ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

OPTIMIZATION AND CHARACTERIZATION OF BRIQUETTES DEVELOPED FROM WHEAT STRAW AND COFFEE HUSK AS AN ALTERNATIVE ENERGY SOURCE IN CEMENT INDUSTRY

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A Thesis submitted to Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering, in partial fulfillment of the requirements of Masters of Science (Process Stream)

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This is to confirm that thesis provided by Misganaw Workneh, entitled "Optimization And Characterization Of Briquettes Developed From Wheat Straw And Coffee Husk As An Alternative Energy Source in Cement Industry" is submitted in partial fulfillment for degree of Masters of Science in process stream under Chemical and Bio Engineering complies with the regulations of the university and meet the accepted standards with respect to originality and quality.

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ACRONYMS

AAU	Addis Ababa University
AAiT	Addis Ababa Institute of Technology
AACNS	Addis Ababa College of Natural Science
ASTM	American Society for Testing Materials
RSM	Response Surface Methodology
FT-IR	Fourier transmission infrared spectroscopy analysis
HHV	High Heating Value
LHV	Lower Heating Value
FC	Fixed Carbon
VM	Volatile Matter
AC	Ash Content
MC	Moisture Content
ml	Milliliter
µm	Micrometer
Kcal/Kg	Kilo Calorie per Kilogram
MJ/Kg	Mega Joule per Kilogram

NOTATIONS

Symbol	Definition	Units
Ms	Mass of sample	g
Mash	Mass of Ash	g
ρ	Bulk density	kg/m^3
V1	volume of container	ml
V	volume of briquette	mm^3
Z	weight of container	g
Y	weight of container and sample	g
r	radius of briquette	mm

ABSTRACT

The process of making cement uses a lot of energy and produces emissions. Both the overall environmental impact of the cement industry and energy security are enhanced by the substitution of alternative fuels for coal. Because they are widely used in the making of cement, fossil fuels like coal, coke, and heavy fuel oil are not renewable and are predicted to release massive volumes of greenhouse gases (GHG) into the atmosphere during their life cycle, which includes mining, processing, transportation, and burning. This study looked at whether briquetting wheat straw and coffee husks would be a suitable alternative energy mix for cement pyro processing. Understanding the physiochemical and thermal properties of raw coffee husk, wheat straw, and mixed briquetted pellet required characterization for proximate analysis, final analysis, calorific value, bulk density, and ash composition of the fuel.

Box Behnken design (BBD) was used to optimize process factors that impact the calorific value, such as particle size (<100µm, 100 ~ 175µm, and 175 ~ 250µm), mixing ratio (30%, 50%, and 70%), and carbonization temperature (300°C, 350°C, and 400°C). The findings indicated that the optimized parameters were as follows: a maximum calorific value of 5616.52 Kcal/kg, a mixing ratio of 70% coffee husk to 30% wheat straw, and a particle size of around 100µm. Lastly, the calorific value, volatile matter, moisture content, ash content, and fixed carbon content of the briquette have all been measured and found to be 5676.24 Kcal/Kg, 52.5%, 3.5%, 7.6%, and 39.84%, respectively

1. INTRODUCTION

1.1. Background

Cement is an important binder used in building that is manufactured in vast amounts all over the world. Because the clinker kilns must reach temperatures between 1450°C and 1500°C and release a significant quantity of CO_2, the manufacturing of cement is an energy-intensive operation (Murray and Price, 2008). Depending on the procedure, the clinker needs between 788 and 955 kcal/kg of heat energy to produce cement (Demján, 2005).

According to Vesterinen et al. (2010), the cement factory uses around 835 kcal/kg of clinker for energy and emits about 1 ton of CO_2 for every ton of clinker, of which about 40% comes from fuel and about 60% from the calcination of the limestone. More than 90% of the energy required to produce cement is used in the pyro process. The remaining 10% is roughly equally divided between the processes involved in clinker grinding, fuel and raw material preparation, and material combining to create the final cement product. Consequently, a large cement mill needs a lot of fuel. Furthermore, the cement industry is mostly dependent on fossil fuels that are high in carbon.

Owing to the distinctive nature of its output, the cement sector contributes around 5% of the world's anthropogenic CO_2 emissions, resulting in approximately four degrees of global warming [WBCSD, 2009]. The primary source of these greenhouse gas emissions is the combustion of fossil fuels during the cement-making process. Additional emissions associated with cement are produced during the production process, which breaks down or calcines limestone ($CaCO_3$) to produce calcium oxide, which is the primary precursor of cement.

It is now necessary to create a new, efficient, and cost-effective renewable and sustainable alternative energy source to address the need for a sustainable energy supply due to energy reliance and the environmental effects of fossil fuel usage. A significant role for biomass as an alternative energy source is anticipated, given it is carbon neutral among the remaining renewable resources (IEA, 2015; J.S. Tumuluru, Wright, Kenny & Hess, 2010). Agricultural wastes like coffee husks and wheat straw are seen as a potentially sustainable and inexpensive source of energy since they are small scale, locally generated, indigenous resources that are readily available.

Ethiopia demands for cement were predicted to rise as a result of the GDP's steady and ongoing expansion. The country has a lot of potential for cement consumption, as evidenced by rising per capita income, fast urbanization, high population growth, a severe housing scarcity, significant infrastructural deficiencies, and the creation of an industrial park.

It is anticipated that as the world's population rises, fuel consumption will rise as well, changing the rate at which various nations are developing their industries. A fuel crisis is likely to occur when demand greatly exceeds supply, necessitating the use of alternative renewable energy sources.

Fuels that deviate from the current standard are known as alternative fuels. This applies to all fuels with the exception of gas, coal, heavy fuel oil, and white spirit. According to Mokrzycki E. et al. (2003), the alternative fuels utilized in the cement industry can be liquid or solid and made from combinations of industrial and municipal waste. Considering the components nature and the amount of organic matter they contain; these fuels need to have the right chemical composition.

1.2. Statement of the problem

Energy is mostly used in the pyro-process of the kiln plant, which produces cement clinker, in the energy intensive cement manufacturing sector. The limited availability of fossil fuels, the need for imported fuels by Ethiopias cement industry, fluctuating and high prices, and above all the increasing greenhouse gas emissions that are causing global warming force the local industries to concentrate on producing energy through the use of alternative carbon-neutral renewable sources.

Moreover, compared to 30~40% in the global comparison, Ethiopian cement plants energy expenses represent over 50~60% of their whole production cost structure. As a result, people continue to view Ethiopian prices as being somewhat higher than those on the global market. More significantly, lowering energy costs by partially substituting alternative energy sources for imported coal is the best way to increase the competitiveness of cement plants. Therefore, in order to lower cement manufacturing costs and prices, investments in alternative energy sources are required.

Alternative fuels, such as biomass and biomass leftovers, might be used by cement factories to heat their kilns. The leftovers from agriculture and agro-industry make for 15% of Ethiopia's overall energy consumption. The remnants are mostly utilized in the house with extremely low power equipment for baking and cooking. The best prospective alternative fuels are coffee husk and wheat straw due to their modest energy value and considerable availability.

The principal drawbacks of utilizing agricultural residues, like coffee husks and wheat straw, as a sustainable substitute for coal and other fossil fuels are their high moisture content, which leaves them vulnerable to degradation by microorganisms, their heterogeneous nature, low calorific value, and higher volume or low bulk density. In order to increase the qualities of the biomass and get around these drawbacks, briquetting was devised. A review of earlier studies on the temperature and pressure at which carbonization occurs in briquetting reveals that numerous publications report carbonization at temperatures and pressures of no more than 300°C and 1 MPa for a variety of biomasses, including coffee husk, corn stalk, bamboo, banyan, willow, blue gum wood, leucaena, sawdust, rice husk, wheat straw, and reed canary grass. But none of them have so far studied in detail the fuel property of mixed carbonized coffee husk and wheat straw briquette more than 300°C and 1MPa.

In order to replace imported fossil fuels, the goal of this study was to develop, optimize the operating parameters, and examine the burning properties in comparison to mixed briquette coffee husk and wheat straws.

1.3. Objectives

1.3.1. General objectives

The main objective of this research were to find out if briquettes composed of wheat straw and coffee husks might be utilized as a substitute energy source to produce clinker for the cement industry.

1.3.2. Specific objectives

- To determine the physico-chemical and thermal properties of raw wheat straw and coffee husks.
- To develop a mixed briquette and physico-chemical characterization.
- To investigation the influence of particle size and proportion on the calorific value of a briquette.
- To optimization the carbonization parameters and comparison of optimal combustible briquettes with non-charred briquettes.

1.4. Significance of the study

For the Ethiopian cement business, society, and most crucially, the environment, these studies provide a solid and safe answer. By optimizing clinker production, substituting of waste and byproducts as alternative fuels lowers greenhouse gas emissions. Because its resources are limitless, it will also provide sustainable energy security (maximum energy recovery from waste) and offer protection against the volatility of the world energy market. It also makes the difficult work of getting rid of rubbish in an eco-friendly way easier. For our nation, which has a strategic plan for a climate-based green economy, it is therefore a win-win situation.

Most cement factories find fuel switching to be beneficial due to its economic and environmental benefits. Lower fuel prices are one financial benefit of switching to alternative fuels, and manufacturers can make more money as biomass fuels can cut carbon emissions from cement plants by a large amount. Benefits like employment creation and currency savings are felt throughout the country.

2. LITERATURE REVIEW

2.1. Overview of Cement Production

Solids (aggregates) are bind together by cement, a substance that solidifies from a plastic condition. For growing nations to reduce poverty and promote economic growth, cement is essential. Cement is a basic component of concrete, along with aggregate and water. As such, it is a necessary building material that makes it possible to construct massive infrastructure projects in the energy, water, and transportation sectors as well as most importantly the construction of contemporary buildings and urban infrastructure (IFC, 2017). There are two steps involved in the process of producing cement.

Firstly, the raw ingredients calcium oxide (42~55%), silicon oxide (10~20%), aluminum oxide (3~10%), and iron oxide (3~8%) are heated to temperatures as high as 1500°C in a rotary kiln to make clinker. The procedure in this stage might be semi-wet, dry, wet, or dry depending on the state of the raw material. The next stage is to mix in gypsum (calcium sulphates) and maybe additional ingredients such fly ash and natural pozzolan once the clinker has been created. After being processed in a cement mill to a fine, uniform powder, the cement is either transported in bulk or in bags (Thrän et al., 2017).

China is by far the world's greatest producer of cement, with estimates of 2.5 billion tons in 2021, followed by India with 330 million tons in the same year, according to data on worldwide cement output. China is the world's largest producer of cement. Global cement output is projected to reach 4.4 billion tons in 2021. Cement output in the globe was just 1.39 billion tons in 1995, illustrating how much the building industry has expanded since then. It is projected that the amount of cement produced worldwide would rise from 3.31 billion tons in 2010 to 4.85 billion tons in 2030.

One of the sectors in Ethiopia that is expanding the quickest is the cement industry. The nation's average per capita cement consumption climbed from 39 kg to 62 kg. This figure is still far less than the 500 kg world average per capita consumption, though. In order to satisfy the demands of the nation going forward, the Ethiopian government intends to upgrade its current cement plants and build new ones. Ethiopia presently has 20 cement plants, 16 of which are integrated factories and the other 16 of which are grinding plants.

By 2025, it is anticipated that each person would need 179 kg of cement. In recent years, Ethiopia has grown to become one of the biggest cement markets in Africa. Furthermore, Ethiopia is now the continent of Sub-Saharan Africa's top exporter of cement. The manufacture of cement in Ethiopia is mostly dependent on imported energy. The high manufacturing costs in this industry are significantly impacted by this predicament.

The Federal Democratic Republic of Ethiopia (FDRE) Ministry of Industry has created new plans to direct the growth of Ethiopia's cement sector for the years 2015~2025. By the end of 2025, the nation is expected to consume 19.97 million tons of cement, while a 25.16 million ton production capacity would be needed. By the end of 2025, eight million tons of extra capacity will be available. By 2025, the average person's cement consumption is predicted to rise from 62 kg to 179 kg. Encouraging the manufacturing of green cement is one of the government's strategic initiatives to boost Ethiopia's cement sector.

Table 1: Cement plants in Ethiopia

Plant	Year of Operation	Clinker capacity (tpd)
Muger Cement Enterprise	1984	2000
Mesebo Cement Factory	2001	2000
Huan Shang P.L.C	2010	860
National Cement S.C	1936	960
Abyssinia Cement P.L.C	2007	288
Jema Cement P.L.C	2008	100
Debresina Bussiness industries P.L.C	2009	288
Dejen Mini Cement Plant	2007	288
Mugher Cement Expansion project	2012	3000
Messobo Cement Expansion Project	2011	3000
National Cement S.C (new)	2014	3000
Derba-dashen Cement Plant	2011	288
Derba MIDROC Main Cement Plant	2012	5000
Dangote Industries P.L.C	2015	5000
Habesha cement S.C	2016	3000

Ethio-Cement Plc.	2014	1340
East Cement Plc.	2011	1675
Pioneer Cement Plc.	2012	1000
Enchini Bedroc Cement Plc.	2012	667

2.2. Cement Chemistry and Impact on The Environment

The production of cement results in significant emissions of greenhouse gases and heavy reliance on fossil fuels (Worrell et al., 2001). According to Lemieux et al. (2004), cement kilns are an energy intensive industry that require an energy input of 3.2 to 5 MJ/kg of clinker produced, depending on the process parameters. About 2.2 MJ/kg of energy are needed for the strong endothermic decarbonization of limestone and the dehydration reaction of kaolinite, whereas approximately 0.45 MJ/kg are released during the process that generates the exothermic phase (C_3S, C_2S, C_3A, and C_4AF; see 3.1). According to Wilitsch et al. (2009), in the dry process, the chemical reaction needs around 50% of the energy used, with the remaining energy coming from radiation losses (roughly 10~12%), exhaust air (about 10%), exhaust gases (up to 20%), clinker (about 2%), and other sources. A range of energy sources are used by cement producers. According to Jacott et al. (2003), fuel oils, several kinds of coal, petroleum coke, and natural gas are the most popular fuel types. Energy is mentioned as accounting for around 30~40% of cement manufacturing costs (Rasul, Widianto & Mohanty, 2005). Cement manufacturers worldwide are embracing the practice of substituting waste products and other alternatives for fossil fuels in cement manufacturing, not only to save energy costs but also to save natural resources, reduce emissions, lessen the need for landfills and other disposal options, and reduce the CO_2 footprint of emissions (Gossman, 2007).

There are three sources of greenhouse gasses in the cement producing process. The first source originates from cement production's intrinsic characteristics. Limestone, the primary ingredient of cement, comprises over 90% calcium carbonate ($CaCO_3$). As demonstrated by chemical reaction 1, when calcium carbonate ($CaCO_3$) is heated, it breaks down into carbon dioxide, a greenhouse gas, and calcium oxide, the primary ingredient in cement.

$\mathbf{CaC}(\boldsymbol{Heat}=\mathbf{870}℃) \rightarrow \mathbf{CaO}+\mathbf{CO_2}$ …………… (1)

About 44 grams of carbon dioxide and 56 grams of calcium oxide are created from 100 grams of calcium carbonate heated to approximately 750 °C in a kiln. As a result, around 44 grams of carbon dioxide are emitted into the environment for every 56 grams of calcium oxide used in building. Burning carbonaceous fossil fuels like coal, methane, furnace fuel, or dirt tires, as well as alternative fuels like biomass, is the second source of greenhouse gasses. It also includes burning garbage from homes and businesses. Reaction 2 uses methane (CH4), the simplest hydrocarbon component, to explain how a carbonaceous fuel burns and produces carbon dioxide.

$\mathbf{CH_4+2O_2 \rightarrow CO_2+2H_2O}$ ………………………… (2)

The European Cement Association estimates that each tons of cement produced in the kiln results in around 335 kg of carbon dioxide emissions overall from fuel burning.

Power plants that burn fossil fuels to create electricity are a third source of carbon dioxide emissions. For every tons of cement produced, this equates to about 50 kg of CO_2, according to the European Cement Association. Electric motors do not emit a significant quantity of carbon dioxide, unlike countries like Ethiopia, where hydropower accounts for the majority of energy generation. However, it is evident that the first two sources of carbon dioxide are produced by the cement factories in these nations. For every tons of cement produced, up to 0.8 tons of carbon dioxide are released into the environment as a result of these three sources. Because of this, the manufacture of cement contributes significantly to greenhouse gas emissions, making up 5% of total emissions worldwide (Ernst Worrell, Lynn Price, Nathan Martin, Chris Hendriks, 2001).

2.3. Alternative Fuels in The Cement Industry

Although there is no formal definition for the word "alternative fuel," it refers here to fuels that are not today's standard or conventional fuels. This implies that the phrase is also dynamic, meaning that what are now considered alternative fuels may eventually be regular or conventional fuels. Therefore, all fuels other than gas, heavy oil, coal, and petcock are considered alternative fuels in the context of the cement business today. Waste fuels and biofuels are the two primary categories into which alternative fuels may be generally separated.

Waste fuels are fuels derived from household waste and industrial waste and include:

- Plastics;

- Paper;
- Used tires;
- Sewage sludge;
- Oil sludge from refineries
- Municipal solid waste, either raw or sorted and refined fractions such as refuse derived fuel (RDF)
- Meat and Bone Meal (MBM)

Biofuels are fuels that are derived from forestry and agricultural waste. The types are many and will reflect the local agriculture and forestry. Examples of biofuel include;

- Wood chips;
- Straw;
- Rice husk;
- Sesame husk;
- Cotton Stalk
- Coffee husk;
- Bio oils (e.g. Palm oil or Jatropha oil);
- Ethanol produced from biomass (Bioethanol);
- Chicken manure;
- Jatropha fruit and biomass
- Prosopis Juliflora Biomass
- Bamboo tree biomass

In the middle of the 1980s, alternative fuels saw their first significant use in the cement sector. Since fuel consumption accounted for over one-third of the cost of producing clinker, the primary objective of fossil fuel replacement was to maintain the industry's economic competitiveness. Any favorable effect on the environment was viewed as an extra advantage. Since then, there has been a rise in understanding of how industry and human activity affect the environment. The use of alternative fuels can significantly reduce greenhouse gas emissions and contribute to ecologically responsible waste disposal in addition to their cost-saving benefits. Because of this, the major cement industry participants have begun to use alternative fuels as a lever to increase their commitment to sustainable development and as a key element of corporate social responsibility (IFC, 2017).

2.3.1. Criteria for Using Alternative Fuel

Since alternative fuels are a blend of various wastes, they must fulfill specific requirements. Legal regulations must be meet by the fuels chemical composition in order to guarantee environmental protection. There is a threshold above which the calorific value must be. The composition of the fuel should be somewhat uniform. The physical shape ought to be transportable and easy to handle. Considering its accessibility, it ought to be financially feasible. Fuels energy, ash, moisture, and volatility contents need special consideration. A flexible fuel feeding system for alternative fuels ought to be created in order to prevent fuel issues.

2.3.2. Selection of The Best Alternative Fuel

After a variety of alternative fuels were evaluated, biomass fuels were chosen because they meet the minimal energy content requirements and were readily available in sufficient quantities. The strongest prospective alternative fuels are thought to be coffee husk and wheat straw among the biomass derived fuels indicated in Table 2.

Table 2: Calorific value of alternative fuels

No.	Energy source type	Kcal/kg	MJ/kg
1	Coffee husk	4118	17.24
2	Wheat straw	3874	16.21
3	Sawdust	4512	18.89
4	Cotton stalk	4179	17.49
5	Solid waste	3168	13.26
6	Sesame husk	4050	16.95

2.3.3. The Advantages Of Using Alternative Fuels In Cement Production

The process of making cement uses a lot of energy. The primary greenhouse gas (GHG) responsible for climate change is carbon dioxide (CO_2), which is produced when energy from fossil fuels like coal and oil is used. On a weight basis, CO_2 accounted for around 69% of all greenhouse gas emissions in 1990. Moreover, CO_2 is produced during the chemical process of producing clinker. Because of these two reasons, the cement industry contributes 5% of the world's man-made CO_2 emissions, of which 40% come from fuel burning and 50% from chemical reactions. The remaining amount is split between transportation and electrical consumption. Governments all throughout the globe are thinking about and enacting levies on industry energy consumption and greenhouse gas emissions in response to global concerns about climate change.

Typically, waste is burnt in incinerators, and the ash that is left over is either disposed of or land-filled. However, when wastes are burned in a cement kiln, the energy contained in the waste is used (energy recovery), and the ash an inorganic component becomes a part of the final product (clinker) (material recovery). However, CO2 emissions occur in both situations. Here, we were comparing net CO_2 emissions using LCA (life cycle approach) approaches.

2.3.4. Current Status of Alternative Fuels in Cement Industries

Environmental protection organizations are putting more and more pressure on the cement production sector to lower emissions. In addition to lowering emissions, using alternative fuels (AFs) in the production of cement provides major ecological advantages by preserving non-renewable resources. The rate at which AFs replace fossil fuels differs from nation to nation. When it comes to the percentage of AFs used, the majority of European nations use them far more than those in other countries.

The top cement manufacturers in the world are now employing AFs extensively and plan to use even more by 2020. Their sustainable development reports provide the percentage of different AFs used by various cement manufacturing groups as well as the conventional fossil fuel replacement rate. The percentage of various wastes that are currently being utilized as AFs in five top cement producing groups is summarized in Table 3.

Table 3: Usage of Alternative Fuels in Different Countries

Country or Region	% Substitution	Country or Region	% Substitution
Netherlands	83	Czech Republic	24
Switzerland	47.8	EU	12
Austria	46	Japan	10
Germany	42	United States	8
Norway	35	Australia	6
France	34.1	United Kingdom	6
Belgium	30	Denmark	4

Sweden	29	Hungary	3
Luxembourg	25	Finland	3

2.4. FUNDAMENTAL ASPECTS OF BRIQUETTING

Compressing bulk fuel into a high-density product is called briquetting. This greatly enhances the material's flammable, chemical, and physical qualities. Storage and transportation have also been enhanced. A lot of work has gone into researching briquettes from different sources. The raw material, type of binder, compaction pressure, temperature, and durability all affect properties like volatile matter, calorific value, relaxed density, compressed density, ash content, dimensional stability, fixed carbon, and compressive strength. It is therefore impossible to generalize these qualities. Because it includes lignin, some of the biomass spontaneously bonds when the right conditions are met during the briquette making process. To finish the process, a binder is needed if these requirements are not met. Among the binders frequently employed are starch, molasses, clay, manure and rubber. These binders influence the properties of the briquette.

Briquette Quality Can Be Determined by The Following:

- Stability and durability in handling, transportation and storage; these are measurable by changes to the weight, dimension, and ultimately the relaxed density and strength of the briquettes.
- Combustion (energy value) or ease of combustion, and ash content.
- Environmental concern, i.e. the toxic emissions during burning.
- Parameters that determine briquette quality are:
- Pressure and/or temperature applied during densification.
- Nature of the material:

Parameters that determine stability and durability of briquettes are:

- Compressive strength, impact strength.
- Compressive time.
- Relaxation: Moisture, length, density (post-briquetting parameter).

Carbonization

Carbonization has been used for thousands of years to produce solid biomass fuel, allowing early humans to extract iron ore and use charcoal as a heat source. The biomass is gradually heated for many hours to temperatures over 400°C in order to begin the carbonization process. In the event that normal charcoal is improved for adsorption and purification, the process yields activated carbon, biochar for use as soil amendments or fertilizer, charcoal for use as fuel, and biocoke for the extraction of metals.

The process of carbonation involves converting organic material into solid leftovers with a high carbon content, often by pyrolysis in an inert environment. The moisture and volatiles are eliminated by this thermal breakdown process, leaving behind a recalcitrant solid (charcoal), liquid (condensation vapor), and gaseous residue. One method of converting biomass into a more valuable commodity is pyrolysis. It is a thermal conversion process that involves treating the material at a final temperature of around 500°C in an inert environment without the presence of air or oxygen.

Temperature and reaction time are the two key factors that affect carbonization, which often happens in batch reactors. For carbonization to occur with minimum energy consumption, the raw materials need to be dry and have a moisture level of no more than 15%. Low density biomass would need to be compressed into wood-like logs known as briquettes under high pressure and temperature in order to be an effective energy replacement for the manufacturing of cement.

Types of carbonization system

The properties of char, as well as its potential value to agriculture in terms of agronomic performance, carbon sequestration, and energy value, are significantly impacted by the carbonization process. Although the temperature and furnace residence time are the two main process parameters, the kind of feedstock also affects the nature of the product as a result of the interaction between the process and its circumstances.

Low-temperature carbonization

The process of slowly heating biomass at low to medium temperatures (300 to 400°C) without oxygen while simultaneously capturing syngas is known as slow carbonization. Feed stocks are fed into a heated furnace and subjected to consistent heating in the form of dry biomass pellets or chips with different particle sizes.

This phase sees the full breakdown of hemicellulose and cellulose as well as the beginning of the degradation of lignin. The structure of the biomass continues to break down and decompose, resulting in a slightly higher fixed carbon content.

It is characterized by: -

- Relatively low reactor temperatures (300~450°C)
- Reactor operating at atmospheric pressure
- Very low heating rates, ranging from 5~80 °C/minute
- Very short thermal quenching rate for carbonization products: minutes to hours.

High-temperature carbonization

Abrupt heating of the feedstock (200~100,000°C/s) results in a significantly higher percentage of bio-oil and reduced amounts of charcoal. Unlike gradual carbonization, which takes minutes or hours to achieve peak temperature, the endothermic process reaches its peak temperature in just one or two seconds. Rapid energy transfer is possible when the feedstock moisture content is kept at 10% or less and fine particle size is used (less than 2 mm.

Intermediate Carbonization

The presence of moderate temperatures (400~600°C) and fast heating rates (less than 2°C/s) are characteristics of intermediate carbonization. Typically, vapor residence periods are around two seconds. Tar and gas production are significantly lower than with gradual carbonization.

Raw Materials for Briquette Fuel Manufacturing

Fuel briquettes can be made from non-carbonized (fresh) raw materials such wheat straw, maize cobs, coffee husks, and leaves. Nevertheless, biomass materials can be carbonized that is, burnt under regulated oxygen to remove volatile gasses and liquid before being compacted into briquettes. The raw materials used in briquetting have an impact on the characteristics of the briquettes that are generated (Asamoah et al. 2016). Fuel briquettes are a great source of fuel briquettes, with a calorific value of 17~25 MJ/kg, which is comparable to fuel coal when the moisture content is less than 14%.

A group of processes called biomass densification are used to turn biomass into fuel. The process, often referred to as briquetting, enhances the materials handling qualities for storage, transportation, and other uses. Since densification increases a fuel's volumetric calorific value, lowers transportation costs, and improves the fuel situation in rural regions, this method can aid in increasing the use of biomass in energy generation.

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 below.

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

Properties (unit)	Requirement
Moisture content (%)	6~14
Ash content (%)	< 4 to avoid slagging
Volatile matter (%)	50~90
Particle size (mm)	< 2
Fixed carbon (%)	9~25
Calorific value (MJ/Kg)	10~35
Bulk density (Kg/m3)	> 50
Carbon (%)	40~55

Hydrogen (%)	5~8
Oxygen (%)	35~48
Nitrogen (%)	0~1
Sulfur (%)	0~2

2.4.1. Binding Mechanisms of Densification

Understanding the physical and chemical characteristics of biomass is crucial for determining its eligibility for briquetting, as these attributes also impact the fuels behavior. Thermal characteristics, void volume, bulk density, and moisture content are examples of physical attributes that are important. Higher calorific value and proximal and ultimate analysis are important aspects of chemical characterization. For any explanation of the binding processes of biomass, physical qualities are vital. By mechanically interlocking and increasing particle adhesion, high-pressure densification of biomass forms intermolecular interactions at the interface.

2.5. BRIQUETTING TECHNOLOGIES

There are basically four primary methods for extrusion densification:

- Piston press briquettors
- Screw press briquettors
- Roll briquettors;
- Pellet mills

2.5.1. Piston Press Briquetting

Material from the charge is forced by a reciprocating piston into a die, where friction and pressure raise the temperature of the raw material to 145~315°C before it is extruded through a die with a diameter of 25~100 mm. To minimize wear, the mold is often water-cooled. The briquettes then go through a cooling channel, where friction creates counter-pressure on the material exiting the matrices, causing cooling to occur at progressively lower pressures. The high temperature water may convert to steam and burst the briquettes if there is an abrupt reduction in pressure. It is frequently possible to modify the back pressure to enable the best possible generation of fuels with various moisture concentrations. The briquettes can be broken or sliced after exiting the cooling chamber to the desired length. The capacity ranges from 150 kg to 1.5tph.

2.5.2. Screw Press Briquetting

- Low production capacity (750~1000kg) per hour
- High amount of friction heating by the screw, resulting in higher die temperatures and increased wear on the screw and die head.

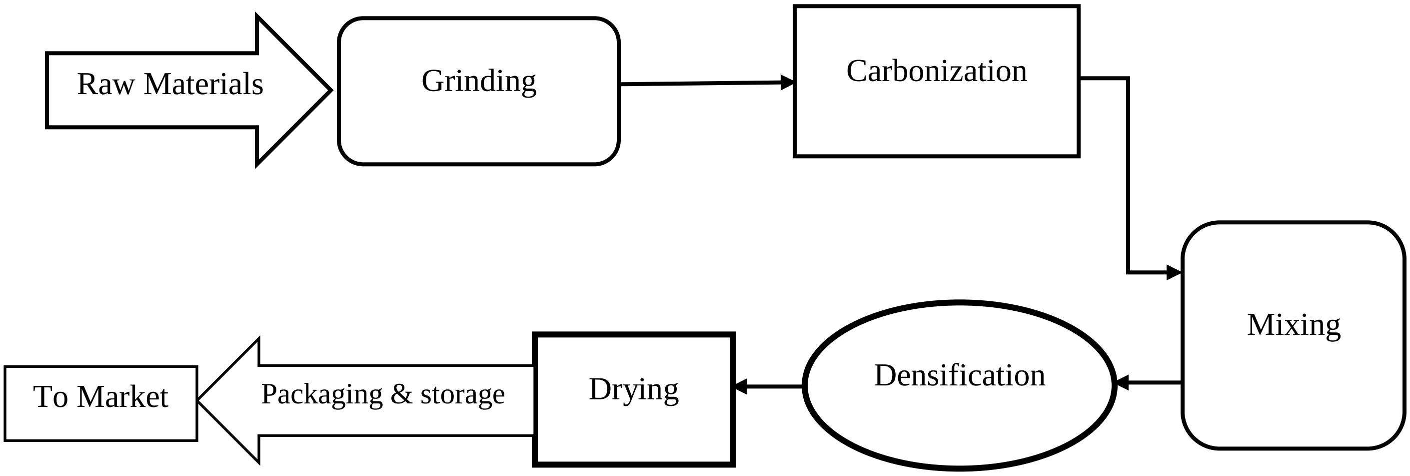
2.5.3. Roll Briquetting

- Feedstock is pre-compressed with a screw feeder and compacted between two rollers with opposing cavities to form pillow-shaped briquettes 25~50 mm in size.
- Rolled briquettes are generally less durable than extruded products unless a binder is used.

2.5.4. Pellet Mill

A pellet mill works by forcing biomass through a dense network of 5~15 mm diameter holes in a strong steel die that is either disc-shaped or cylindrical. The pellets can be severed at a predetermined length typically less than 30 mm when they are extruded from the perforations. The pellet is best suited for bulk handling and storage because to its distinct qualities, which include its tiny size, smooth, rounded edges, high bulk density, and durability.

Figure 1: Schematic Flow Diagram of Briquetting Process



Important Chemical and Physical Properties of Briquette Fuel

The following are the main physical and chemical properties of briquette fuels.

The raw materials moisture content might raise manufacturing energy costs since it takes more energy to decrease the water content during densification and drying. Flakiness in the raw materials might be caused by low moisture content. Accordingly, enough moisture is also necessary to promote the raw material's adhesion process (Asamoah et al. 2016).

The portion of biomass known as volatile matter is that which may be released when the biomass is heated, as during carbonization.

The quantity of total carbon present in the trash that may be burnt to provide heat is known as total carbon. Fixed carbon is helpful since it establishes how much solids are left over after the carbonization process is finished, which can then be utilized to create briquettes. In this instance, burned briquettes with a greater carbon content in the raw material should be robust and long-lasting mechanically.

Ash content is the powdery residue that remains after something is burned. It is made up of inflammable substances (such minerals). Ash slag is the result of a greater ash concentration. This prevents the combustion process, which encourages the smoker to overheat and eventually corrode. Therefore, in order to regulate the combustion process and protect the machine components, the raw material must have an ideal ash level.

High shear strength and durability are provided by bulk density. This may result in higher transportation costs for the raw material in terms of volume or weight, depending on whether there is high or low density involved. The capacity of the raw materials used to make briquettes to bind is often enhanced by the use of smaller particle sizes. However, employing a range of particle sizes also improves binding capacity because bigger particles fill in around smaller ones to form an interlocking link.

The quantity of energy released during the full combustion of a unit mass of briquette is determined by the calorific value (Asamoah et al. 2016). The three primary physicochemical factors to take into account while creating high-quality briquettes are moisture content, ash content, and flow characteristics. First, there should be as little moisture content as possible since too much moisture would make it difficult to fire and take a lot of energy to dry, which will lower the combustion quality. Second, since large alkaline earth metals make up the majority of high ash biomass, the ash concentration of biomass should be less than 4%. These components have a low fusing temperature, which raises the slagging potential. Thirdly, a high degree of flow characterization ought to exist. The procedure of briquetting 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. 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.

3. MATERIALS AND METHODS

3.1. Raw Material Preparation And Collection

For this study, the biomass was gathered as leftovers from coffee husks in Addis Ababa and wheat straw in the Holeta town area of the Oromia region. By drying in the sun for six to seven days, the first moisture decrease was accomplished. Following that, the two residues were crushed and sieved to particle sizes of (<100μm), (100~150μm), and (150~250μm). Four distinct institutes hosted the experiments. The FT-IR analysis was carried out at AAU, AACNS, while the grinding, sieving, carbonization, and briquetting processes were carried out in the School of Chemical and Bioengineering and Mechanical Workshop, AAiT. At Habesha Cement Share Company, ash chemistry and calorific value were assessed. On the other hand, ultimate analysis was conducted at Dangote Cement Plc Ethiopia.

3.2. Equipment and Chemicals Used

3.2.1. Equipment Used

Centrifuge mill, grinder, sieve, electrostatic balance, ceramic crucibles, platinum crucibles, drying oven, muffle furnace (0~1200°C), desiccators, elemental analyzer, CT–5000A bomb calorimeter, flask, condenser, funnel, porcelain dish, pipette, burette, beaker, hot plate, Bunsen burner, metallic crucibles, drying oven, stove, and plastic cup were the main pieces of equipment used.

3.2.2. Chemicals Used

Raw materials; coffee husk and wheat straw

Chemicals that were used include: ammonium hydroxide, nitric acid, copper sulfate, ethylene diamine tetra acetic acid (EDTA), hydrochloric acid, sulfuric acid, PAN indicator, sulfosalsalic acid indicator, phenolphthalein, calcine methyl phenolphthalein (CMP), methyl red indicator, barium chloride, potassium fluoride, potassium chloride, sodium hydroxide, sodium carbonate, tri ethanol amine (TEA), filter paper and distilled water.

3.3. Characterization of Raw Wheat Straw and Coffee Husk

3.3.1. Proximate Analysis

Moisture Content (MC)

Within a biomass, moisture can take on several forms. For example, i) surface or free moisture refers to water that is retained on the surface of biomass particles. ii) Water retained in pores by capillary action is known as inherent (residual) moisture. iii) Decomposition moisture: water resulting from the thermal breakdown of biomass's organic components. Therefore, surface and inherent moisture make up the overall moisture content of biomass, which is expressed as a mass percentage of the biomass as received.

%Total moisture = %Free moisture + %Inherent moisture

The coffee husk, wheat straw, and mixed briquette moisture content were obtained gravimetrically by the oven drying method.

For this work, two samples (coffee husk and wheat straw) are taken and put into oven using aluminum foil at about 105°C.

Figure 2: Oven Drying of Wheat Straw and Coffee Husk

Free Moisture (%FM)

A silicon crucible was filled with around 100 grams of a finely ground (<1mm) air-dried biomass sample, which was subsequently heated to 105 ± 5°C using an electric hot oven. After the biomass sample-filled crucible had been in the oven for one and a half hours, it was taken out using tongs, allowed to cool in a desiccator for around fifteen minutes, and then weighed. The weight loss is expressed in free moisture (on percentage basis). The equation is given below:

$$MC = \frac{A - B}{A - C} * 100\%$$

Where, MC= moisture content

C= mass of crucible in g

A= mass of sample+ crucible in g (before heating)

B= weight of sample+ crucible in g (after heating)

Inherent Moisture (%IM)

After the surface free moisture biomass sample was about 50 grams finely powdered (~90µm), it was weighed in a silica crucible and heated to 105±5˚C using an electronic hot air oven. After being in the oven for around three hours, the crucible containing the biomass sample was removed using a pair of tongs, allowed to cool in a desiccator for fifteen minutes, and then weighed. Inherent moisture is used to describe the weight loss (on a percentage basis).

The equation is given below:

$$MC = \frac{A - B}{A - C} * 100\%$$

Where, MC= moisture content (%)

C= mass of crucible in g

A= mass of sample + Crucible in g (before drying)

B= mass of sample + Crucible in g (after drying)

Figure 3: Moisture Determination by Oven Drying

Determination of the ash content (AC)

First, a silica crucible was weighed and oven dried until its weight was constant. One gram of the dry basis sample, around 90µm in size, was weighed and placed in an empty silica crucible. After the cupel was burned for 30 minutes in an electric furnace, it was removed and burned for four hours at 550°C. The cupel was then removed from the high temperature furnace and allowed to cool to room temperature for 25minutes before being weighed to the nearest 0.002g.

$$AC(\%) = \frac{A - B}{C - B} * 100$$

Where B= mass of crucible

C= mass of crucible + masst of sample before heating

A= mass of crucible + mass of sample after heating

Figure 4: Weighing Balance and Muffle Furnace

Volatile Matter (VM %)

The volatile matter was calculated using the 2004 ASTM D3175-02 standard. It was ascertained by calculating the weight loss that occurred when a sample was heated under strictly regulated circumstances. After weighing about 1 gram of finely powdered (<90µm) air-dried coal sample, it was weighed in a VM crucible to the closest 0.002g and put inside a muffle furnace that was kept at 925˚C. The crucible's lid was then placed on top. After precisely seven minutes of heating, the crucible was taken out, let to cool in the open air, and then placed within a desiccator before being weighed once more. The calculation is done as per the following:

$$C = \frac{A-B}{A} * 100\%$$

C= weight loss in (%)

A= mass of sample used (oven dried) in grams before heating

B= mass of sample in grams after heating

VM =C-D

Where:

VM= volatile matter in %

D= moisture (%)

Fixed Carbon (FC %)

The proportion of ash content, moisture content, and volatile matter were subtracted from 100 to determine the percentage fixed carbon (PFC).

%FC= 100- (%VM+%AC+%TMC)

3.3.2. Ultimate Analysis

Using an elemental analyzer, this is the conventional procedure for figuring out the amount of carbon, hydrogen, nitrogen, and sulfur in raw coffee husks and wheat straw both before and after heat treatment. The samples were added to the analyzer together with extra oxygen, a reference flow, and helium, the carrier gas. They were ascertained using an elemental analyzer (EA 1112 Flash CHNS/O analyzer) in accordance with ASTM procedures. A tin cap containing an average sample weight of 1.5 to 2 mg was used to load the device. Next, in an oxygen-rich atmosphere with a high temperature, the tin was put into the combustion tube. With a carrier gas flow of 120 mL/min, a reference flow of 100 mL/min, an oxygen flow of 250 mL/min, a furnace temperature of 900°C, and a furnace temperature of 75°C, an exothermic reaction was produced. Carbon dioxide, water, nitrogen dioxide, and sulfur dioxide are the products of the reaction between the oxygen and other elements in the sample, such as carbon, hydrogen, nitrogen, and sulfur.

A thermal conductivity detector (TCD) was used to detect the combustion products after they had been separated by column chromatography. The TCD produced an output signal that was proportionate to the quantity of each component in the mixture. This establishes the sample's components comparable compositions. By deducting the total of the compositions of carbon, hydrogen, nitrogen, and sulfur from 100, the composition of oxygen was calculated based on these.

Calorific Value Determination

Using an oxygen bomb calorimeter and comparable techniques, the sample's calorific value was ascertained (ASTM D 5468, 1999). The oxygen bomb was loaded after a 1gram sample was prepared. Two thousand grams of distilled water were put into a calorimeter bucket, which was then placed inside the calorimeter. The controller was used to bring the temperature of the jacket and bucket into balance while the calorimeter ran for five minutes. Subsequently, the bomb was detonated, and after 20 seconds of firing, the temperature inside the bucket reached. After burnout, temperature was measured for approximately six minutes. Until the temperature reached a steady maximum and stayed that way for at least two minutes, the thermometer was read every minute. The final temperature was then recorded. After the recording, the thermometer was raised and the bomb removed from the bucket. After being cleaned with distilled water, the bomb's inside surfaces were gathered in a beaker. To calculate the net quantity of burnt wire, all unburned bomb electrode fuse wire fragments were taken out, straightened, and their total length in centimeters measured. The bomb washes were then titrated using a normal sodium carbonate solution that included methyl orange. The gross calorific value of the sample was then calculated using the following equation.

$$\text{Calorific value} = \frac{((Tf-Ti)*14470)-40}{4.185m}$$

Where; m=mass of the sample, (g)

Tf=final temperature

Ti= initial temperature

3.3.3. Ash composition of wheat straw, coffee husk, and Mixed Briquette

Ash Chemistry of the raw wheat straw and coffee husk were performed in order to determine the percentage of different oxides such as SiO_2, Fe_2O_3, Al_2O_3, CaO and MgO.

The sample was first prepared following the procedures;

- Each sample's oxide content was measured using 1.0 g, which was then oven dried for an hour at 105 °C, ashed for an hour at 950 °C, and chilled in a desiccator.
- In a platinum crucible, 2.5g of fusion mixture ($NaKCO_3$) and 0.5g of samples were weighed. The surface of the mixture was then coated with an additional 0.5g of $NaKCO_3$. After that, a lid was put over the crucible, and it was heated to 1000 for 20 minutes in a muffle furnace.
- The sample was removed from the furnace & gently swirled in order to spread the melton the sides of the crucible.
- The sample was then put in a porcelain basin and submerged in around 50 milliliters of the basin's cold distilled water. After that, the crucible and lid were taken out of the basin and put on a dry porcelain dish. After that, the fuse was released using around 20 milliliters of concentrated hydrochloric acid. Distilled water was used to rinse the crucible and lid.
- After that, the dish's contents were evaporated to dryness on a water bath. As it dried, wash with an additional 20ml of concentrated HCl.
- After being taken out of the water bath, it was cooked at 105°C for an hour in a drying oven. Removed from the oven, let to cool, and then 20 milliliters of HCl were added and allowed to digest for ten minutes.
- Using coarse filter paper, the contents were filtered while still hot in a 500 ml volumetric flask. Filled to the brim after being regularly washed in hot water and let to cool.
- Whereas the filtrate was utilized for CaO, MgO, Fe_2O_3, and Al_2O_3 analysis, the precipitate was utilized for SiO_2 analysis. The above-prepared filtrates and other laboratory reagents were then used to determine the main oxides.

Determination of CaO

A 25 ml solution filtrate was pipetted into a 300 ml beaker. The solution was diluted to 200ml after adding 10ml of KF (20g/l) and letting it sit for 5 minutes. The addition of 5 milligrams of CMP indicator and 5 milliliters of TEA (triethylamine) rendered Fe_2O_3 and Al_2O_3 inactive. After that, 25 milliliters of KOH were added to the liquid to bring its pH down to 10.2. Finally, yet importantly, the solution's green hue became crimson when 0.015M EDTA was added to it.

$$\%\mathrm{CaO} = \frac{\mathrm{V_{EDTA}} * \mathrm{T_{CaO}}}{\mathrm{Ms}}$$

Where: V_{EDTA} = volume of EDTA added

M_S= mass of ash

T_{CaO}= 0.784

Determination of Fe_2O_3

In a 300 ml beaker, 25 ml of the solution was diluted with distilled water to make 100 ml. The solution was heated to 2 pH and drops of NH_4OH (1 gm/l) were added until a yellow tint appeared. After that, endpoint determination was achieved by adding ten drops of indicators for sulfosalicylic acid. Titrate the solution with EDTA until the reddish-brown hue turns colorless.

$$\%\mathrm{Fe2O3} = \frac{\mathrm{V_{EDTA}} * \mathrm{T_{Fe2O3}}}{\mathrm{M}s}$$

Where: V_{EDTA} = volume of EDTA added

M_S= mass of ash

T_{Fe2O3}= 0.784

Determination of Al_2O_3

Following the completion of the Fe_2O_3, 15 milliliters of EDTA were added, the pH was raised to 4.3, and the mixture was heated. The solution that $CuSO_4$ (0.015 mol/l) was used to titrate was mixed with five drops of PAN indicator. When the solution's yellow hue became violet, endpoint determination was finally achieved.

$$\%\mathrm{Al2O3} = \frac{1.33(\mathrm{K} * \mathrm{V_{CUSO4}}) * \mathrm{T_{Al2O3}}}{\mathrm{M}s}$$

Where: K = Excess EDTA+ $CUSO_4$ consumption

M_S= mass of ash

T_{Al2O3}= 0.7355

Determination of MgO

A 300 ml beaker was filled with a 25 ml filtrate via pipetting. Following the addition of 10ml of KF (20g/l) and a 5 minute incubation period, the solution was diluted to 200ml. Next, 20 milliliters of ammonia hydroxide (pH adjusted to 12.5), 5 milliliters of TEA, 1 milliliter of potassium sodium tartrate, and 6 drops of KB indicator were added. When the solution was titrated with EDTA, its brown hue became blue.

$$\%\mathrm{MgO} = \frac{(\mathrm{V_{MgO}} - \mathrm{V_{CaO}}) * \mathrm{T_{MgO}}}{\mathrm{Ms}}$$

Where: M_S= Mass of ash

V_{MgO} = Volume of MgO

V_{CaO}= Volume of CaO

T_{MgO}= 0.5816

Determination of SiO_2

To a 250 ml plastic cup, 50 ml of the previously specified solution was measured. After adding 15 milliliters of concentrated HNO_3, the mixture was allowed to cool in a cold-water bath for 15 minutes. Subsequently, 3 spatulas full of solid KCl were added until it was saturated, and 10 milliliters of KF (150 g/l) was added to increase the SiO_2 concentration. Give the fluid fifteen minutes to dissolve following the addition of 8 drops of phenolphthalein and 10 ml of ($KCl+CH_3CH_2OH$) to the solution, the mixture was filtered through filter paper, which was then washed three times with KCl (150 g/l) (10, 10, 5 ml) in the preceding plastic beaker. The solution was then titrated with NaOH (0.15 g/l) until a pink hue appeared. The solution was then titrated by adding hot water up to the 200 ml mark, three drops of 0.1 g/NaOH, and one drop of phenolphthalein. When titrated by EDTA (0.015 mol/l), the solution turned from colorless to light pink to yellow.

$$\%\mathrm{SiO2} = \frac{0.5 * \mathrm{V_{NaOH}} * \mathrm{T_{SiO2}}}{\mathrm{Ms}}$$

Where: M_S=mass of the ash

V=Volume of the NaOH solution T_{SiO_2}= 2.04

3.4. Fourier Transform Infrared Spectroscopy analysis (FT-IR)

The Perkin Elmer Spectrum 65 FTIR spectrometer was the apparatus that was employed. A significant method made it simple to determine whether specific functional groups are present in an organic molecule. Vibration frequencies within functional groupings are exclusive to that group. The infrared (IR) frequency range corresponds to these vibration frequencies. As a result, the organic compound's functional groups vibrate at particular frequencies when an IR signal passes through it. The infrared region of the electromagnetic spectrum corresponds to these frequencies (4000 ~ 400 cm^{-1}). To prepare the sample for infrared analysis, potassium bromide particles were added at the beginning since those substances absorb infrared light. The mixture was then pressed to a small thickness below 1mm and prepared as a pellet required for FTIR analysis.

3.5. Bulk Density

The major equipment that were used was electrostatic balance and baker. The bulk density of powdered cotton stalk and coffee husk was measured.

Figure 5: Bulk Density Determination of Raw Coffee Husk and Wheat Straw

3.6. Carbonization of coffee husk and wheat straw

Coffee husk and wheat straw carbonization studies were carried out in a muffle furnace fitted with a temperature and time controller. To establish an oxygen-free atmosphere or reduce the amount of oxygen in the oven, samples of dried coffee husks and wheat straw were weighed, placed on a tandoori, and completely covered with aluminum foil. Three factors temperature, fineness, and mixing ratio at three different levels minimum, center point, and maximum were tested, and the effects of each were tracked as it related to the carbonation outcomes with a calorific value. The temperature effect was maintained at three levels: 300, 350 and 400 °C, with appropriate particle sizes for <100µm, 100 ~ 150µm and 150 ~ 250µm and fixed mixing ratios of 70, 50 and 30% of coffee husk to wheat straw. Following carbonization, the solid char was taken out of the furnace and dried in a desiccator before being ground up, sieved, and ready for further processing.

Figure 6: Pulverized Raw Materials Prepared for Carbonization

<100µm 150 ~ 250µm 100 ~ 150µm

Figure 7: Carbonization of Pulverized Materials Using Muffle Furnace

Figure 8: Carbonized Materials

100 ~ 150µm <100µm 150 ~ 250µm

3.7. Experimental Design and Statistical Analysis

Response Surface Methodology (RSM) is a collection of mathematical and statistical approaches that are helpful for modeling and evaluating issues where several factors impact a response of interest and the goal is to maximize this response, according to Douglas C. Montogomory (2001). Utilizing the response surface approach, the study evaluated the influence of carbonization factors and optimized the circumstances after taking individual impacts and interactions into account.

The statistical package used in this study is Design-Expert version 7.0.0 (Statistics – Ease, Inc.). Box-Behnken experimental setup with three numerical factors, namely particle size <100µm, <150µm and <250µm, mixing ratio (30%, 50% and 70%) and carbonization temperature (300℃, 350℃ and 400℃) in appropriate amounts, which affect the response variable (calorific value). As shown in the table below, the design included seventeen randomized series with five repeats of the midpoint to minimize bias. Factors and levels are listed in Table 4. and the number of runs was calculated using Box Behnken Design software. In this experiment, 17 experimental runs were performed with the BBD.

Table 4: Experimental Factors and Levels

Code	Independent variable	Units	Levels		
			Low (-1)	Medium (0)	High (+1)
A	Temperature	℃	300	350	400
B	Particle size	µm	100	150	250
C	Ratio of coffee husk to wheat straw	%	30	50	70

Following the design of the experimental run given by the software, Design-Expert 7.0.0 the carbonization process was done according to the given data. The experimental runs design was shown below.

Effect of Operation Variables on the Responses

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A: Temperature (°C)	B: Particle size (µm)	C: Mixing Ratio (%)	Calorific value (Kcal/Kg)
2	1	400.00	100.00	50.00	
13	2	350.00	175.00	50.00	
4	3	400.00	250.00	50.00	
8	4	400.00	175.00	70.00	
11	5	350.00	100.00	70.00	
10	6	350.00	250.00	30.00	
9	7	350.00	100.00	30.00	
1	8	300.00	100.00	50.00	
6	9	400.00	175.00	30.00	
14	10	350.00	175.00	50.00	
15	11	350.00	175.00	50.00	
7	12	300.00	175.00	70.00	
5	13	300.00	175.00	30.00	
12	14	350.00	250.00	70.00	
3	15	300.00	250.00	50.00	
16	16	350.00	175.00	50.00	
17	17	350.00	175.00	50.00	

Statistical Analysis

A second-order polynomial equation, also known as a quadratic equation, will be used to ascertain the relationship between the response (calorific value) and the independent variables or parameters (temperature, particle size, and mixing ratio). The following will apply to the three factors that were chosen:

$$Y = \beta 11A2 + \beta 22B2 + \beta 33C2 + \beta 12AB + \beta 13AC + \beta 23BC + \beta 1A + \beta 2B + \beta 3C + \beta 0 + \varepsilon$$

Where, βi represents the coefficients of a linear interaction effect, $\beta 0$ is a constant, βij represents the coefficients for cross-product interaction effect, βii represents the coefficients for quadratic interaction effect, Y is the response, and ε is the random error.

To do the regression analysis and estimate these coefficients, Stat-Ease, Inc.'s Design-Expert version 7.0.0 statistical software was utilized. The adequacy of the model equations was evaluated using analysis of variance (ANOVA). At five percentile levels of the Least Significance Difference (LSD), the major comparison was conducted. The F-test, coefficient of determination (R2), adjusted coefficient of determination (adj-R2), prediction coefficient of determination (Pred R2), and coefficient of variation (CV) were used to represent the model equations' quality of fit and statistical significance.

Optimization of Quality Briquette Fuel

Design-Expert version 7.0.0's optimization module looks for a set of levels and factors that together fulfill the demands made on every response and factor. Prior to applying optimization, each answer must be examined in order to determine the best model given the engineering considerations and cost-benefit analysis. Using the Box Behnken Design (BBD) approach, the briquette quality with the highest calorific value was determined by analysis of the experimental data obtained.

Briquetting

Using a hydraulic press operating at pressures more than 150 bar, the well-mixed and carbonized samples were put into a cylindrical mold with a diameter of 21mm and a maximum height of 45mm. Supata et al. (2013) state that the carbonized briquettes were mostly compressed using a hydraulic press. Following an hour of waiting and physical pressing, the briquette is taken out of the cylindrical mold.

Mechanical Tests to Measure the Strength and Durability of Briquettes

Consideration must be given to a number of qualities, including durability and strength. Compressive strength, impact resistance, water resistance, and a number of other characteristics demonstrate the strength of certain briquettes. The diametric compression test is used to evaluate the compressive strength, which is the maximum crushing load that briquettes can bear before breaking or shattering. A single briquette will be tested by sandwiching it between two parallel, flat platens that are larger than the briquette's anticipated area. The briquettes were subjected to increasing weights until they broke or cracked.

Briquettes can also be used to measure their relative durability by weighing them after each of four drops onto a flat steel plate from a height of 2.0 meters. The ratio of the briquette's final mass maintained after the four drops to its original mass was used to calculate the durability percentage. The duration needed for a briquette to completely dissolve in water was used to measure the briquette's water resistance.

1. Shatter resistance test

Briquette hardness is assessed using the shatter test. The briquette is repeatedly dropped three times on a concrete floor from a height of two meters. The following formulas were used to determine the briquettes' shatter resistance. By recording, the sample briquettes' weight both before and after they broke, the percentage of shatter resistance could be determined.

Weight loss (%) = $\frac{A-B}{A}$*100%

Shatter resistance (%) =100% - weight loss (%)

Where A is initial weight (g), whereas B represent final weight (g)

2. Tumbling resistance test

Briquettes' durability index was determined by the tumbling or abrasion resistance test, which also shows how the briquette behaves throughout the transportation phase. Fuel particles colliding with the walls of a spinning chamber and with each other subjected the briquette to regulated shocks. According to EN 15210-2 (2010), the tumble procedure was carried out for five minutes in a clockwise manner at a speed of 35 rpm.

The equations used to determine the tumbling resistance of the briquette were calculated as follows:

Weight loss (%) = $\frac{A-B}{A}$*100%

Tumbling resistance (%) =100% - weight loss (%)

Where A is weight of briquette before tumbling (g), whereas B is weight of briquette after tumbling (g).

3. Water resistance test

To find the percentage of water resistance to penetration, the briquette is submerged in water that is kept at room temperature for thirty seconds. It illustrates how the briquettes will behave when exposed to water or during rainy seasons.

The immersion test was used to gauge the solid fuels' water resistance. 100 ml of room temperature water was added to a 200 ml beaker. Prior to the submerging, each briquette's original weight was noted. The duration of the immersion was also recorded at 30 seconds using a timer. The briquette was taken out of the beaker following the immersion, and the final weight was recorded.

The percentage of water gained by each briquette was calculated by using the equations as followed:

Weight gained (%) = $\frac{A-B}{B}$*100%

Water resistance (%) =100% - weight gained (%)

Where B is weight of briquette before immersion while A is weight of briquette after immersion.

The value of shatter resistance, tumbling resistance and water resistance test should be higher in order to ensure the strength of the briquettes.

4. Compressive Strength Test

The diametric compression test is used to evaluate the compressive strength, which is the maximum crushing load that briquettes can bear before breaking or shattering. A single briquette will be tested by sandwiching it between two parallel, flat platens that are larger than the briquette's anticipated area. The briquettes were subjected to increasing weights until they broke or cracked. The test was performed on an Ultimate Tensile Machine (UTM) with a working load capacity of up to 100kN. The UTM was configured to compress half of the briquette's thickness or to fail.

4. RESULTS AND DISCUSSION

4.1. Characterization of Coffee Husk and Wheat Straw

4.1.1. Characterization of Coffee Husk

Proximate analysis

Proximate analysis which involved completing two replications on average for each sample are determined and presented in Table 5, including information on moisture content, ash content, volatile matter, and fixed carbon.

Table 5. Proximate Analysis of Coffee Husk

Parameters	Coffee husk	Imported coal (South Africa)
Moisture content (%)	8.0	5.5
Ash content (%)	2.25	19.29
Volatile matter (%)	79.50	29.69
Fixed carbon (%)	18.25	45.52

Moisture content

[Bolesław Karwat et al., 2014] state that 20% is the maximum moisture content required by the cement sector and that this is the ideal moisture level for alternative fuels. [A. Uliasz-Bochenczyk, B. Mokrzycki, 2003]. Since there was no surplus moisture in the material, the moisture in the coffee husks had no effect on ignition or rate of burning. Woody biomass stores moisture in the voids left by dead cells and cell walls, which accounts for the comparatively greater moisture content of coffee husks as compared to imported coal.

Ash content

The non-combustible residue that remains after burning biomass is known as the ash content of biomass. The design and functionality of biomass distribution systems are impacted by the composition and amount of ash. This is dependent on the biomass's inherent qualities as well as the methods for collection and treatment (Akdeniz et al., 2004). As per [Sarn et al., 2003; SPC, 2008: Trezza, Scian, 2005], alternative fuels must have an ash content of around 15%, whereas the cement sector requires an ash content of approximately 35% [B. Mokrzycki, A. Uliasz-Bochenczyk, 2003]. Coffee husks have a very low inorganic content, as seen by the preceding data, which shows that their ash content of 8.25% is lower than that of imported coal.

Volatile Matter

Fuels volatile content is made up of the vapors that are generated during heating, both condensable and non-condensable. This characteristic aids in the estimation of flame length as well. Due to a decreased lignin concentration, the volatile content of coffee husks was much greater than that of South African coal [BISYPLAN., 2012], as the table illustrates. The coffee husk may so ignite at low temperatures with ease. Because these volatile chemicals remove volatiles during pyrolysis, they burn more quickly. Additionally, it will draw attention to the coffee husk throughout the burning process [Xing Yang et al., 2017].

Fixed Carbon

Fixed carbon is the solid, flammable residue that remains after volatiles are removed from a biomass molecule by heating. The proportion of moisture, volatiles, and ash in the sample is subtracted to find it. The calorific value may be roughly estimated from the carbon fixed in the substance. The result indicates that the carbon content in the coffee husk residues was not as high as that in the coal and that this is the case with the imported coal having a high calorific value. It was discovered that the fixed carbon in the coffee husks had less fixed carbon than the imported coal.

Ultimate analysis

To determine the carbon, hydrogen, and oxygen content of a material, elemental analysis has been used. The concentration of these components provides detailed information about the biomass's energy content, storability, and general quality. The following table displays the elemental analysis findings for coffee husk. The sample's oxygen concentration was determined by adding the contents of carbon, hydrogen, nitrogen, and sulfur and computing the difference of 100%.

Table 6: Ultimate Analysis of Coffee Husk in Dry Basis

Elements	Coffee husk	Imported coal
Carbon (%)	49.01	70
Hydrogen (%)	5.10	4
Nitrogen (%)	0.56	2
Sulfur (%)	0.03	2
Oxygen (%)	43.56	22

Calorific Value

A clear indicator of the energy value of biomass is its calorific value (CV). As the most extensively used benchmark for fuel quality and, consequently, its economic worth, it is one of the most significant characteristics that characterizes the quality of alternative fuel and is also one of the most often used parameters in categorization systems. It is the quantity of heat emitted when burning. It establishes the primary factor that determines how much conventional fuel may be replaced throughout the clinker manufacture process. Only when proper temperature conditions are maintained in each part of the kiln which is influenced by the calorific value of the fuel used can high-quality clinker be generated and by the way of its combustion [Malgorzata Wzorek, 2012]

Typically, the CV is given as either the net calorific value (which is the lower heating value) or the gross calorific value (which is the larger heating value). As a result of condensation of the water vapor created during burning, the latent heat of calorific value (NCV) differs from the gross calorific value (GCV). The GCV makes the assumption that every drop of vapor created during the burning of biomass moisture has completely condensed. The NCV makes the assumption that water is not completely condensed and is eliminated along with the combustion products.

According to Małgorzata Wzorek (2012), the minimum gross calorific value of alternative fuels is ≥13.0 MJ/kg (3104.9 Kcal/Kg), which guarantees both correct kiln operation and a good level of clinker product quality. The gross calorific outcome (heat of combustion) of coffee husk was found to be 4118 Kcal/Kg.

Ash Composition Analysis

The mineral components of burnt coffee husk include silicon, aluminum, iron, calcium, magnesium, titanium, manganese, sodium, and potassium oxides; these oxides are also partially mixed as silicates, sulphates, and phosphates. In an ash study, the primary and minor elements are therefore often given as their oxides. When producing clinker, knowing the chemical makeup of the ash in alternative fuels is very beneficial for designing the raw mix. In the kiln, some waste materials and byproducts that contain beneficial minerals like calcium, silica, alumina, and iron can be utilized in place of raw materials like clay, sandstone, and limestone.

The following table shows the results of the ash mineral composition of coffee busk and the results were compared with the imported (South African) coal.

Table 7: Ash Major Oxide Analysis of Coffee Husk

Minerals composition	Coffee husk	Imported coal
SiO_2(%)	17	46.94
CaO (%)	22	8.42
MgO (%)	6.5	1.23
Fe_2O_3(%)	1.06	17.74
Al_2O_3(%)	28.2	20.08
SO_3(%)	1.08	1.12

4.1.2. Characterization of wheat straw

All proximate sample analysis was performed in duplicate forms and their average was taken.

Table 8: Proximate Analysis of Wheat Straw

Parameters	Wheat straw	Imported coal (South Africa)
Moisture content (%)	11.5	5.5
Ash content (%)	10.5	19.29
Volatile matter (%)	70.52	29.69
Fixed carbon (%)	18.5	45.52

Moisture content

[Bolesław Karwat et al., 2014] state that 20% is the maximum moisture content required by the cement sector and that this is the ideal moisture level for alternative fuels. [A. Uliasz-Bochenczyk, B. Mokrzycki, 2003]. Since there was not an excessive amount of moisture present, the wheat straw's moisture content had no effect on ignition or rate of burning. The woody biomass in wheat straw stores moisture in the voids left by dead cells and cell walls, which accounts for its comparatively greater moisture content as compared to imported coal.

Ash content

The non-combustible residue that remains after burning biomass is known as the ash content of biomass. The design and functionality of biomass distribution systems are impacted by the composition and amount of ash. This is dependent on the biomass inherent qualities as well as the methods for collection and treatment (Akdeniz et al., 2004). As per [Sarn et al., 2003; SPC, 2008: Trezza, Scian, 2005], alternative fuels must have an ash content of around 15%, whereas the cement sector requires an ash content of approximately 35% [B. Mokrzycki, A. Uliasz-Bochenczyk, 2003]. Wheat straw has a very low inorganic content, as seen by the preceding data, which shows that its 10.5% ash concentration is lower than that of imported coal.

Volatile Matter

Fuels volatile content is made up of the vapors that are generated during heating, both condensable and non-condensable. This characteristic aids in the estimation of flame length as well. Due to a lower lignin level, wheat straw had a substantially greater volatile content than coal from South Africa [BISYPLAN., 2012], as the table illustrates. Consequently, at low temperatures, the wheat straw may burn with ease. Because these volatile chemicals remove volatiles during pyrolysis, they burn more quickly. Additionally, it will draw attention to the wheat straw throughout the burning process [Xing Yang et al., 2017].

Fixed Carbon

When a biomass particle is heated and the volatile stuff is released, fixed carbon a solid, combustible residue remains. The proportion of moisture, volatile matter, and ash in the sample is subtracted to find it. A materials heating value can be roughly estimated based on its fixed carbon content. The wheat straw's fixed carbon content was found to be lower than that of the imported coal. This suggested that the carbon content of the wheat straw residue was lower than that of the coal, which is also the reason why the South African coal has a high heating value.

Ultimate analysis

To determine the carbon, hydrogen, and oxygen content of a material, elemental analysis has been used. The concentration of these components provides detailed information about the biomass's energy content, storability, and general quality. The following table displays the elemental analysis findings for coffee husk. The sample's oxygen concentration was determined by adding the contents of C, H, N, and S and computing the difference of 100%.

Table 9: Ultimate analysis of wheat straw

Elements	Wheat straw	Imported coal
Carbon (%)	44	70
Hydrogen (%)	5.9	4
Nitrogen (%)	3.5	2

Sulfur (%)	0.2	2
Oxygen (%)	38.25	22

Calorific Value

It is the quantity of heat emitted when burning. It establishes the primary factor that determines how much fossil fuel may be replaced throughout the clinker manufacture process. Only when proper temperature conditions are maintained in each part of the kiln which is influenced by the energy value of the fuel used can high quality clinker be generated. Therefore, the gross calorific value of wheat straw found to be 3785Kcal/Kg.

Ash Composition Analysis of wheat straw

The mineral components of wheat straw burn to produce an ash residue that is mostly made up of silicon, aluminum, iron, calcium, magnesium, titanium, manganese, sodium, and potassium oxides, with some silicates, sulphates, and phosphates also present. In an ash study, the primary and minor elements are therefore often given as their oxides. When producing clinker, knowing the chemical makeup of the ash in alternative fuels is very beneficial for designing the raw mix. In the kiln, some waste materials and byproducts that contain beneficial minerals like calcium, silica, alumina, and iron can be utilized in place of raw materials like clay, sandstone, and limestone.

The following table shows the results of the ash mineral composition of wheat straw and the results were compared with the imported (South African) coal.

Table 10: Ash major oxide analysis of wheat straw

Minerals composition	Wheat straw	Imported coal
SiO_2(%)	75.92	46.94
CaO (%)	4.21	8.42
MgO (%)	2.18	1.23

Fe_2O_3(%)	0.6	17.74
Al_2O_3(%)	1.15	20.08
SO_3(%)	0.9	1.12

4.2. Design Expert Results

4.2.1. Experimental design

Three factors were examined in order to look into high quality fuel briquettes with good calorific values meant for alternative energy sources. Particle size, temperature, and mixing ratio were these crucial variables. Three elements at three different levels defined the calorific value, which was the response of the experiment that was carried out. Table 11, showed the three components experimental designs at three different levels together with the corresponding response values.

Table 11: Experimental design and response results of RSM BBD design

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A: Temperature (℃)	B: Particle size (µm)	C: Mixing Ratio (%)	Calorific value (Kcal/Kg)
2	1	400.00	100.00	50.00	5258.18
13	2	350.00	175.00	50.00	4804.20
4	3	400.00	250.00	50.00	4418.34
8	4	400.00	175.00	70.00	5084.27
11	5	350.00	100.00	70.00	5469.18
10	6	350.00	250.00	30.00	3804.12
9	7	350.00	100.00	30.00	3964.60
1	8	300.00	100.00	50.00	4456.54

6	9	400.00	175.00	30.00	4173.48
14	10	350.00	175.00	50.00	4604.21
15	11	350.00	175.00	50.00	4794.94
7	12	300.00	175.00	70.00	4504.32
5	13	300.00	175.00	30.00	3428.45
12	14	350.00	250.00	70.00	4814.38
3	15	300.00	250.00	50.00	4114.14
16	16	350.00	175.00	50.00	4824.34
17	17	350.00	175.00	50.00	4898.64

4.2.2. Analysis of variance (ANOVA)

An analysis of variance was used to assess the model statistically (ANOVA). Next, using software design expert version 7.0.0, an ANOVA was performed for the fitted quadratic polynomial model to see how each element affected the calorific value and how each variable interacted with the other. The results are displayed below.

Analysis of variance (ANOVA) for calorific value

Response 1 Calorific value

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	
Model	4.437E+006	9	4.930E+005	32.77	< 0.0001	significant
A-Temperature	7.386E+005	1	7.386E+005	49.09	0.0002	
B-Particle size	4.988E+005	1	4.988E+005	33.15	0.0007	

C-Mixing Ratio	2.533E+006	1	2.533E+006	168.35	< 0.0001	
AB	61861.64	1	61861.64	4.11	0.0822	
AC	6812.85	1	6812.85	0.45	0.5226	
BC	61088.07	1	61088.07	4.06	0.0837	
A^2	2.028E+005	1	2.028E+005	13.48	0.0080	
B^2	67.81	1	67.81	4.507E-003	0.9484	
C^2	3.028E+005	1	3.028E+005	20.13	0.0028	
Residual	1.053E+005	7	15045.83			
Lack of Fit	57707.01	3	19235.67	1.62	0.3194	not significant
Pure Error	47613.80	4	11903.45			
Cor Total	4.543E+006	16				

The model is deemed significant based on its F-value of 32.77. Noise has a mere 0.01% probability of producing a "Model F-Value" of this magnitude. "Prob > F" values less than 0.0500 suggest the significance of the model terms. A, B, C, A2, and C2 are important model terms in this instance. The model terms are not important if the value is bigger than 0.1000. Model reduction might make your model better if it has a large number of unimportant model terms (apart from those needed to maintain hierarchy).

The 1.62 "Lack of Fit F-value" indicates that the Lack of Fit is not statistically significant in comparison to the pure error. A "Lack of Fit F-value" this large might be the result of noise with a 31.94% possibility. It is desirable for there to be a non-significant lack of fit in the model.

With a determination coefficient (R2) of 0.9768 and no statistically significant lack of fit at $p > 0.05$, the quadratic regression model was able to account for 96.68% of the data. According to the findings, the response variable's model fit was sufficient to capture the link between the response and the independent variables and was significant ($p < 0.0001$) [24]. The F-test was used to assess the model's relevance and revealed that the model's F-value was extremely high (F = 32.77). The correlation metric for determining if the regression equation fits the data well is called R2 adj (adjusted determination coefficient). This model's R2 adj value is 0.9470, meaning that just 5.30% of the total variations could not be explained by model. Meanwhile, a relatively lower value of coefficient of variation (CV = 2.69%) showed a better precision and reliability of the experiments carried out.

There is a fair amount of agreement between the "Adj R-Squared" of 0.9470 and the "Predicted R-Squared" of 0.7804. This suggested that the experimental and anticipated values agreed rather well. It is acceptable that the discrepancy between the Adjusted R^2 and the Predicted R^2 is less than 0.2. An additional model fit statistics parameter that quantifies the signal to noise ratio is called "Adeq Precision." It displays the expected dependent variable's range of variation together with a standard error estimate. It was obtained by dividing the expected value's average standard deviation by the minimum and maximum anticipated values, respectively. Ideally, the ratio should be higher than 4. An appropriate signal is indicated by the analysis ratio of 21.889. Consequently, one may utilize this approach to traverse 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 lower values of Coefficient of Variance imply the reliability of the experiment is high. In this experiment, it was shown that the Coefficient of Variance was 2.69, which was lower and the experiment was reliable, and has good precision.

Table 12: Fit Statistics

Std. Dev.	122.66	R-Squared	0.9768
Mean	4553.90	Adj R-Squared	0.9470
C.V. %	2.69	Predicted R-Squared	0.7804
PRESS	9.977E+005	Adeq Precision	21.889

Sequential Model Sum of Squares [Type I]

Table 13: Sequential Model Sum of Squares

Source	**Sum of Squares**	**df**	**Square**	**Value**	**Prob > F**	
Mean vs Total	3.525E+008	1	3.525E+008			
Linear vs Mean	3.770E+006	3	1.257E+006	21.15	< 0.0001	
2FI vs Linear	1.298E+005	3	43254.19	0.67	0.5879	
Quadratic vs 2FI	5.373E+005	3	1.791E+005	11.90	0.0039	Suggested
Cubic vs Quadratic	57707.01	3	19235.67	1.62	0.3194	Aliased
Residual	47613.80	4	11903.45			
Total	3.571E+008	17	2.101E+007			

From the lack of fit test, it is clear that the second-order quadratic model suggested by design expert was suitable because the lack of fit was insignificant (prob>F is 0.3194).

The experimental values of the independent variables and the actual values of the dependent (response) of 17 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.

Table 14: Coefficients of Fitted Model

Factor	Coefficient Estimate	df	Standard Error	95%CI Low	95%CI High	VIF
Intercept	4785.27	1	54.86	4655.55	4914.98	
A-Temperature	303.85	1	43.37	201.30	406.40	1.00
B-Particle size	-249.69	1	43.37	-352.24	-147.14	1.00
C-Mixing Ratio	562.69	1	43.37	460.14	665.24	1.00
AB	-124.36	1	61.33	-269.38	20.66	1.00
AC	-41.27	1	61.33	-186.29	103.75	1.00
BC	-123.58	1	61.33	-268.60	21.44	1.00
A^2	-219.45	1	59.78	-360.81	-78.10	1.01
B^2	-4.01	1	59.78	-145.37	137.34	1.01
C^2	-268.18	1	59.78	-409.54	-126.83	1.01

The quadratic model equation for the carbonization of a coffee husk and wheat straw expressed in terms of coded factors is given as equation below. 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:

Final Equation in Terms of Coded Factors:

$$\text{Calorific value} = +4785.27 + 303.85 * A - 249.69 * B + 562.69 * C - 124.36 * A * B - 41.27 * A * C - 123.58 * B * C - 219.45 * A^2 - 4.01 * B^2 - 268.18 * C^2$$

Final Equation in Terms of Actual Factors:

$$\text{Calorific value} = -14091.32122 + 75.39086\,\text{Temperature} + 12.6467 * \text{Particle size} + 124.04229 * \text{Mixing Ratio} - 0.033163 * \text{Temperature} * \text{Particle size} - 0.041270 * \text{Temperature} * \text{Mixing Ratio} - 0.082387 * \text{Particle size} * \text{Mixing Ratio} - 0.087781 * (\text{Temperature})^2 - 7.13422\text{E-}004 * (\text{Particle size})^2 - 0.67046 * (\text{Mixing Ratio})^2$$

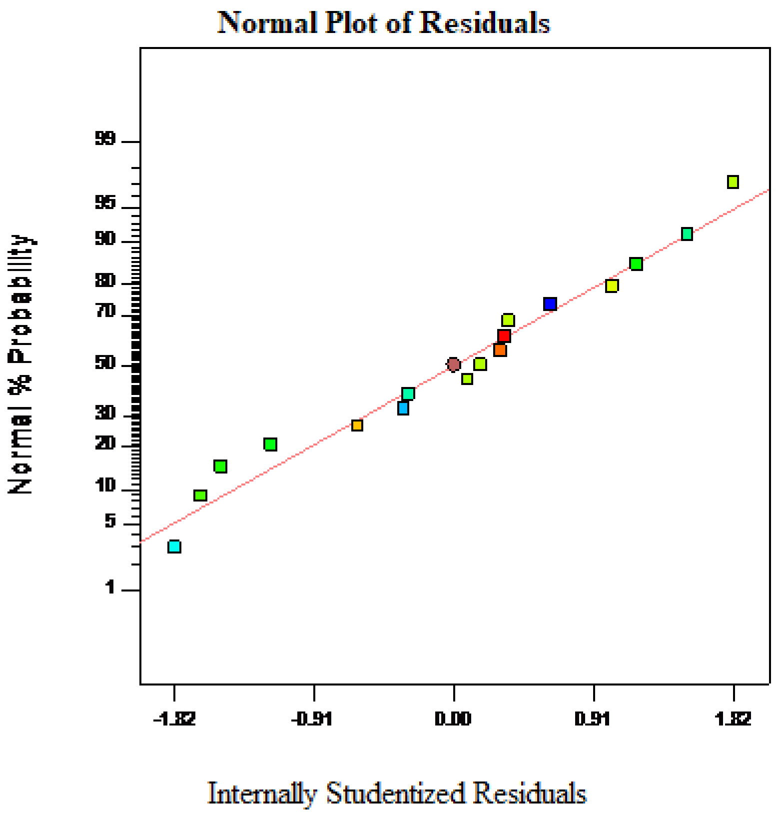
4.2.3. Diagnostics Plots

The graphical depiction of the experimental investigation is shown via model graphs and diagnostic plots. A smooth, linear graph of normal probability displays a straight line. With the options of internally studentized and raw residuals, externally studentized residuals are the default. The standard errors of the residuals vary unless the leverages of every run in a design are the same. The default is to use externally studentized residuals based on a deletion procedure as they are better at identifying issues with the study. While available, internally studentized residuals are less adept at identifying issues of this nature.

Normal Probability

The normal probability plot indicates whether the residuals follow a normal distribution, thus follow the straight line. In this case, the residuals were followed a linear line which implies the error distribution is normal as it can be seen in figure 9.

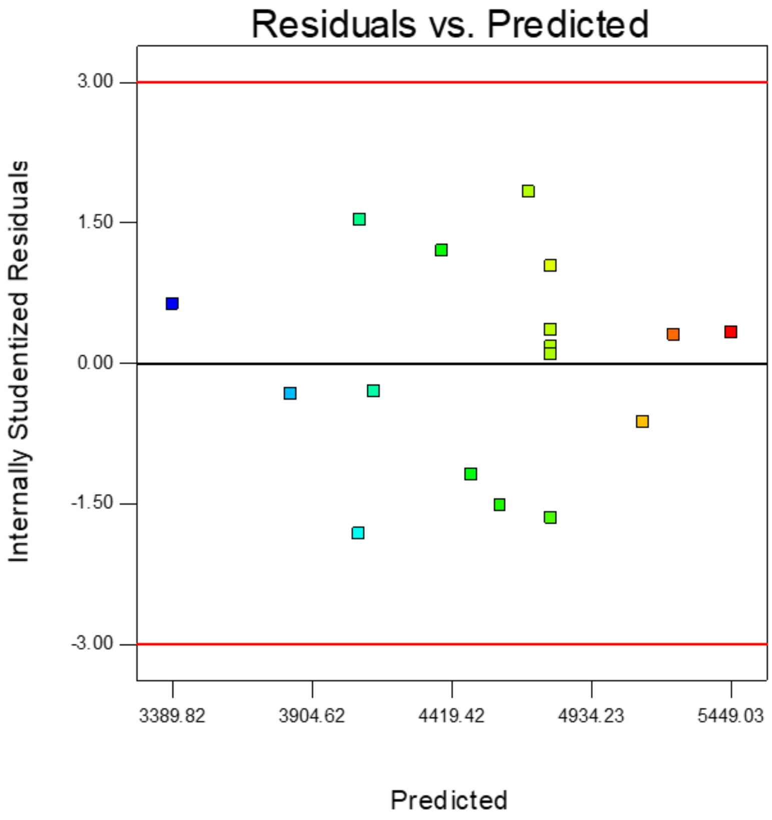
Figure 9: Normal Probability Plot



Residuals versus Predicted

This is a plot of the residuals versus the ascending predicted response values. The plot is a random scatter, constant range of residuals across the graph.

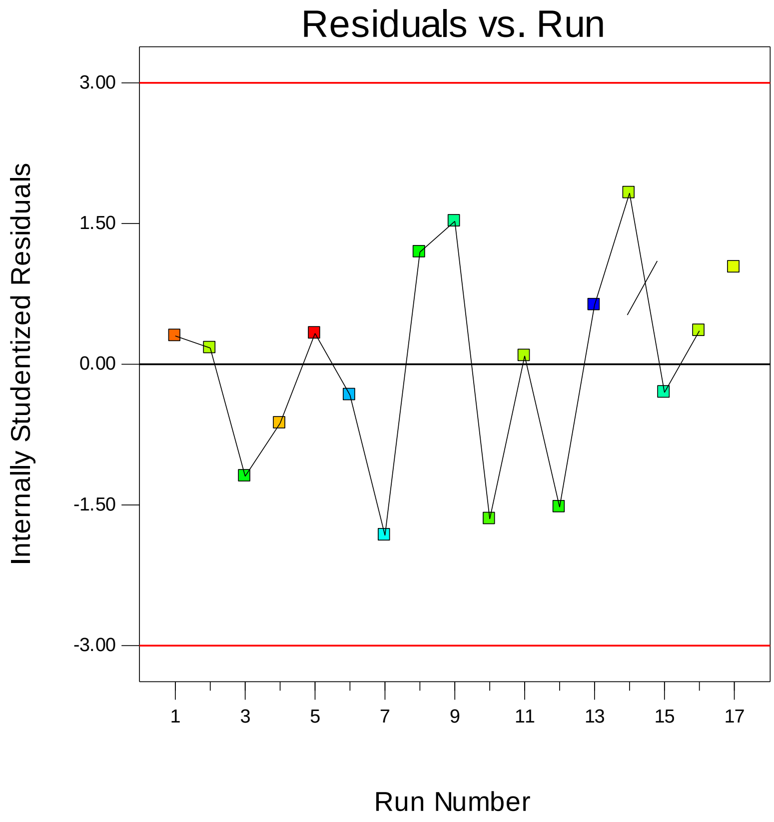
Figure 10: Residuals Vs Predicted



Residuals versus Run

The residual versus run plot indicated how the experimental run was randomized.

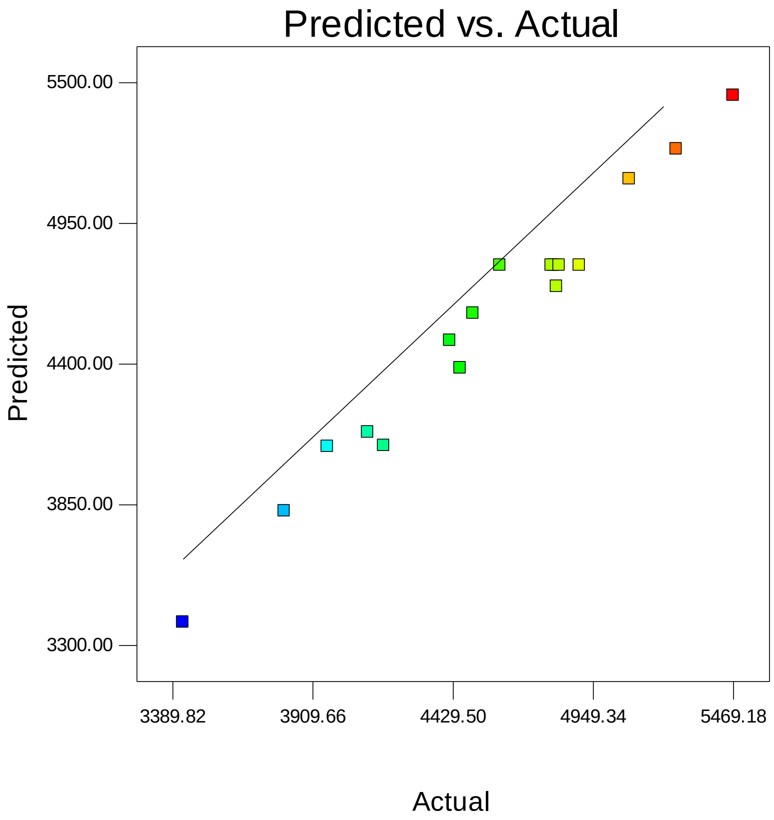
Figure 11: Residuals vs Run



Predicted versus Actual plot

A comparison between the response values that were obtained and those that were anticipated. Finding a value, or set of values, that the model finds difficult to predict is helpful. The 45° should be used to divide the data points equally. The experimental data were very precisely described by the quadratic model's regression equation. The linear straight line passes through all of the spots.

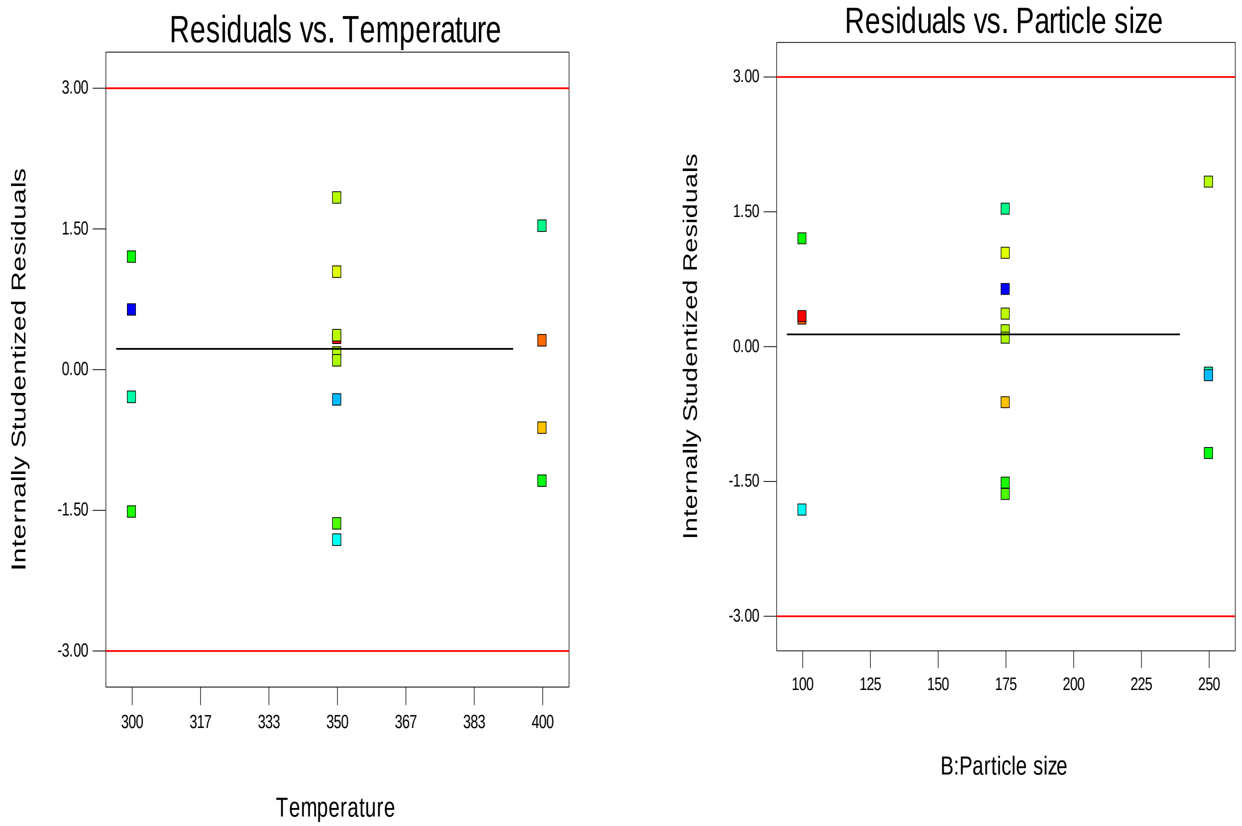
Figure 12: Predicted vs Actual

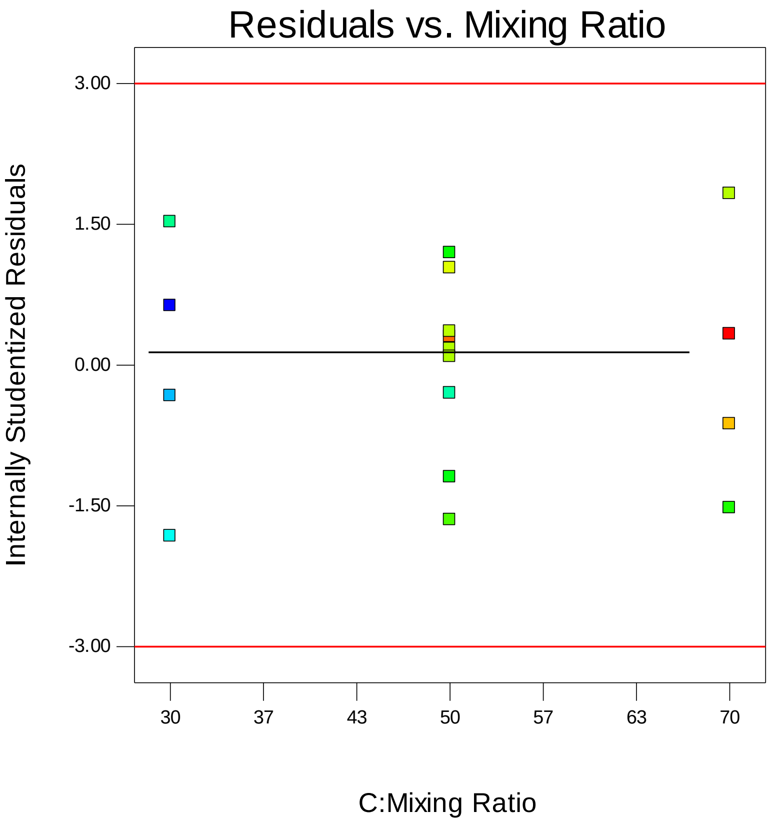


Residuals versus Factor

The residuals are plotted against each of the factors in this diagram. It determines if the variation that the model is unable to account for varies depending on the factor's level. In a perfect world, the plot would show a random spread. A noticeable curvature might be a sign of a systematic independent factor contribution that the model is unable to account for.

Figure 13: Residuals Vs Factor

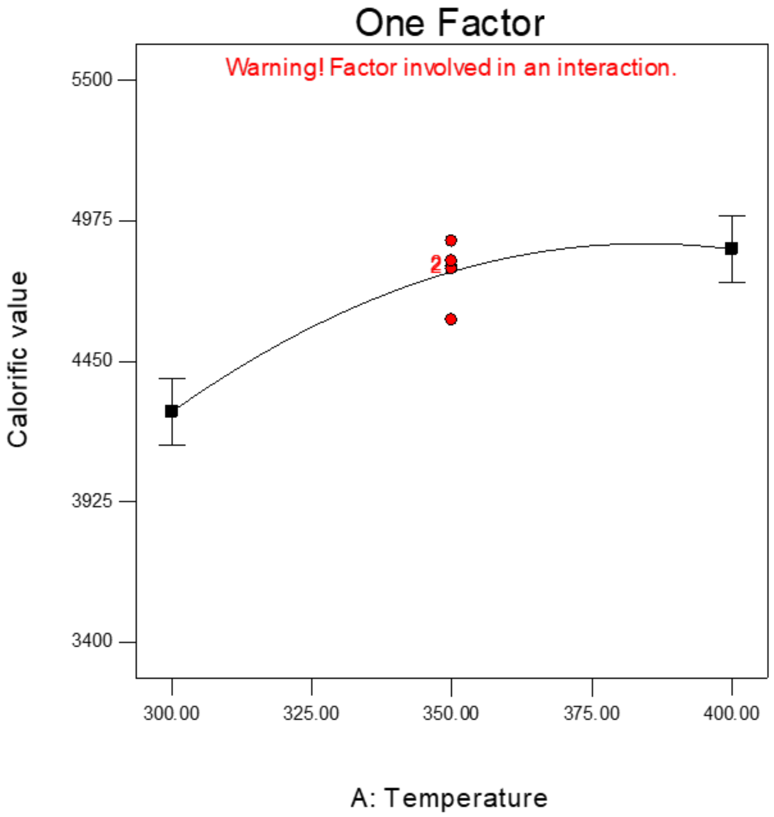




4.2.4. Effects of Individual Process Variables on The Response

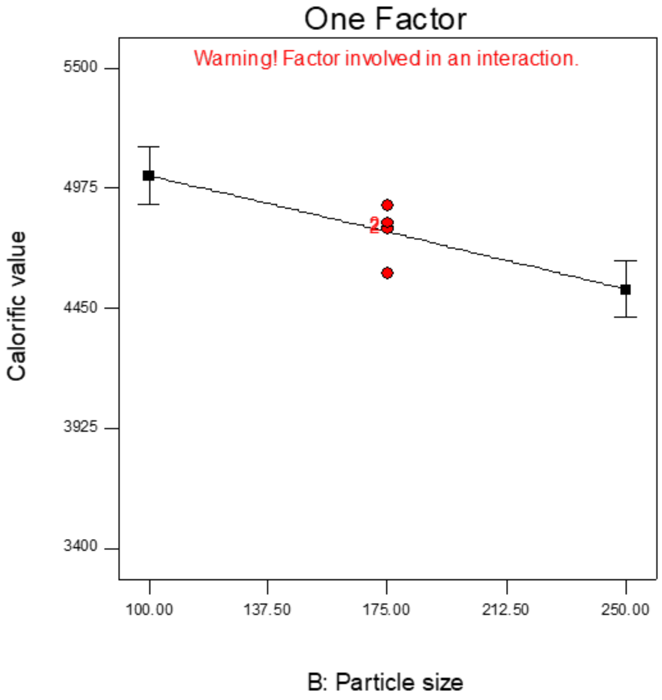
The effect of each factor on calorific value was analyzed by keeping the other variables constant. As it was shown in the quadratic model equation, each independent variable has an interaction effect on the dependent variable (calorific value). Temperature and mixing ratio were affecting the calorific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

Effect of temperature on calorific value



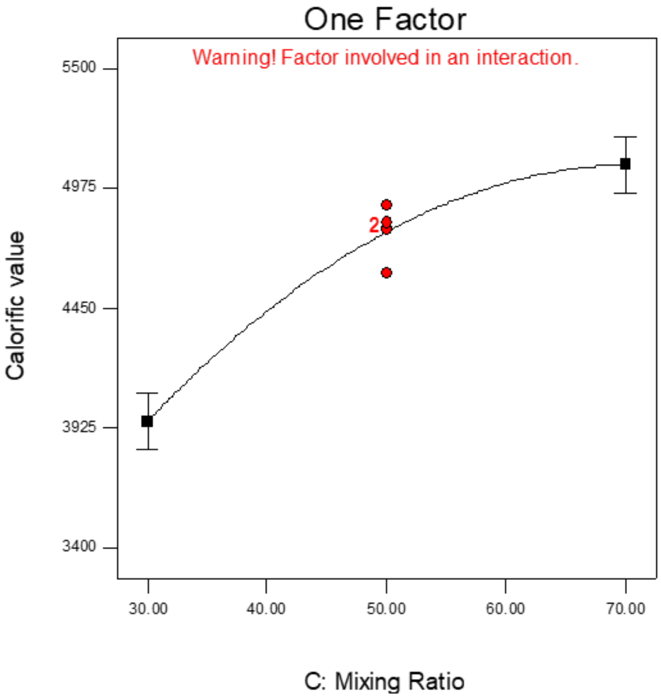
The effect of carbonizing temperature on calorific value was determined by fixing the effect of particle size and mixing ration at 175µm and 50% respectively. As shown in Figure when the temperature was increased from 300°C to 350°C the calorific value was significantly increased.

Effect of particle size on calorific value



To determine the effect particle size on calorific value, mixing ratio and carbonization temperature were fixed at 50% and 350℃ respectively. It was observed that as a particle size increased from 100µm to 250µm, the calorific value of the briquette was decreased. This is may be due to the fact that the amount of heat required depends on the size and biomass properties.

Effect of Mixing Ratio on Calorific Value



The effect of mixing ratio on calorific value was determined by fixing the particle size and carbonization temperature at 175µm and 350℃ respectively. It was observed that as the mixing ratio increased from 3% to 70%, the calorific value of the briquette was increased.

4.2.5. The Interaction Effect of The Process Variable

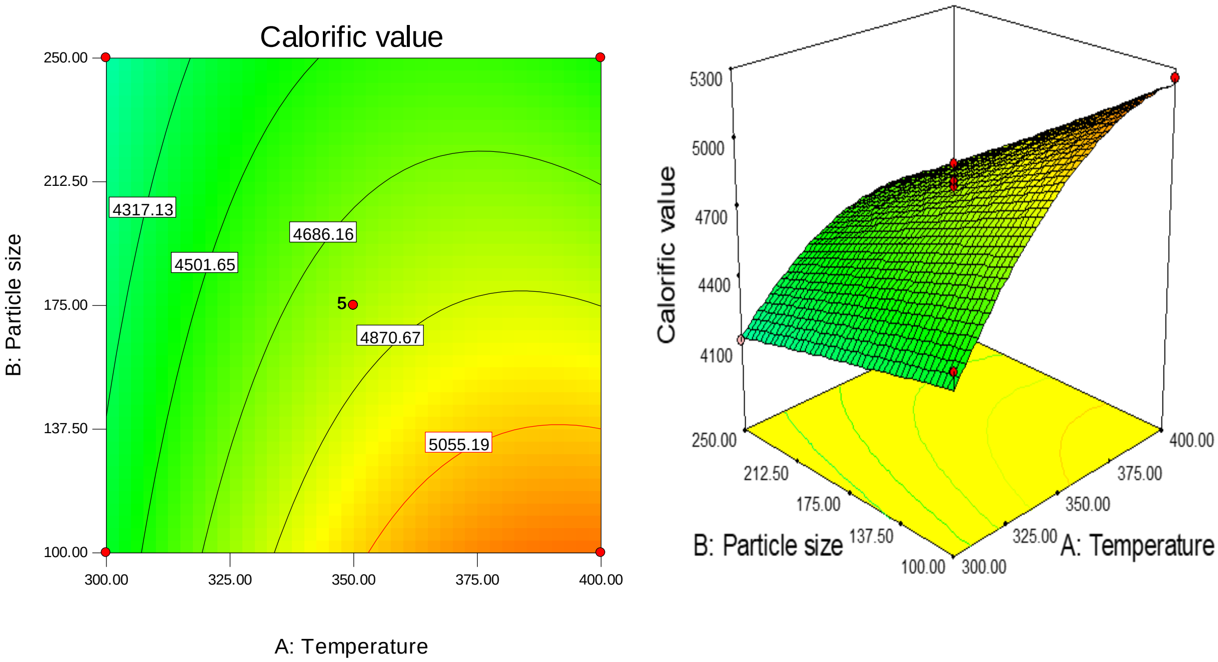
The result of ANOVA revealed that process variables interaction could affect the calorific value at a significant level. Particularly, temperature with particle size and temperature with mixing ratio interactions were the process interaction variables that affect the process significantly. The interaction between the independent variable and the dependent variable was plotted in the form of three-dimensional (3D) response surface and contour plots (Figure 14).

Interaction Effect of Temperature and particle size on Calorific Value

These plots illustrate the relative effect of any two variables by maintaining the third variable constant; and furthermore, it used to predict the optimum condition for the given process variables. In Figure 4.6, the increase in calorific value was observed at lower particle size 130µm

(<150µm) and 375℃ of carbonization temperature. However, the decrease in calorific value was observed at higher particle size 210µm (<250µm) and the lower carbonization temperature 310℃. This may be due to, at a higher temperature, smaller particle size has a better heat transfer rate. This indicated that the carbonization temperature and particle size have significant effect on the process.

Figure 14: Interaction effect

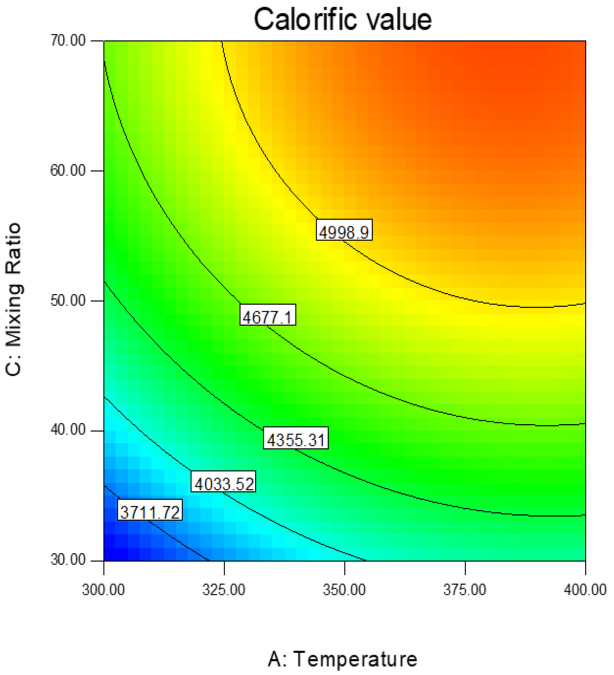


a) Contour Plots

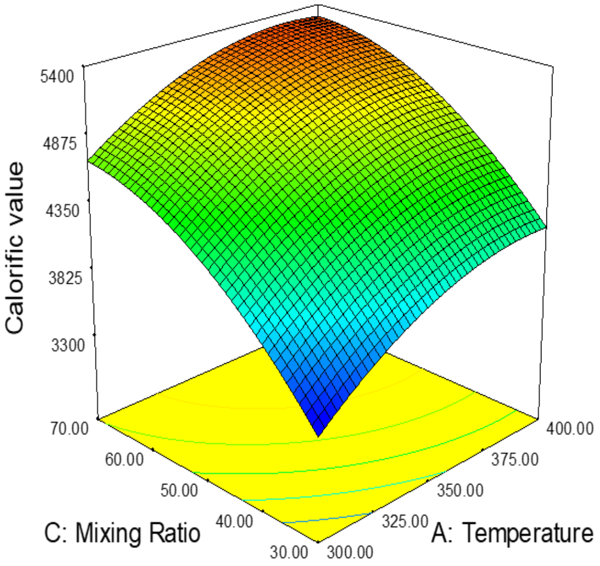
b) 3D Response Surface

Interaction Effect of Temperature and Mixing Ratio on Calorific Value

As shown from the graph, calorific value increased when both carbonization temperature and mixing ratio increased.



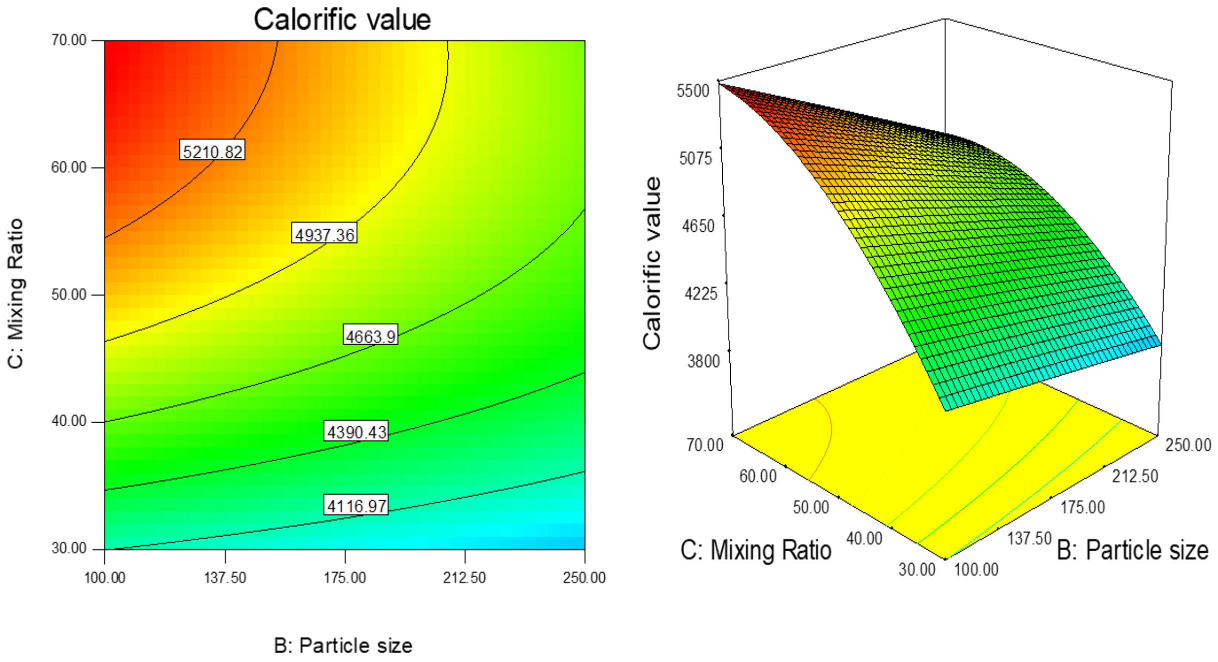
a) Contour Plots



b) 3D Response Surface

Interaction Effect of particle size and Mixing Ratio on Calorific Value

The increase in calorific value was observed at particle size of 150µm and 70% of mixing ratio. However, the decrease in calorific value was observed at higher particle size 250µm and the lower mixing ratio of 30%.



a) Contour Plots b) 3D Response Surface

Fig. Interaction effect of particle size and mixing ratio a) Contour plot b) 3D Response Surface

4.3. Optimization of the Process Parameters

The numerical optimization tool of Design-Expert 7.0.0 was utilized to ascertain the ideal circumstances for each of the three criteria. The highest desirability was taken into consideration while choosing the optimal variables. Depending on the goal of the study, the objectives were set at maximum, in range, or at minimum. Because coffee husk has a larger energy content during the mixing process, carbonization at higher temperatures with lowest particle size and mixing ratio were optimized to provide the greatest calorific value.

Table 15: Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Temperature	maximize	300	400	1	1	3
Particle size	minimize	100	250	1	1	3
Mixing Ratio	maximize	30	70	1	1	3
Calorific value	maximize	3428.45	5469.18	1	1	3

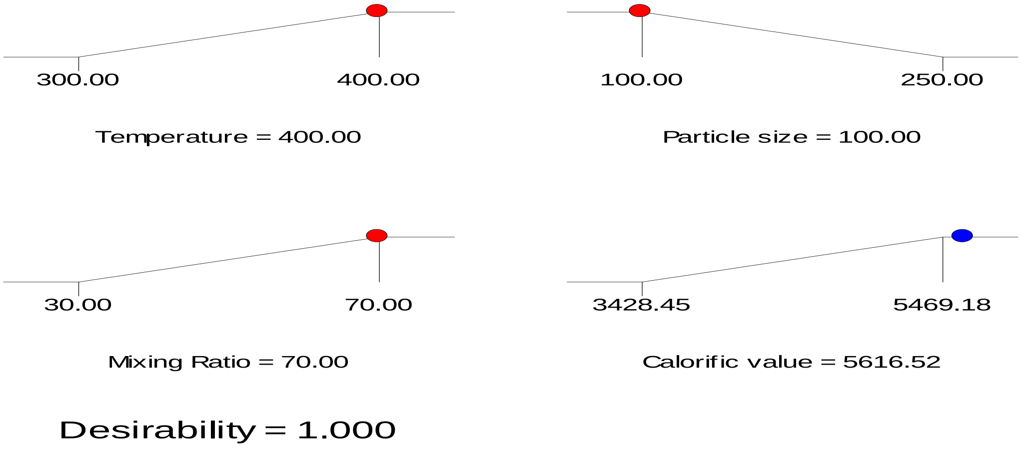
Table 16: Optimized Possible Solutions

Number	Temperature (℃)	Particle size (µm)	Mixing Ratio (%)	Calorific value	Desirability	
1	400.00	100.00	70.00	5616.52	1.000	Selected
2	399.61	100.00	69.98	5616.78	0.999	
3	400.00	102.09	70.00	5602.85	0.996	
4	400.00	100.00	69.16	5611.5	0.995	
5	399.99	100.00	67.83	5601.59	0.986	
6	392.86	100.00	70.00	5619.46	0.982	
7	400.00	100.00	65.75	5581.27	0.972	
8	400.00	122.65	70.00	5468.3	0.960	
9	383.21	100.00	70.00	5609.22	0.955	
10	400.00	100.00	61.43	5520.69	0.941	
11	392.90	133.73	70.00	5406.39	0.914	

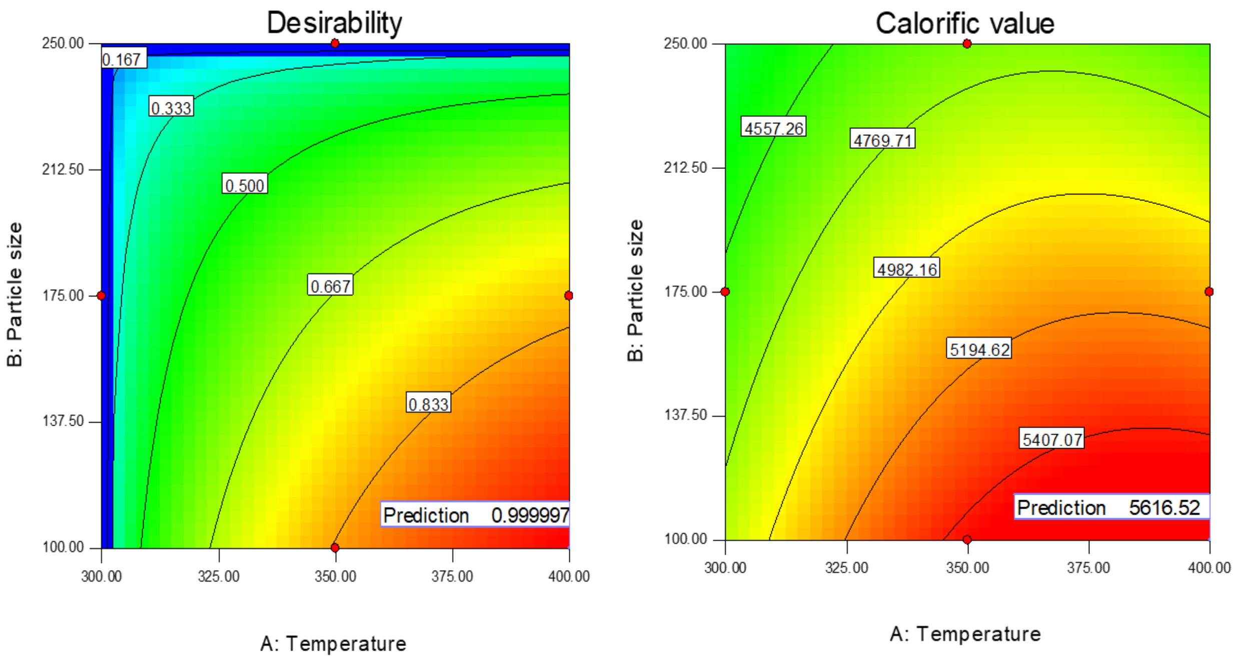
To validate the optimum condition predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized carbonization process conditions and calorific value of 5616.52Kcal/Kg with a desirability value of 1.00 was obtained.

Model Validation of Calorific Value

Response	Desirability	Temperature	Particle size	Mixing ratio	predicted	experimental	Error
Calorific value	1.00	400	100	70	5616.52		



a) 2D plot



b) Contour plot

Figure 15: Optimization Result with Desirability A) 2D Plot B) Contour Plot

4.4. Characterization of Optimum Carbonized Mixed Briquette

4.4.1. Proximate Analysis

The contents of moisture, ash, and volatile matter are provided via proximate analysis. The de-volatilization that occurs during carbonization, which results in an increase in ashes content and fixed carbon as well as a decrease in moisture content and volatile matter, can be used to explain the differences between the values of the coffee husk briquette, wheat straw briquette, and carbonized mixed sample. This is shown in Table 17 below. Optimum mixed carbonized briquette analytical findings were attained with a weight percentage of 30% wheat straw and 70% coffee husk with a particle size of below 90µm.

Table 17: Proximate Analysis of Mixed Briquette

Sample	Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)
Coffee husk	8.0	2.25	79.50	18.25
Wheat straw	11.5	10.5	71.49	17.5
Optimum mixed carbonized briquette	3.85	7.66	52.50	39.84

Moisture Content

Thermal treatment at 400°C for one hour resulted in a drop in the moisture content of the ideal carbonized mixed briquette to 3.85%. The increased thermal efficiency during the carbonized briquette's thermal combustion is implied by the decrease in moisture content. Additionally, it resists moisture absorption and degradation while being transported and stored. Lower moisture concentrations, according to Miranda et al. (2015), permit greater flame temperatures with improved heat transmission and temperature gradients, as well as the completion of combustion and shorter residence durations in the combustion chamber.

Ash Content

The carbonized mixed briquette's ash concentration rose to 7.66%. The outcome showed that inorganic species or trace elements were present in the mixed briquette. A higher ash content increases the burning rate's effect and lowers the briquette's heating value.

Volatile Content

Due to the breakdown and de-volatilization events, carbonization pushes away the volatile stuff from both biomasses. The ideal blended briquette's volatile content dropped to 52.50%, as seen in table 17 above. Because the briquette has a low volatile content, this leads to a decrease in the biomass burnout rate. The burning of the biomass in briquettes takes longer than that of raw biomass.

Fixed Carbon

The fixed carbon result of the mixed briquette climbed to a greater value than the raw biomass, as determined by the difference. Due to the breakdown process, some fixed carbon is driven out of the coffee husk and wheat straw during the carbonization process. The proportion of fixed carbon in the ideal carbonized mixed briquette increased to 39.84% even if the absolute amount of fixed carbon reduces after carbonization.

4.4.2. Ultimate Analysis

The final examination of the carbonized mixed briquette, as shown in Table 18, reveals that while the concentration of hydrogen and oxygen reduced during the carbonization process, the content of carbon rose. Compared to raw wheat straw and coffee husk, the carbonized mixed briquette has a lower atomic ratio of O/C and H/C due to a change in chemical composition. This is because during carbonization, volatile substances rich in hydrogen and oxygen are released, including carbon dioxide, water, and carbon monoxide. Since more oxygen than carbon is lost in the form of volatiles as a result of this shift in biomass's chemical composition, its quality as an energy source will improve due to an increase in energy density (Darr & Potter, 2010). There were essentially none at all of Nitrogen and Sulphur detected in carbonized mixed briquette, which is a typical characteristic of biomass (Nhuchhen et al. 2014). Therefore, the use of biomass residues has the added benefit of reducing the cement's nitrogen oxide (NOx) emissions.

Table 18: Ultimate Analysis of Carbonized Optimum Briquette

Ultimate Analysis of Carbonized Optimum Briquette	
Carbon (%)	71.89
Hydrogen (%)	3.24
Oxygen (%)	24.38
Nitrogen (%)	0.46
Sulfur (%)	0.025

4.4.3. Calorific Value

The calorific value of mixed optimized briquettes higher than that of coffee husk and wheat straw due to during carbonization, the biomass loses relatively more oxygen and hydrogen which increase the calorific value of the product to be 5676.24kcal/kg.

4.4.4. Ash Composition

Ash composition optimum carbonized briquette were determined and shown below in the table 19

Table 19: Major Oxide Ash Analysis of Optimum Carbonized Mixed Briquette

Mineral composition	Optimum carbonized mixed briquette
SiO_2 (%)	22.31
CaO (%)	28.69
MgO (%)	5.62
Fe_2O_3 (%)	2.45
Al_2O_3 (%)	32.09

4.4.5. Fourier Transform Infrared Spectroscopy Analysis (FT-IR)

The study employed Fourier transform infrared spectroscopy to examine alterations in the chemical composition of mixed carbonized briquette under ideal conditions for raw coffee husk and wheat straw. The primary cause of this alteration is the decreased presence of oxygen-containing functional groups resulting from the thermal breakdown of organic groups, particularly hemicellulose. The OH stretching vibration zone at around 3209-3512 cm^{-1} exhibits a broadband because of the crystalline cellulose's intra- and intermolecular hydrogen bonding and band properties. The hydrophilic property of biomass is caused by this hydroxyl group, which has the ability to generate ions and draw in water molecules.

Oxygen-containing compounds were gradually broken down and removed throughout the carbonization process, which reduced the oxygen content and simplified the organic content of the carbonized mixed briquette.

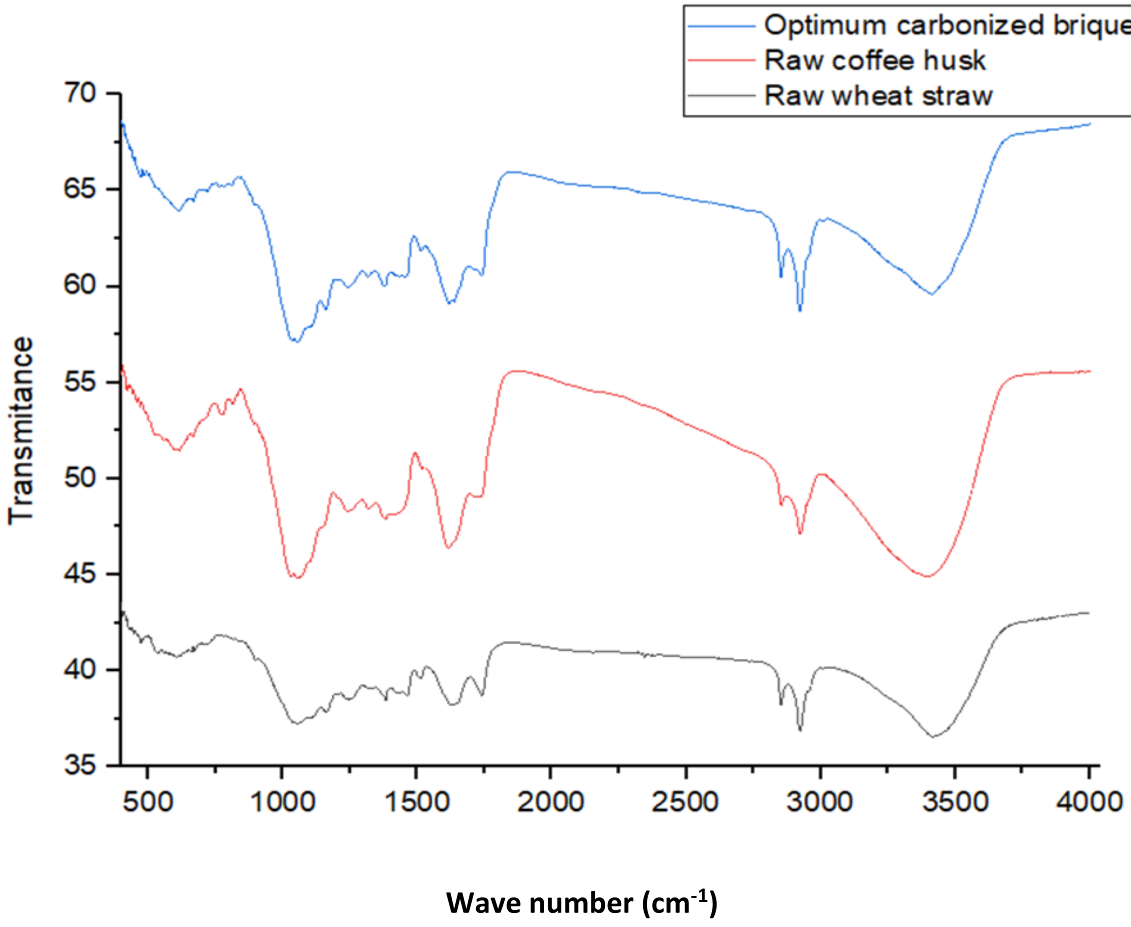


Fig: FT-IR analysis of raw wheat straw, raw coffee husk, and optimum carbonized briquette

Bulk Density

The produced mixed carbonized briquette has a bulk density of 1062.07 kg/m3. The resulting bulk densities were 655 kg/m3, 273.3 kg/m3, 1385.76 kg/m3, and 1028.35 kg/m3 for powdered coffee husk, powdered wheat straw, and briquetted coffee husk. As a result, without the addition of a binding agent, the bulk density of the mixed briquetted is much higher than that of the powdered coffee husk and wheat straw.

Mechanical Tests

Several characteristics such as strength and durability must be considered. Parameters that show strength of certain briquettes are compressive strength, impact resistance, water resistance and several others.

1. Shatter Resistance Test

Weight loss (%) = (A-B)/A*100%

Shatter resistance (%) =100% - weight loss (%)

Where A is initial weight (g), whereas B represent final weight (g)

i. Raw wheat straw

A (initial mass) = 8.8g B (final mass) = 7.4g

Weight loss= (8.8-7.4)/8.8= 15.91%

Shatter resistance = 100-15.91= 84.09%

ii. Raw coffee husk

A (initial mass) = 13.2g B (final mass) = 13.1g

Weight loss= (13.2-13.1)/13.2= 0.75%

Shatter resistance = 100-0.75= 99.25%

iii. Optimum carbonized briquette

A (initial mass) = 12.6g B (final mass) = 11.7g

Weight loss= (12.6-11.7)/12.6 = 7.14%

Shatter resistance = 100-7.14= 92.86%

2. Tumbling Resistance Test

The equations used to determine the tumbling resistance of the briquette were calculated as follows:

Weight loss (%) = (A-B)/A*100%

Tumbling resistance (%) =100% - weight loss (%)

Where A is weight of briquette before tumbling (g), whereas B is weight of briquette after tumbling (g).

i. Raw wheat straw

A (Initial mass) = 25.1g B (final mass) = 24.7g

Weight loss= (25.1-24.7)/25.1 = 1.60%

Tumbling resistance (%) =100% - 1.60% = 98.40%

ii. Raw coffee husk

A (Initial mass) = 30.4g B (final mass) = 30.2g

Weight loss= (30.4-30.2)/30.4 = 0.65%

Tumbling resistance (%) =100% - 0.65% = 99.35%

iii. Optimum carbonized briquette

A (Initial mass) = 60.4g B (final mass) = 59.8g

Weight loss= (60.4-59.8)/60.4 = 0.99%

Tumbling resistance (%) =100% - 0.99% = 99.01%

3. Water Resistance Test

The percentage of water gained by each briquette was calculated by using the equations as followed:

Weight gained (%) = (A-B)/B*100%

Water resistance (%) =100% - weight gained (%)

Where B is weight of briquette before immersion while A is weight of briquette after immersion.

The value of shatter resistance, tumbling resistance and water resistance test should be higher in order to ensure the strength of the briquettes.

i. Raw wheat straw

A (Initial mass) = 8.9g B (final mass) = 16.1g

Weight gained= (16.1-8.9)/16.1 = 44.72%

Water resistance (%) =100% - 44.72% = 55.28%

ii. Raw coffee husk

A (Initial mass) = 7.6g B (final mass) = 8.2g

Weight gained= (8.2-7.6)/8.2 = 7.31%

Water resistance (%) =100% - 7.31% = 92.69%

iii. Optimum carbonized briquette

A (Initial mass) = 12.5g B (final mass) = 14.3g

Weight gained= (14.3-12.5)/14.3 = 12.58%

Water resistance (%) =100% - 12.58% = 87.42%

The briquettes produced from different combination at this optimized mixing ratio were shown to have above the required target which is shatter resistance and tumbling resistance ≥90% and also water resistance ≥85%.

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

This study's primary goal was to increase the calorific value of briquettes made from a carbonization method that included coffee husk and wheat straw. The BBD of RSM was used to investigate and optimize the carbonation of wheat straw and coffee husk as a substitute energy source for the cement industry's clinker production.

Using sets of experimental data, quadratic model equations were constructed and then analyzed and optimized using Design Expert version 7.0.0 software. The temperature (300, 350, and 400 °C), fineness (<100µm, 100~175µm, and 175~250µm), and mixing ratio (30%, 50%, and 70%) changes throughout the carbonization process for the dependent variable (calorific value) may all be calculated and improved using the quadratic model. With a maximum calorific value of 5676.24 Kcal/Kg, the ideal circumstances were particle size (<100µm), mixing ratio (70% of coffee husk), and carbonization temperature (400°C). This demonstrates that we can completely replace South African imported coal, which has a calorific value of 5245~6230 kcal/kg. The fixed carbon would rise as the temperature of carbonization and biomass fineness increased and as a result, the calorific value was also increasing.

It was demonstrated that the briquettes made from various combinations at this ideal mixing ratio had greater mechanical strength and durability in terms of water resistance, tumbling resistance, and shatter resistance. Thus, the research conducted for this work shown that the use of alternative energy sources made from wheat straw and coffee husk briquettes can help address the energy problem caused by the depletion of non-renewable energy resources.

5.2. RECOMMENDATION

Production, optimization and characterization of fuel briquette from a mixture of wheat straw and coffee husk was done. Based on this research work the following tasks are recommended to be done by other researchers:

- Further studies in carbonization of biomass by bio chemical solution must be investigated.
- The use of alternative fuels in cement industries must be adapted in order to reduce fossil fuels and to prevent environmental solution.
- Further researches could be done on the carbonization temperatures above 400℃ and particle size of under 45µm.
- Briquette press with preheating die should be designed with appropriate compression pressure.
- Compressive strength test of briquettes should be analyzed since it’s not addressed because of there is no compression load of 100KN and below.

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APPENDICES

Appendix A: Proximate Analysis Experimental Method

A1: Moisture Content

By measuring the sample's weight loss during heating under strictly regulated temperature, time, and environment conditions, as well as sample weight and equipment parameters, moisture was ascertained. The sample's moisture content was calculated using (ASTM D3173-03, 2004). After being weighed and baked to 105°C in the oven, the empty crucible was covered, placed in a desiccator for 15 to 30 minutes, and allowed to cool to room temperature. One gram of the material, ground to a size of 250 µm, was weighed to the closest 0.1 gram, put inside the crucible, and sealed. The sample was immediately placed into the preheated oven and baked for one hour after the cover was removed. After being taken out of the oven, the samples were placed in a desiccator and allowed to cool to room temperature while covered 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.

$$MC = \frac{A - B}{A - C} * 100\%$$

Where, MC= moisture content

C= mass of crucible in g

A= mass of sample + crucible in g (before heating)

B= mass of sample + crucible in g (after drying)

A2: Ash Content

As a result, the ash content was calculated (ASTM D3174-02, 2004). Weighing the residue that remained after burning the sample under well monitored conditions (sample weight, temperature, duration, environment, and equipment specifications) allowed us to quantify the amount of ash. An empty silica crucible was filled with about 1 gram of finely powdered (<90µm) dry basis sample, which had been weighed. Next, the crucible and its contents were weighed to the closest 0.002g. The cupel was first burned for 30 minutes in an electric furnace. It was then removed and burned for four hours at 550°C in a high-temperature furnace. Finally, it was cooled to room temperature in a dryer and weighed after 25 minutes.

$$AC(\%) = \frac{A - B}{C - B} * 100$$

Where B= mass of crucible

C= mass of crucible + mass of sample before drying

A= mass of crucible + mass of sample after drying

A3: Volatile Matter

The volatile matter was calculated using the 2004 ASTM D3175-02 standard. It was ascertained by calculating the weight loss that occurred when a sample was heated under strictly regulated circumstances. 1.0g of fine powdered material (<90µm) air-dried sample was weighed in a VM crucible to the closest 0.002g, and it was then put inside a muffle furnace that was kept at 925˚C. The crucible's lid was then placed on top. After precisely seven minutes of heating, the crucible was taken out, let to cool in the open air, and then placed within a desiccator before being weighed once more.

The calculation performed as per the following:

$$\mathrm{C} = \frac{\mathrm{Y-Z}}{\mathrm{Y}} * 100\%$$

C= weight loss in (%)

Y= mass of sample used (oven dried) in g before drying

Z= mass of sample in grams after drying

VM =C-D

Where:

VM= volatile matter in %

D= moisture (%)

A4: Fixed Carbon Content

The percentage fixed carbon (PFC) was computed by subtracting the sum of the percentage of ash content, moisture content and volatile matter from 100.

%FC= 100- (%VM+%AC+%TMC)

Where: FC= Fixed carbon

AC= Ash content

VM= Volatile matter

TMC= Total Moisture content

Appendix B: Bulk Density Determination

B1: Bulk density for powdered coffee husk and cotton stalk

A digital balance was used to weigh an empty 100 mL bottle to the closest 0.0001 g. The sample was placed inside the container, and to make sure there are no big empty areas, the material will be gently crushed. Next, the sample and the container were weighed. Three replicates were carried out. The wet bulk density of the sample was then calculated from the following equation.

$$\rho = \frac{Y - Z}{V1}$$

Where: ρ = bulk density of the sample (g/ml)

Y= mass of the container and sample (g)

Z= mass of the container (g)

V1= volume of the container (ml)

Bulk density for powdered wheat straw:

Mass of sample =Y-Z = 16.3g

V1= 60ml

ρ=16.3g/60ml= 0.2733g/ml=273.3kg/m^3

Bulk density of powdered coffee husk:

mass of sample =Y-Z =39.3g   volume of container = 60ml

ρ=39.3g/60ml = 0.655g/ml = 655kg/m^3

B2: Bulk Density for Briquette

The weight of the briquette was weighted using digital balance. The volume of the briquette was approximated cylindrical shape by measuring the diameter and the height of the briquette. The bulk density was then calculated from the following equation.

$$\rho = \frac{Ms}{V}$$

$V= \pi r^2 h= (\pi d^2 h)/4$

Where: Ms= mass of briquette V= volume of briquette   r= radius of briquette h= height of briquette

For optimized carbonized mixed briquette:

Ms =10.3g   d = 21mm   h=28mm

V= 9698.096mm^3=9.698096cm^3

ρ =10.3/9.698096 = 1.06207g/cm^3=1062.07kg/m^3

For coffee husk briquette: ρ= 7.4g/5.340cm^3= 1.385767g/cm^3= 1385.767Kg/m^3

For wheat straw briquette: ρ= 5.14g/ 5.0cm^3 = 1.028g/cm3=1028Kg/m^3

Appendix C: Determination of Ash Composition

Ash Chemistry of the raw wheat straw and coffee husk were performed in order to determine the percentage of different oxides such as SiO_2, Fe_2O_3, Al_2O_3, CaO and MgO using ASTM procedure.

Determination of CaO

A 300 ml beaker was pipetted with a filtrate of 25 ml solution. Following the addition of 10ml of KF (20g/l) and a 5-minute incubation period, the solution was diluted to 200ml. Fe_2O_3 and Al_2O_3 were rendered inactive by the addition of 5 milligrams of CMP indicator and 5 milliliters of TEA (triethylamine). The pH of the mixture was then adjusted to 10.2 by adding 25 milliliters of KOH. Last but not least, the solution's green hue became crimson when 0.015M EDTA was added to it.

$$\%\mathrm{CaO} = \frac{\mathrm{V_{EDTA}} * \mathrm{T_{CaO}}}{\mathrm{Mash}}$$

Where: V_{EDTA} = volume of EDTA added

Mash= mass of ash

T_{CaO}= 0.784

Determination of Fe_2O_3

In a 300 ml beaker, 25 ml of the solution was diluted with distilled water to make 100 ml. The solution was heated to 2 pH and drops of NH_4OH (1 gm/l) were added until a yellow tint appeared. After that, endpoint determination was achieved by adding ten drops of indicators for sulfosalicylic acid. Titrate the solution with EDTA until the reddish-brown hue turns colorless.

$$\%\mathrm{Fe2O3} = \frac{\mathrm{V_{EDTA}} * \mathrm{T_{Fe2O3}}}{\mathrm{Mash}}$$

Where: V_{EDTA} = volume of EDTA added

Mash= mass of ash

T_{Fe2O3}= 0.784

Determination of Al_2O_3

Following the completion of the Fe_2O_3, 15 milliliters of EDTA were added, the pH was raised to 4.3, and the mixture was heated. The solution that $CuSO_4$ (0.015 mol/l) was used to titrate was mixed with five drops of PAN indicator. When the solution's yellow hue became violet, endpoint determination was finally achieved.

$$\%\mathrm{Al2O3} = \frac{1.33(\mathrm{K} * \mathrm{V_{CUSO4}}) * \mathrm{T_{Al2O3}}}{\mathrm{Mash}}$$

Where: K = Excess EDTA+ $CUSO_4$ consumption

Mash= mass of ash

T_{Al2O3}= 0.7355

Determination of MgO

A 300 ml beaker was filled with a 25 ml filtrate via pipetting. Following the addition of 10ml of KF (20g/l) and a 5minute incubation period, the solution was diluted to 200ml. Next, 20 milliliters of ammonia hydroxide (pH adjusted to 12.5), 5 milliliters of TEA, 1 milliliter of potassium sodium tartrate, and 6 drops of KB indicator were added. When the solution was titrated with EDTA, its brown hue became blue.

$$\%\mathrm{MgO} = \frac{(\mathrm{V_{MgO}} - \mathrm{V_{CaO}}) * \mathrm{T_{MgO}}}{\mathrm{Mash}}$$

Where: Mash= Mass of ash

V_{MgO} = Volume of MgO

V_{CaO}= Volume of CaO

T_{MgO}= 0.5816

Determination of SiO_2

To a 250 ml plastic cup, 50 ml of the previously specified solution was measured. After adding 15 milliliters of concentrated HNO3, the mixture was allowed to cool in a cold water bath for 15 minutes. Subsequently, 3 spatulas full of solid KCl were added until it was saturated, and 10ml of KF (150 g/l) was added to increase the SiO2 concentration. Give the fluid fifteen minutes to dissolve. After the solution was filtered through filter paper, 10 ml of (KCl+CH3CH2OH) and 8 drops of phenolphthalein were added to the mixture, and the paper was washed three times with KCl (150g/l) (10,10,5 ml) in the previous plastic beaker. Hot water was added up to the 200 ml mark, along with three drops of 0.1 g/NaOH and one drop of phenolphthalein. The solution was then further titrated by NaOH (0.15 g/l) until colorless changed to light pink and then yellow when it was titrated by EDTA (0.015 mol/l). This process continued until pink color appeared.

$$\%\mathrm{SiO2} = \frac{0.5 * \mathrm{V_{NaOH}} * \mathrm{T_{SiO2}}}{\mathrm{Mash}}$$

Where: Mash= mass of the ash

V=Volume of the NaOH solution

T_{SiO2}=2.04

Appendix D: Laboratory Photos

Raw Coffee Husk

Raw Wheat Straw

Raw material preparation

Pulverized Wheat Straw

Pulverized Coffee Husk

Electric Muffle Furnace

Drying Oven

Water Bath

Ash Determination Carbonization

175~ 250µm 100 ~ 175µm <100µm

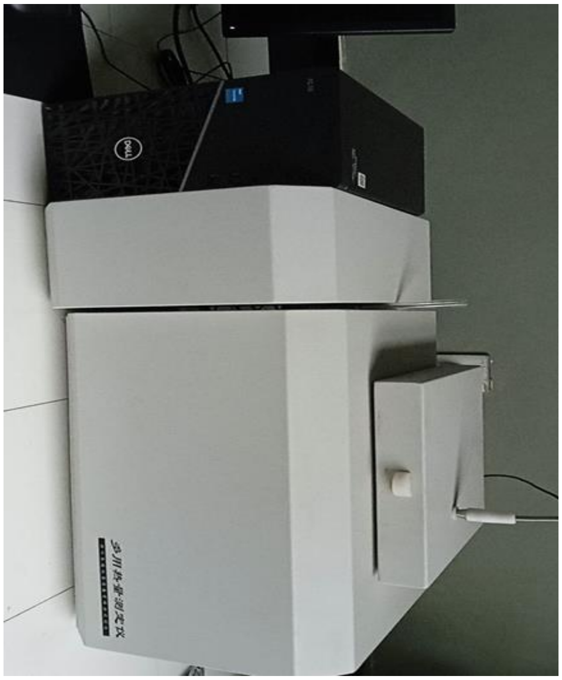
Carbonized Sample

Hydraulic Press

Raw Briquette

Mixed Carbonized Briquette

Prepared Sample for calorimeter

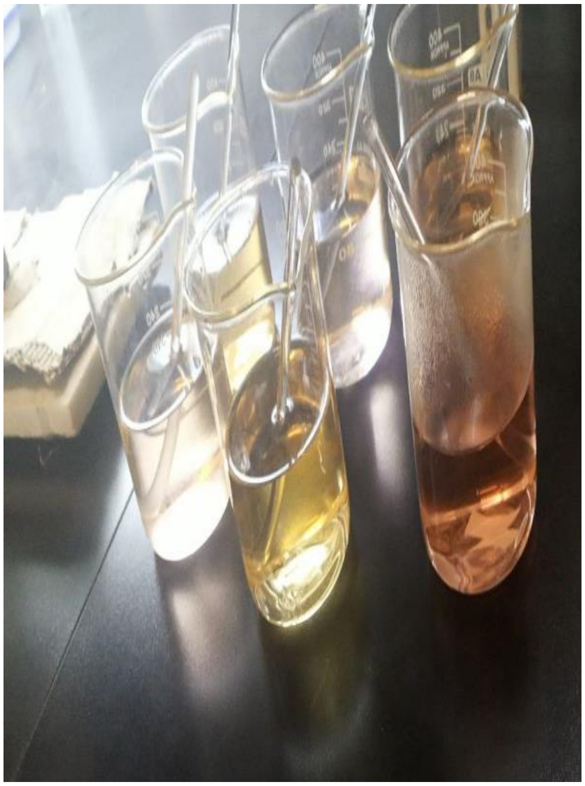


CT-5000A Calorimeter Instrument

Powder Chemicals

Prepared and Reagent Solutions

Reagent Bottles



Titrated Solution

Pipettes and Burettes

Tumbling Resistance Test

Water Resistance Test