
20	360.646	60.001	75.000	4657.363	0.948
21	350.000	70.518	75.000	4389.711	0.941
22	350.000	71.796	75.000	4353.001	0.935
23	350.048	60.000	68.823	4606.813	0.934
24	350.000	60.001	68.596	4601.125	0.932
25	350.000	60.000	68.304	4593.406	0.929
26	350.000	120.000	75.000	4298.040	0.926

27	350.000	119.999	74.716	4302.420	0.925
28	350.000	120.000	74.538	4305.174	0.924
29	350.000	119.999	74.339	4308.205	0.924
30	350.434	120.000	75.000	4290.676	0.923
31	351.045	120.000	75.000	4280.300	0.920
32	350.000	120.000	73.049	4327.464	0.919
33	351.760	120.000	75.000	4268.133	0.915
34	350.000	119.999	72.128	4340.666	0.915
35	367.219	60.000	75.000	4592.135	0.914
36	350.000	119.998	71.613	4347.886	0.913
37	350.097	120.000	71.279	4350.983	0.911
38	350.000	115.719	75.000	4198.078	0.908
39	350.000	119.917	70.385	4362.252	0.907
40	350.000	115.231	75.000	4187.980	0.907
41	350.000	114.378	75.000	4170.969	0.904
42	353.936	120.000	75.000	4231.083	0.902
43	350.000	80.259	75.000	4155.821	0.901
44	350.000	113.526	75.000	4154.801	0.901
45	350.000	111.463	75.000	4118.964	0.894
46	372.306	60.000	75.000	4541.008	0.888
47	350.000	108.617	75.000	4077.331	0.886
48	350.000	86.021	75.000	4067.287	0.884
49	350.000	107.373	75.000	4061.968	0.883
50	350.000	104.667	75.000	4034.503	0.878
51	350.000	103.700	75.000	4026.674	0.877
52	350.000	90.184	75.000	4026.350	0.877
53	350.000	93.123	75.000	4009.088	0.873
54	350.000	100.403	75.000	4007.809	0.873
55	350.000	95.813	75.000	4001.732	0.872
56	368.462	120.000	56.648	4271.308	0.739

Table C.2: Design summary

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	2.546E+08	1	2.546E+08			
Linear vs Mean	1.681E+06	3	5.604E+05	2.19	0.1288	
2FI vs Linear	3.004E+06	3	1.001E+06	11.96	0.0005	
Quadratic vs 2FI	**8.611E+05**	**3**	**2.870E+05**	**12.64**	**0.0010**	**Suggested**
Cubic vs Quadratic	25275.42	4	6318.85	0.1879	0.9362	Aliased
Residual	2.017E+05	6	33623.44			
Total	2.603E+08	20	1.302E+07			

Table C.3: diagnostics report

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals	Cook's Distance	Influence on Fitted Value DFFITS	Standard Order
1	3570.55	3407.43	163.12	0.118	1.153	1.175	0.018	0.430	19
2	3754.37	3691.04	63.33	0.793	0.924	0.917	0.328	1.796	6
3	3409.17	3407.43	1.74	0.118	0.012	0.012	0.000	0.004	18
4	3309.44	3407.43	-97.99	0.118	-0.693	-0.673	0.006	-0.247	20
5	3782.37	3775.66	6.71	0.491	0.062	0.059	0.000	0.058	9
6	4764.58	4761.08	3.50	0.793	0.051	0.048	0.001	0.095	5
7	3238.04	3198.41	39.63	0.793	0.578	0.558	0.128	1.093	2
8	3267.55	3335.99	-68.44	0.491	-0.637	-0.617	0.039	-0.606	14
9	4291.91	4298.04	-6.13	0.793	-0.089	-0.085	0.003	-0.166	7
10	4429.29	4459.12	-29.83	0.793	-0.435	-0.417	0.073	-0.817	3
11	2501.33	2493.59	7.74	0.793	0.113	0.107	0.005	0.210	8
12	3978.76	3948.76	30.00	0.793	0.438	0.419	0.073	0.821	4
13	*3760.59*	*3407.43*	*353.16*	*0.118*	*2.496*	*3.857*	*0.083*	*1.412*	*17*
14	3325.55	3407.43	-81.88	0.118	-0.579	-0.558	0.004	-0.204	16
15	3104.68	3170.22	-65.54	0.491	-0.610	-0.589	0.036	-0.579	13
16	3705.19	3837.41	-132.22	0.491	-1.230	-1.266	0.146	-1.244	11
17	2844.77	2985.46	-140.69	0.491	-1.309	-1.364	0.165	-1.339	10
18	3000.12	2974.36	25.76	0.793	0.376	0.359	0.054	0.703	1
19	3979.29	3981.06	-1.77	0.491	-0.016	-0.016	0.000	-0.015	12
20	3337.24	3407.43	-70.19	0.118	-0.496	-0.477	0.003	-0.174	15

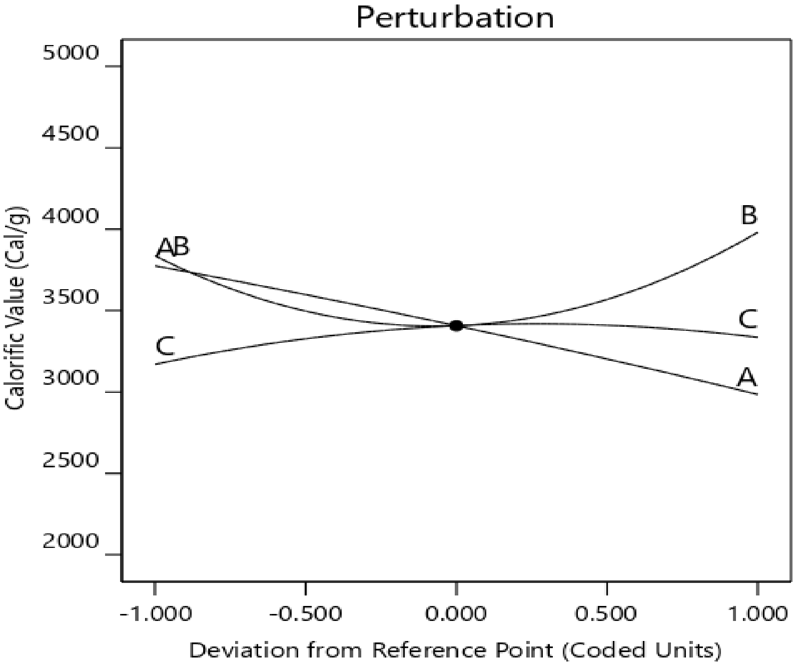


Figure C.1: Perturbation effect of all independent variables

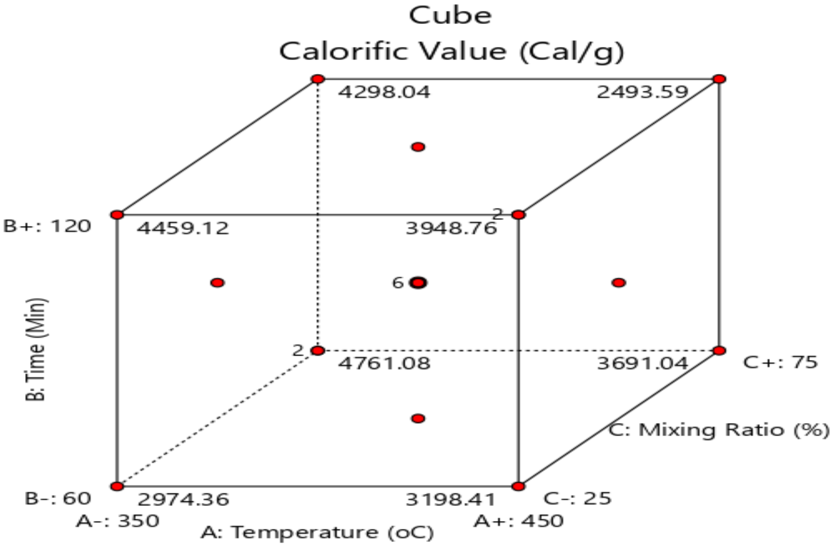


Figure C.2: Cubic effect of Temperature, Time and mixing ratio