ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)
SCHOOL OF CHEMICAL AND BIO ENGINEERING

Co-pelletization of Torrefied Cotton Stalk and Coffee Husk as an Alternative Energy Source for Cement Pyroprocessing

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University, Institute of Technology, in Partial Fulfilment of Requirement of Degree of Masters of Science in School of Chemical and Bio Engineering (Environmental Stream)

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This is to confirm that thesis provided by Yeayneabeba Tadesse, entitled “Co-pelletization of Torrefied Cotton stalk and Coffee Husk as an Alternative Energy Source for Cement Pyroprocessing” is submitted in partial fulfillment for degree of Masters of Science in Environmental Engineering 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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DECLARATION

I, the undersigned, declare that this thesis entitled “**Co-Pelletization of Torrefied Cotton Stalk and Coffee Husk as an Alternative Energy Source for Cement Pyroprocessing”** is my original work, and has not previously been submitted by any other person for the award of a degree in this or any other university, and that all resources of material used for this thesis have properly acknowledged.

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ABSTRACT

*Cement manufacturing is an energy and emission intensive process. The use of alternative fuels to replace coal contributes to energy security and the total environmental footprint of the cement industry. This study investigated the suitability of co-pelletized torrefied coffee husk and cotton stalk as alternative energy mix for cement pyroprocessing. Process parameters which affect the calorific value such as particle size (100-125μm, 125-250 μm and, 250-500 μm), mixing ratio (0.33, 0.5 and 0.67) and torrefaction temperature (200℃, 250℃ and 300℃) were optimized via Box Behnken design (BBD). Characterization of raw coffee husk, cotton stalk and mixed torrefied pellet for proximate analysis, ultimate analysis, calorific value, bulk density, ash composition, Thermogravimetric analysis (TGA) and Fourier transmission infrared spectroscopy analysis (FT-IR) were determined to understand the physiochemical and thermal property of the fuel. Based on the results, the optimal conditions were (particle size=100-125μm, mixing ratio=0.62 and torrefaction temperature of 300℃), with a maximum calorific value of 5320.72kcal/kg. The optimum mixed torrefied pellet showed a decrease in moisture content (1.67%), volatile content (50.45%), hydrogen to carbon ratio (0.044) and oxygen to carbon (0.4239), while the fixed carbon (37.14%), elemental carbon (*68.1195%*) and calorific value (5322.31kcal/kg or 22.283 MJ/Kg) increased considerably. As shown in the FT-IR analysis, loss of -OH groups resulted in decreased hydrogen-bonding capacity which makes the mixed torrefied pellet more hydrophobic. Moreover, the TGA analysis showed that the lignin content at higher torrefaction temperature was higher which was responsible for the higher heating value of mixed torrefied pellet. In view of the results obtained in this study, the proposed mixed torrefied pellet has a potential to be used as a source of alternative energy for cement industries.*

Keywords: Torrefaction, Co-pelletization, Alternative energy, Cotton stalk, Coffee husk

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ACRONYMS

ASTM	American society for testing and materials
CHNS	Carbon, Hydrogen, Nitrogen, and Sulphur
CMP	Calcine methyl phenolphthalein
FT-IR	Fourier transmission infrared spectroscopy analysis
GDP	Gross domestic product
HHV	High Heating Value
IEA	International energy agency
TBP	Torrefied biomass pellet
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis

NOTATIONS

Symbol	Definition	Units
m	Mass of the sample	g
T_f	Final temperature	℃
T_i	Initial temperature	℃
ρ_b	Bulk density	g/ml and Kg/m^3
W_1	Weight of the container	g
W_2	Weight of the container and sample	g
V_1	Volume of the container	ml
V_2	Volume of the pellet	mm^3
r	Radius of the pellet	mm

1. INTRODUCTION

1.1. Background

Cement is one of commonly used construction material in the world. The manufacturing of cement is an energy intensive which requires a temperature between 1450℃ and 1500℃ and emits a large quantity of CO_2 (Kaddatz et al., 2013; Vesterinen et al., 2010). Globally, the cement sector is responsible for roughly 5% of greenhouse gas emissions from human activity each year (The Pembina Institute and Environmental Defence Funding, 2014).

Energy use in cement factory is about 3500 kJ/kg clinker and emission is about 1 ton of CO_2 per ton clinker, of which about 40% is from the fuel and about 60% from calcination of limestone (Vesterinen et al., 2010). Pyro processing consumes more than 90% of the cement manufacturing energy. The remaining 10% is consumed in almost equal amounts by activities related to fuel and raw material preparation, grinding of clinker and blending of materials to prepare the finished cement product. Thus, the fuel demand of a large cement factory is enormous. Besides, cement industries rely heavily on carbon-intensive fossil fuels. According to Lemi et al. (2015), coal (53 percent) and petroleum coke products (29 percent) accounts for more than 80 percent of energy consumption.

In Ethiopia, the demand for cement would increase due to continuous and robust gross domestic product (GDP) growth. The increment in per capital income, rapid urbanization, high rate of population growth, significant housing deficit, large infrastructural gap, development of industrial park indicates the strong potential cement demand in the country. Moreover, In order for the nation to realize the dream of being a middle incoming country by 2025, several mega projects will be undertaken in the year to come (Lemi et al., 2015). Currently, new entrants are coming into the cement manufacturing in addition to the existing cement industries. If all plants are going to run at their full capacity the supply is expected to surplus the demand which shall make the Ethiopian cement price competition fierce and demand for energy would also increase. However, the energy-intensive nature of cement manufacturing coupled with the dependency of the country on the imported fossil fuel (furnace oil, coal, and petcock) and spiraling price of fossil fuel would stress the need for alternative fuel. Besides, in order to make a cement industry to grow sustainably, there should be a way to cut down sectorial greenhouse emission.

The energy dependency and environmental consequence derived from the consumption of fossil fuels have made necessary to develop a new alternative energy source which is renewable and sustainable, efficient and economically effective, to meet the demand of a sustainable energy supply. Among renewable resource, residual biomass is carbon-neutral and destined to play an important role as an alternative energy source (IEA, 2015; J. S. Tumuluru, Wright, Kenny, & Hess, 2010). Since agricultural residues such as coffee husk and cotton stalk are indigenous resources generated in large scale, thus, is largely available and rather inexpensive, these materials are considered as potential renewable and economically safe way of providing energy.

However, large amounts of agricultural residues remain unutilized due to its structural heterogeneity, non-uniform physical property, low energy density, high moisture content, and a hydrophilic nature have become a major problem in its efficient and economic transport, handling, storage and conversion into bioenergy products. The direct burning of these agricultural residues in domestic and industrial applications is also inefficient and associated with wide-scale air pollution (Rajkumar & Venkatachalam, 2013). Prior to cost-effective use in energy applications, the energy density and the shelf life of the biomass has to be improved. This can be possible by combining torrefaction and pelletization as a pretreatment method.

Torrefaction is a thermal pre-treatment method that improves the fuel properties of biomass and makes it more suitable for co-firing with coal. When combined with pelletizing, torrefaction results in energy-dense pellets with a high calorific value and other properties such as a hydrophobic nature and improved grindability characteristics compared to untreated biomass (Nunes et al. , 2014).

Therefore, this thesis was aimed to study the fuel property of raw coffee husk and cotton stalk in comparison with mixed torrefied coffee husk and cotton stalk pellet. The physiochemical and thermal properties and effect of torrefaction temperature, particle size and mixing ratio on the calorific value of the pellet were investigated.

1.2. Statement of the problem

Cement manufacture is an energy-intensive industry in which energy is mainly consumed in the pyro-process of the kiln plant for producing cement clinker. For land-locked countries like Ethiopia, imported fossil fuels such as furnace oil, coal, and petcock provide most of the energy needs of cement industries. The finite nature of fossil fuel resources, high and unstable prices and most importantly, their damaging effect on the environment underscore the need to develop alternative fuels.

Moreover, the energy cost for Ethiopian cement firms accounts nearly 50 to 60% of the total production cost structure as a contrast to 30 to 40% of global standards. Consequently, price in Ethiopia is still perceived to be relatively higher as compared to global price. Most importantly, the major opportunity for improving the competitiveness of cement firms mainly revolve around reducing energy cost through partly replacing imported coal with local and alternative energy source use. Therefore, it is imperative to invest in alternative energy sources in order to reduce the cost of production and cement price.

Agricultural and agro-industrial residues constitute 15% of the total energy consumed in Ethiopia. Residues are currently used ineffectively, which are combusted in three stone open fire stoves in villages. In different parts of the country, various types of crops are cultivated and, as a result, a considerable volume of crop residues is also generated. Due to their availability in enough amounts and fulfilling minimum energy content coffee husk and cotton stalk are considered as the best candidate alternative fuels. Despite ample availability, cotton stalk and coffee husk have never been used in Ethiopia as an effective source of energy, but have been left to decompose or burned in open field or dumped into nearby rivers causing air and water pollution respectively.

The disadvantage of using agricultural residues such as coffee husk and cotton stalk as sustainable alternative fuel to coal and other fossil fuels are mainly attributed to its low energy density, high moisture content (which makes it susceptible to biological attack and biodegradation), heterogeneity, low calorific value, high oxygen to carbon and hydrogen to carbon ration, hygrophilic nature and larger volume or low bulk density. In order to overcome these drawbacks, torrefaction in combination with pelletization is introduced in order to improve biomass properties.

Reviewing past literatures concerning torrefaction indicate that many literatures are reported on torrefaction of different biomass such as cotton stalk, corn stalk, bamboo, banyan, willow, marula seeds, blue gum wood, leucaena, sawdust rice husk, wheat straw and reed canary grass. Only a few studies are reported on combined torrefaction and pelletization of biomass. However, to the best of the author's knowledge, none have so far studied in detail the fuel property of mixed torrefied coffee husk and cotton stalk pellet.

Hence, this study was aimed to investigate the fuel property of raw coffee husk and cotton stalk in comparison with mixed torrefied coffee husk and cotton stalk pellet. The physiochemical and thermal properties and effect of torrefaction temperature, particle size and mixing ratio on the calorific value of the pellet were studied.

1.3. Objectives

1.3.1. General objective

The main objective of this thesis was to study if co-pelletized torrefied cotton stalk and coffee husk can be used as an alternative energy source for cement industries.

1.3.2. Specific Objectives

The specific objectives of this study were:

- To observe physiochemical and thermal characteristics of raw cotton stalk and coffee husk
- To torrefy each biomass at different temperature and to pelletize both biomass at different particle size and biomass ratio.
- To examine the effect of particle size, biomass ratio and torrefaction temperature on the calorific value of the pellet and to optimize torrefaction and pelletization parameters using response surface method.
- To investigate the physiochemical and thermal characteristics of optimum torrefied mixed pellet

1.4. The scope of the Study

The scope of the research work was to explore and cover the torrefaction and pelletization of coffee husk and cotton stalk as an alternative energy source for partial energy substitution in cement industries. Initially, both coffee and cotton residues were subjected to sun drying for around seven days and both residues were ground and milled at three different particle size (125-125µm, 125-250µm, and 250-500µm). Powdered raw coffee husk and cotton stalk were then characterized by performing proximate analysis, ultimate analysis, calorific value, ash composition, bulk density, TGA and FT-IR. Torrefaction of both residues was undertaken at three different temperatures (200℃, 250℃ and 300℃) for one hour at a constant nitrogen flow rate. The mixing of torrefied coffee husk and the cotton stalk was performed as three different mixing ratio (0.33, 0.5 and 0.67) and pelletized at constant compression pressure and holding time. The best calorific value was determined by RSM considering the main parameters (particle size, mixing ratio, torrefaction temperature). The fuel property of selected pellet was performed in terms of proximate, ultimate, calorific value, ash composition, TGA, FT-IR, bulk density, appearance, and durability.

1.5. The significance of the study

This study became necessary in view of the recent interest in the use of agro-residues for energy production. Thus, the study seeks to find a productive way of utilizing agro-residues as a renewable energy source. It also has a significant role in contributing to promoting renewable energy for improved energy access and security, climate change mitigation and adaptation and environmental sustainability in general. Besides this research work seeks to provide a clean and environmentally sound energy for clinker production without compromising its final product quality.

Utilization of indigenous energy sources like cotton stalk and coffee husk as an alternative fuel to partially substitute the existing imported coal is expected to benefit the company by providing energy security and by contributing to the effort in cutting off the production cost to keep the cement company competitive in the cement market. It also has financial benefits arising from added revenue from the Clean Development Mechanism (CDM), as biomass fuels can reduce CO_2 emissions from cement plants substantially.

In addition, it benefits the environment by keeping the carbon footprint to a minimum and by providing value-added waste management option. Moreover, it assists society by improving the livelihood of the pastoral community by creating job opportunity and also the country as a whole by easing the scarce foreign currency shortage.

Generally, this research work would serve as a starting for further research studies on combined torrefaction and pelletization of biomass to produce energy-dense pellets with a high calorific value and other improved properties for the aforementioned benefits.

2. LITERATURE REVIEW

2.1. Overview of cement production

Cement is paramount for economic development and poverty reduction in emerging markets. Along with aggregates and water, cement is the key ingredient in the production of concrete, and, as such, is an essential construction material that enables large infrastructure projects in energy, water, and transport, as well as, importantly, the construction of modern buildings and urban infrastructure (IFC, 2017).

Cement production is a two-step process. First, clinker is produced from raw materials (calcium oxide (65%), silicon oxide (20%), alumina oxide (10%) and iron oxide (5%)) by heating in a rotary kiln at temperatures of up to 1,500°C. This step can be a dry, wet, semi-dry or semi-wet process according to the state of the raw material. After the clinker is produced, the second step involves gypsum (calcium sulfates) and possibly additional materials, such as coal fly ash, natural pozzolanas being added to the clinker. These are then ground to a fine and homogeneous powder in a cement grinding mill, after which, the cement is dispatched either in bulk or bagged (Thrän et al., 2017)

According to the statistic of Global cement production (2017), China produces the most cement globally by a large margin, at an estimated 2.4 billion metric tons in 2017, followed by India at 270 million metric tons in the same year. China produces over half of the world’s cement. Global cement production is expected to increase from 3.27 billion metric tons in 2010 to 4.83 billion metric tons in 2030.

As reported by Jemaneh (2017), the construction industry is booming in Ethiopia. Years ago, the country had been importing cement at huge costs for its developmental projects. In 2010/11 the country imported 0.3 million tons cement by spending millions of USDs. However, owing to the growing numbers of cement factories,13 factories with over 12 million tones design capacity, the country has begun exporting beyond meeting local consumption. Furthermore, as listed in Table 2.1 and 2.2, new entrants are coming into the cement manufacturing in addition to the existing cement industries.

Ethiopia has greater potential for higher cement consumption at least for a decade to come mainly due to continued and robust GDP growth which is also estimated to sustain, improving political stability; increasing per capita income and emergence of middle class; increasing government capital budget expenditure; rapid urbanization (4.3 %); high rate of population growth (2.6%); significant housing deficit; large infrastructural gap and development of industrial parks (29.37million square meters) among others. Besides, in order for the nation to realize the dream to join middle-income countries by 2025, several other mega projects will be undertaken in years to come (Lemi et al., 2015).

Table 2. 1: Ethiopian cement factories design and actual production capacity (2009E.C)

Company name	Design capacity (ton)	Actual production (ton)	Accomplishment in %
Large cement factories			
Dangotie Cement PLC	2,500,000	2,055,622.53	82.22
National Cement	1,200,000	615,334	51.28
Messebo Cement	2,160,000	1,794,472.52	83.08
Derba Cement	2,300,000	1,544,277	67.14
Mugher Cement	2,160,000	1,064,927.00	49.30
Small cement factories			
Capital Cement	450,000	289,019.10	64.23
Ture Cement	300,000	216,814.50	72.27
Dashen Cement	180,000	83,835.70	46.58
Inchini Bedrock	300,000	102,050	34.02
East Cement	450,000	238,761.70	53.06
Zhongshan Cement	250,000	194,847.73	77.94
Pionner Cement	450,000	246,587.48	54.80
Abysiniya Cement*	90,000	20,158	22.40

*Half year production

Source: Chemical and Construction Inputs Industry Development Institute (CCIIDI) (2009E.C)

As reported in Ethiopian cement industry utilization strategy (2015-2025), it is difficult to make firm and detail industry level energy utilization comparison with global standards due to lack of energy audit in Ethiopia, with the exception of Muger cement. However, the current energy efficiency status of the cement industry is assumed to very low as compared to the international standard. It was reported that energy cost accounts of the total cost structure of cement firms are nearly around 50-60%. This Figure indicates that the energy incurred in Ethiopian cement factories is higher than the global standard which is between 30-40%.

Table 2. 2: Ethiopian cement industries under construction phase

Company name	Design capacity (ton)
Jema Cement	105,000
Debresina business	90,000
Huang Shang	435,000
Huwayu Cement	150,000
CH clinker manufacturing *	1,200,000
Ethio cement	850,000

* Increased by 300,000 tons from the previous one

Source: Chemical and Construction Inputs Industry Development Institute (CCIIDI), (2009E.C)

2.2. Cement chemistry and impact on the environment

Cement production is a large user of fossil fuels and producer of greenhouse gases (Worrell et al, 2001). In cement production, there are three sources of greenhouse gases. The first source comes from the inherent nature of cement production. Cement is made from limestone, which predominantly contains more than 90% calcium carbonate ($CaCO_3$). As shown in a chemical reaction1, when heat is applied to $CaCO_3$ it dissociates into calcium oxide, which is the main ingredient for cement, and carbon dioxide, which is a greenhouse gas.

$$\mathbf{CaCO_3 \xrightarrow{\mathit{Heat}=850℃} CaO + CO_2} \text{……………………………………………..…Reaction 1}$$

For every 100 grams of calcium carbonate heated in a kiln above 750°C, about 44 grams of carbon dioxide and 56 grams of calcium oxide are produced. In effect, for every 56 grams of calcium oxide that is used by the construction industry, about 44 grams of carbon dioxide are released into the atmosphere. The second source of greenhouse gases comes from the combustion of carbon-containing fossil fuels such as methane, furnace fuel, coal or alternative fuels such as biomass, re-ground tires, and household and industrial wastes. The mechanism by which carbon-containing fuel burns to give off carbon dioxide is given in reaction 2 using the smallest hydrocarbon compound, methane (CH_4).

$$\mathbf{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O} \ldots\ldots\ldots\ldots\ldots\ldots \text{Reaction 2}$$

According to the European Cement Association, the overall carbon dioxide production from combustion of fuel in the kiln is approximately 335 kg of CO_2 per ton of cement.

The third source of carbon dioxide derives from the use of electricity produced by power stations that are burning fossil fuels. Based on the European cement association, this accounts for approximately 50 kg of CO_2 per ton of cement produced. Countries, such as Ethiopia, that generate a significant fraction of their electricity from hydroelectric power stations do not produce large quantities of carbon dioxide from the use of electrical motors. However, cement plants in these countries do, of course, produce carbon dioxide from the first two sources. The carbon dioxide produced from the three source releases up to 0.8 ton of carbon dioxide into the atmosphere per ton of cement produced. This makes cement production one of the largest sources of greenhouse gases, producing 5 percent of global emissions (Ernst Worrell, Lynn Price, Nathan Martin, Chris Hendriks, 2001)

Generally, Production of cement is relatively energy intensive and emits a large quantity of CO_2. Energy use is about 3500 kJ/kg clinker. Thus, the fuel demand of a large cement factory is enormous. For most producers, coal is the major energy source in production, even though some cement factories already use biomass in proportions which in some cases reach up to 50%. The kilns are suited for using a range of different fuels, but it would be difficult to supply such high amounts of biomass that the share of biomass in the total energy mix would be considerable. On the other hand, the cement industry can easily use even wet and low-calorific value fuels in small portions. For example, municipal waste, sewage sludge, animal meal, waste wood, paper sludge, and crushed tires are used in different cement factories in different European countries (Vesterinen et al., 2010).

2.3. Alternative fuels in the cement industry

The first major use of alternative fuels in the cement manufacturing industry emerged during the mid-1980s. The primary goal in substituting fossil fuels was to enable the industry to remain economically competitive, as fuel consumption accounts for almost one-third of the cost of producing clinker. Any positive impact on the environment was considered an added benefit. Since then, there has been an increased sensitivity to the environmental impact of human and industrial activities. Beyond the cost-cutting benefits of alternative fuels, use of these fuels can contribute greatly to the environmentally sound disposal of waste and to the mitigation of greenhouse-gas emissions. Therefore, key cement players started to consider alternative fuels as a lever to improve their contribution to sustainable development and as a key component of corporate social responsibility (IFC, 2017).

2.3.1. Types of alternative fuel

As clearly reviewed by Seboka et al., (2009), in cement industries, there are three sources of fuels used for pyro-processing. These are fossil fuels, biomass, and non-renewable waste.

Fossil Fuels: Fossil fuels represent the main sources of energy used in cement production. Principal fossil fuels used are coal, petcoke and petroleum-based fuels such as natural gas and heavy furnace fuel.

Biomass: These materials are, in principle, ‘renewable’ because they can be re-grown at a rate equal to, or greater than, the rate of harvesting; they are ‘carbon-neutral’ because plants absorb carbon dioxide as they grow. Biomass waste such as forest products, fuelwood, foliage, shavings, agricultural crops, cotton stokes, coffee husk, rice straw, sugarcane, flower farm waste, and wheat straw are widely used as renewable and carbon-neutral fuels. Industrial-scale animal wastes, such as bones, fats, meats, and other animal wastes, also fall under the biomass category.

Non-renewable wastes: These materials are wastes or materials at the end of their service lives. They can be burnt in the cement kiln to recover energy and conserve fossil fuels that would have otherwise been used. Some, such as plastics and rubber wastes, can also cause environmental hazards when dumped in landfills. Rubber tires, plastics, hydraulic oil, grease, and hydrocarbon-based house-hold or industrial wastes can be used as an energy source in cement factory kilns.

2.3.2. Criteria for using alternative fuel

Alternative fuels are a mixture of various wastes and therefore these fuels must fulfill certain criteria. The chemical contents of the fuel must meet regulatory standards to ensure environmental protection. It must have the calorific value above a certain level. The fuel should have a fairly homogeneous composition. The physical form must allow easy handling for transportation. It should be economically viable along with its availability. The energy, ash, moisture and volatiles contents of the fuels should be given an important consideration. A flexible fuel feeding system needs to be developed for alternative fuels to avoid problems associated with the feeding.

The following properties are expected to be considered as alternative fuels (Kaddatz et al., 2013; Madlool et al., 2011; Mokrzycki & Uliasz- Bocheńczyk, 2003; Patil & Khond, 2014):

- The physical state of the fuel (solid, liquid, gaseous)
- The content of circulating elements (Na, K, Cl, S)
- Toxicity (organic compounds, heavy metals)
- Composition and content of ash, Content of volatiles
- Calorific value (over 14.0 MJ/kg)
- Chlorine content (less than 0.2%)
- Sulfur content (less than 2.5%)
- PCB content—less than 50ppm
- heavy-metals content—less than 2500ppm [out of which: mercury (Hg)—less than 10ppm, and total cadmium (Cd), thallium (Tl) and mercury (Hg)—less than 100ppm].
- Physical properties like scrap size, density, homogeneity, grinding properties, moisture content
- proportioning technology
- the emissions released
- the cement quality and its compatibility with the environment must not decrease,
- Alternative fuels must be economically viable.

As a mixture of various wastes, alternative fuels must be produced in conformity with certain rules (Mokrzycki et al., 2003; Patil & Khond, 2014):

- The chemical quality of the fuel must meet regulatory standards assuring environmental protection,
- The calorific value must be stable enough to allow the control of the energy supply to the kiln; the objective is to arrive at a fairly homogeneous composition, and
- The physical form must allow easy handling of the material for transportation and a stable, adjustable flow of material in the cement plant

In general, substitution of alternative fuels for fossil fuels will help reduce energy costs, providing a competitive edge for a cement plant using this source of energy. Furthermore, this will reduce the burden of waste disposal considerably. The conditions in rotary kilns, such as high temperature, the high speed of the gas stream and the long particle-storage period, guarantee that the use of alternative fuels is ecologically safe (Patil & Khond, 2014).

2.4. Biomass energy

Biomass has always been a major source of energy for mankind and accounts for about 14% of the world’s total energy supply. The term biomass refers to all organic materials that originate from living organisms e.g. wood, agricultural residues, animal manure etc. Biomass sources are therefore diverse. Biomass is a clean energy resource that shows high potential as a substitute for fossil fuels and to meet the world’s increasing energy demand (Royal University of Phnom Penh, 2013).

Plant residues from the major agricultural crops (wheat, rice, corn, soybean, sugarcane, coffee, and cotton) are abundantly available renewable resources that can be used to supply energy through thermochemical conversion processes (Zhang et al., 2012).

Agricultural residues are defined as a biomass by-product from the agricultural system and include straws, husks, shells, and stalks. These residues can be divided into 2 groups: crop residues, which remain in the field after harvest, for example, cotton stalk, and agricultural residues, which are the by-products of the industrial processing of crops, for example, coffee husk. Agricultural residues constitute a major part of the total annual production of biomass residues and are an important source of energy both for domestic as well as industrial purposes (Akdeniz et al.,2004).

2.4.1. Potential biomass resource in Ethiopia

Ethiopia has low access to modern energy services and its energy supply is primarily based on biomass. According to International energy agency (IEA) 2014 report, percent share of biomass and waste energy of Ethiopia is 92.2% followed by oil (5.7%), Hydropower (1.6%), coal (0.1%) and geothermal, solar/ wind (0.4%). Biomass plays a major part in fulfilling the energy needs of developing countries like Ethiopia. Ethiopia has huge potential to develop thermal energy for its cement firms from biomass.

Biomass-based first generation biofuels generation using food crops is under criticism over sustainability issues on food security. However, second-generation biofuel, derived from agricultural wastes and forest residue and a number of fast-growing trees, and grown specifically for energy purposes, could provide opportunities for energy production (Mhilu, 2014). Among several kinds of second-generation biofuel, agro-residues have become one of the most promising choices (Rajkumar & Venkatachalam, 2013). Haile-Meskel, (2015) also reported a potential for energy production from agro-processing industries such as sugarcane bagasse, cotton stalk, coffee hull, and oilseed shells. There is also encouraging initiatives at Messebo to use sesame husk as an alternative energy source for cement factories (Lemi et al., 2015).

Agricultural and agro-industrial residues constitute 15% of the total energy consumed in Ethiopia. Residues are currently used ineffectively, which are combusted in three stone open fire stoves in villages. In different parts of the country, various types of crops are cultivated and, as a result, a considerable volume of crop residues is also produced. The agricultural residue potential depends on the number of crops and agricultural land. The availability measurements of the crop processing area are very difficult because of unavailability of actual residue generation data. Therefore, the amount of residue is estimated on the bases of residue production ratio (RPR). Generally, for use as fuel, crops with a higher residue-to-production ratio provide the largest volume of potential biomass. However, it is often not desirable, socially and environmentally acceptable or, indeed, economically viable to divert all types of biomass residue for fuel (Teka, 2015).

As explained by Teka (2015), agricultural residues have different uses. Residues from wheat and maize, for example, may be left on the ground or burned in the field to recycle soil nutrients; some parts are used as animal feed, as building materials, and as cooking fuel. The fraction that is available for fuel is limited and varies from crop to crop. In the small-scale farming context, residues are generally better used for ecological, agricultural or construction purposes than for fuel. However, in large commercial farms and in agro-industries a large proportion of the residue available cannot be used on-site due to limited demand in the immediate vicinity. As a consequence, residue tends to be disposed of wastefully (Teka, 2015).

2.4.2. Selection of the best alternative fuel

Varieties of alternative fuels have been assessed, among them biomass drives fuel have been selected due to their availability in enough amounts and fulfilling minimum energy content. Out of the listed biomass-derived fuels in Table 2.3, coffee husk and cotton stalk are considered as the best candidate alternative fuels. Table 2.4 also confirm the availability of both biomasses.

Table 2. 3: the Heating value of alternative fuels

NO.	Energy source type	Kcal/kg	MJ/kg
1	Coffee husk	3936	16.479
2	Sawdust	4512	18.89
3	Cotton stalk	4179	17.497
4	Solid waste	3168	13.264
5	Sesame husk	4050	16.957

Source: (FDRE, 2015) and self-computation

2.4.3. Coffee growing in Ethiopia

In its wild state, Arabica coffee is a forest plant restricted to the highlands of Ethiopia and a small area in neighboring South Sudan. It has been used in Ethiopia as a food and beverage for many hundreds, if not thousands, of years. Thus, Ethiopia can be considered as the biological and cultural home of coffee. Its early use was no doubt restricted to gathering fruits from the wild forests, with semi-domestication possibly coming soon afterward.

Today, an estimated 525,000 hectares (5,250 km^2) of coffee is planted in Ethiopia, although the actual area is probably in excess of 20,000 km^2. Coffee provides Ethiopia with its most important agricultural commodity, contributing around one-quarter of its total export earnings (Kew Royal BotanicGardens, 2017).

The main coffee growing areas are found within Oromia Region and Southern Nations, Nationalities, and Peoples' Region (SNNPR), with modest production in Amhara Region and minor output in Benishangul-Gumuz Region.

2.4.4. Cotton growing in Ethiopia

Cotton has been produced in Ethiopia since very ancient times. cotton is one of the more valuable and extensively grown field crop plants in the mild altitudes and lowland areas of Ethiopia. It has great importance in the social, cultural and spiritual way of life of the people. Both medium staple and short staple cotton are produced in the country. According to the report of the ministry of agriculture, at the national level in 2013/14 cropping season, 55,523 ha of land was covered by both cotton and over 83,284 quintals of seed cotton is produced. It is used to manufacture a wide verity of handwoven dresses and industrial processed textile fabrics, in addition to edible and protein rich-seed cake production for human and animal consumption respectively. The cotton stalk is also used as feed, fuelwood and fencing material. However, the use of cotton stalk as livestock feed is not suitable due to Endosulfan contamination and very poor feeding value (Akhmedov et al, 2017).

Cotton is grown predominantly as a mono-crop, once in a year. The main season, normally known as summer season, relies either on June to September rainfall or an irrigation water that lasts, depending on the location, for about 126 days. The major cotton-producing regions are Amhara, Tigray, Afar, Gambella, and south nations and nationalities people regions accounting for 96.8% of the total annual cotton production.

The government of Ethiopia is now working towards the development of cotton, textile and garment sector as a priority within the planning of industrial park development. Many foreign companies are moving closer to their raw material base, the cotton producing countries like

Ethiopia. Therefore, for the foreseeable future, the demand for cotton is expected to outstrip the current supply and drive local and foreign investors to look for large-scale cotton production.

Table 2. 4: Coffee husk and cotton stalk potential of Ethiopia

No	Biomass residue	Area (Province)	Name of deposits	Biomass residue (Ton/yr.)
1	Dry Processing Coffee	SNNPR	Coffee residue	49,496
		Oromia	Coffee residue	132,911
		Gambela	Coffee residue	1,458
		Others	Coffee residue	158
			Total	184,023
2	Wet-processed Coffee	SNNPR	Coffee residue	16,533
		Oromiya	Coffee residue	6,959
		Gambela	Coffee residue	1,519
		Others	Coffee residue	9
			Total	25,020
	Total coffee residue			**209,043**
3	Cotton	Tigray	Cotton residue	42,822
		Afar	Cotton residue	46,100
		Others	Cotton residue	150,000
			Total	**238,922**

Source: (Lemi et al., 2015) and own Computation

2.4.5. Temporal availability of cotton and coffee residue

Agricultural residues such as cotton stalk, coffee husk, and others are seasonal. Collection and storage of residues during the months of availability will be necessary; alternatively, different residues could be sourced at different times of the year. The seasonal availability of cotton stalk and coffee husk are shown in Table 2.5.

Table 2. 5: Seasonal availability of selected cotton and coffee residues

Biomass Type	Season (months) of Availability
Coffee husk	
Washed Coffee pulp	September to January
Sun-dried coffee	December to July
Cotton stalk	November to February

Source: (Seboka et al., 2009)

In Ethiopia, biomass residues are distributed over a large area in small quantities: farms are scattered. But for some wastes, such as cotton stalk and coffee husks, a few large-scale suppliers are available (Seboka et al., 2009)**.**

2.4.6. The advantage of the use of cotton stalk and coffee husk

According to MCF (2015), the use of biomass such as cotton stalk and coffee husk have advantages such as:

- To ensure natural resource preservation and total emission reduction
- To enhance the use of waste material (as a fuel)
- To ensure environmentally sustainable waste management and important saving of agricultural wastes.
- To use of suitable alternative materials because it does not have any negative impact on emission.
- To encourage environmental, social, economically equally and friendly relationship.
- To improve Ethiopian’s climate resilient green economy strategy.
- The company may obtain acceptance from international and financial institutions as well as from governmental institutions because it supports current globalization issues.
- To create job opportunity for the local community (small and micro enterprises)
- To reduce greenhouse gases emission.
- To obtain revenue from carbon trade.
- To insure socio economic and ecological sustainability.

- To reduce foreign currency.

2.5. Biomass convention technologies

Biomass can be converted to more valuable energy forms via a number of processes including thermal, chemical, biochemical, and thermochemical conversion processes. During thermal conversion, biomass is converted into another form of energy by using heat with or without the presence of oxygen. While in chemical conversions, biomass is converted into liquid fuel in the presence of chemical agents. In contrast with the thermochemical conversion which uses chemical and heat to produce energy, biochemical conversion process uses enzymes, bacteria, and other microorganisms to break down biomass to fuel. Table 2.6 outlined the current biomass conversion technologies in use.

Table 2. 6: Current biomass conversion technologies

	Technology/ technique	Description
Pre-processing	Pelletization	Physical process where biomass is dried and pressed under high pressure to produce cylindrical pieces of compressed and extruded biomass.
	Torrefaction	Thermochemical process where water and other volatile compounds in biomass are removed in the absence of oxygen at a temperature of 200-300℃.
Conversion to heat and/or power	Combustion/ co-firing	Thermochemical process where biomass is burnt in the presence of oxygen to produce heat.
Chemical routes to biodiesel from oil	Transesterification	A chemical process where an alcohol (such as methanol) combined with vegetable oil to produce a fatty acid alkyl ester
	Hydrogenation	The chemical process of adding hydrogen to vegetable oils to create hydrocarbon chain.
Biological routes to bioethanol from carbohydrate	Hydrolysis and fermentation	A biochemical process (usually aided by physical/chemical preparation of feedstock) where sugars are fermented into products (particularly ethanol) where starch-based feedstock is used, an additional stage – saccharification - is required before fermentation where the starches are converts into simpler sugar molecules by enzymatic hydrolysis.

Table 2. 6 (Continued)

	Technology/ technique	Description
	Lignocellulosic hydrolysis and fermentation	After various pretreatments to liberate carbohydrates, numerous organisms and process variants are being investigated for their ability to convert cellulosic feedstocks into alcohol-based fuels.
Biological route to biogas	Anaerobic digestion	A biological process where consortia of microbes break down solid biomass into methane and CO2 via successive processes of metabolisms
Thermochemical routes to fuels or power	Gasification	Thermochemical process using a high temperature (600-1,100℃) to turn biomass in to into syngas in the absence of oxygen
	Pyrolysis	The thermochemical process where the feedstock is subjected to high temperatures (475-490℃) in the absence of oxygen to produce a liquid 'bio-oil', a light syngas or a solid bio-charcoal (biochar)
	Carbonization	Thermochemical process where the feedstock is subjected to high temperature (300-600℃) and slow heating rate results in higher yield of charcoal.

Source: (Ayla et al., 2008; Basu, 2013; Davis et al., 2014)

Pre-treatment techniques like pelletization and torrefaction can enhance the utilization and conversion of biomass resource. Pelletization is a densification technique used to enhance the thermochemical conversion efficiency, handling, and transportation of biomass resource (Bevan, Ahmad, Johari, Amran, & Abdullah, 2015). In another hand, torrefaction is a thermal pre-treatment method that improves the fuel property of biomass and makes it more suitable for co-firing with coal. When combined with pelletization, torrefaction results in the energy-dense pellet with high calorific value and other properties such as hydrophobic nature and improved grindability characteristic compared to untreated biomass (Nunes et al., 2014).

The biological treatment process seems to be a promising technology, as it avoids the use of chemicals, consumes less energy, produces minimal byproducts, works at mild operating conditions, and does not harm the environment. However, the biological pretreatment process is very slow and it requires a large space and a controlled environment for the effective pretreatment, which makes the process costly compared to other pretreatment methods (Nhuchhen, Basu, & Acharya, 2014).

The major thermal biomass conversion techniques are gasification, pyrolysis, and carbonization. Combustion means 100% oxidation of all organic contents of the fuel using air/oxygen. Unlike combustion, gasification involves chemical reactions in an oxygen-deficient environment producing product gases with heating values. In pyrolysis we only heat but without adding air and thereby gaseous components of the organic material are evaporated and later condensed as liquid hydrocarbons. Carbonization covers a broad range of processes by which the carbon content of organic materials is increased through thermochemical decomposition. In a more restrictive sense for biomass, it is a process for the production of charcoal from biomass by slowly heating it to the carbonization temperature in an oxygen-starved atmosphere (Basu, 2013).

2.6. Co-firing biomass with coal

Co-firing is a term used to describe incorporating a secondary fuel with a primary fuel (Stephen Gent et al., 2017). Since biomass can be converted into solid fuel, it is a good candidate to be co-fired with coal. Therefore, equipment designed to burn coal should be able to easily use biomass as well (College of Agricultural Sciences, 2008). However, the co-firing of biomass causes some special problems due to the following basic differences between coal and biomass (Basu, 2013):

1) The elemental and proximate analysis of coal is much different from that of biomass.
2) Unlike coal, the properties of biomass are highly variable and heterogeneous. Even different parts of a tree could have a different composition.
3) Unlike coal, when stored for an extended period, biomass absorbs moisture and besides the adverse effect on thermal efficiency moisture could also lead to the development of harmful fungus.
4) Biomass is less brittle and more fibrous than coal which results in significantly different grinding characteristics

These differences are important when considering the supply and storage of fuel for co-firing. One possible method for reducing these problems is to convert the biomass to torrefied biomass (College of Agricultural Sciences, 2008). Torrefaction of biomass could offer some relief to the above problems and make biomass co-firing more viable. Such relief is due to the following intrinsic properties of torrefied biomass (Basu, 2013).

1) The fuel preparation for co-firing greatly benefits from the torrefaction of the biomass feed because this process makes biomass more brittle and less fibrous. The least cost option for co-firing uses the existing pulverization mills and feeds biomass directly into them along with coal. Though torrefaction cannot make biomass as grindable as coal, it makes a significant improvement in the grindability of the biomass. As a result, the existing mills can grind the required amount of biomass without requiring additional energy. This allows the boiler to feed its burner with the required amount of coal and biomass to match the furnace heat input of the existing boiler. Furthermore, in cases where separate mills are used for coal and biomass, the improved grindability of torrefied wood allows the mills to produce particles of a right size and in the right quantity.
2) Capital investment for covered biomass storage could be a major component of the total cost of biomass co-firing upgrade of an existing plant. The carrying charge of that could tip the economic balance against co-firing. Even that may not prevent dried biomass from picking up additional moisture from the atmosphere and cause a health hazard due to fungal attack on biomass. Torrefied biomass, being relatively hydrophobic, does not pick up moisture even when stored outdoors and experience a very little fungal attack. Thus, it obviates the need for expensive covered fuel storage allowing the plant to use parts of the existing coal yard to store the biomass.
3) Torrefaction acts like a quality leveler for multiple fuel feed. The difference between different biomass feedstock is reduced through torrefaction. Thus, while the quality of the delivered biomass supply is variable, the actual variation in quality experienced by the burner is much less. Torrefaction helps reduce the difference in combustion characteristics and heating value of the biomass feed.

2.7. Torrefaction

Torrefaction is a thermal pretreatment technology. It is also defined as isothermal pyrolysis of biomass occurring in temperature ranges of 200–300°C and performed at atmospheric pressure in the absence of oxygen (J. S. Tumuluru, Sokhansanj, Hess, Wright, & Boardman, 2011a).

Torrefaction removes most of the smoke-producing compounds and other volatiles, resulting in a final product that has approximately 70% of the initial weight and 80–90% of the original energy content. The major decomposition reactions affect the hemicelluloses, and, to a lesser degree, the lignin and cellulose. Torrefaction helps to develop a uniform feedstock and improves binding during pelletization by increasing the number of available lignin sites, breaking down the hemicellulose matrix, and forming fatty unsaturated structures, resulting in bulk densities of 750–850 kg/m3 and energy densities exceeding 20GJ/m3 (J. S. Tumuluru, Wright, Hess, Kenney, & National, 2011).

Torrefaction has also been called mild pyrolysis. Raw biomass is characterized by its high moisture content, low calorific value, hygroscopic nature, and larger volume or low bulk density. However, after undergoing torrefaction the properties of biomass are improved to a great extent. The benefits accomplished by torrefaction include (1) higher heating value or energy density; (2) lower atomic O/C and H/C ratios and moisture content; (3) higher hydrophobicity or water-resistivity; (4) improved grindability and reactivity; and (5) more uniform properties of biomass. Figure 2.1. shows a summary of changes in biomass properties before and after torrefaction (Chen et al., 2015).

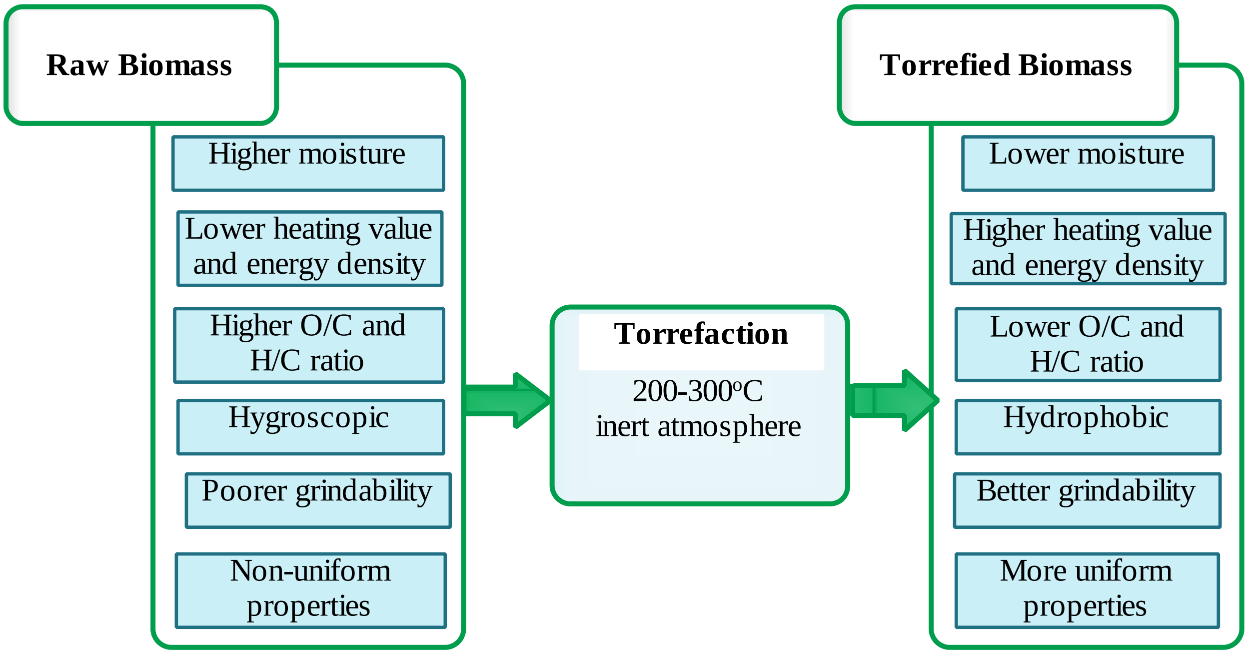


Figure 2. 1: A schematic of the property variation of biomass undergoing torrefaction

2.7.1. Mechanism of Torrefaction

The thermochemical changes in biomass during torrefaction may be divided into five regimes (Basu, 2013; Tumuluru et al., 2011). Each is discussed below.

1. **Regime A (50-120℃):** This is a nonreactive drying regime where there is a loss in physical moisture in biomass but no change in its chemical composition. The biomass shrinks but may regain its structure if rewetted. Upper temperature is higher for cellulose.
2. **Regime B (120-150℃):** This is softening of lignin regime which makes the biomass more suitable for densification, as the softened lignin serves as a binder.
3. **Regime C (150-200℃):** This is called "reactive drying" regime that results in structural deformity of the biomass that cannot be regained upon wetting. This stage initiates breakage of hydrogen and carbon bonds and depolymerization of hemicellulose. This produces shortened polymers that condense within solid structures.
4. **Regime D (200-250℃):** This regime along with regime (E) constitutes torrefaction zone for hemicellulose. This regime is characterized by limited devolatilization and carbonization of solids structure formed in regime (C). It results in the breakdown of most inter- and intramolecular hydrogen, C-C and C-O bonds forming condensable liquids and non- condensable gases.
5. **Regime E (250-300℃):** This is the higher part of the torrefaction process. Extensive decomposition of hemicellulose into volatiles and solid products takes place. Lignin and cellulose, however, undergo only a limited amount of devolatilization and carbonization. Biomass cell structure is completely destroyed in this regime making it brittle and non-fibrous.

2.7.2. Torrefaction products

As Tumuluru et al. (2011) provided, the three different products produced during torrefaction are: (1) brown to black uniform solid biomass, which is used for bioenergy applications, (2) condensable volatile organic compounds comprising water, acetic acid, aldehydes, alcohols, and ketones, and (3) non condensable gases like CO_2, CO, and small amounts of methane. The release of these condensable and non-condensable products results in a change of properties of biomass. These products are further illustrated in Figure 2.2 (Tumuluru et al., 2011).

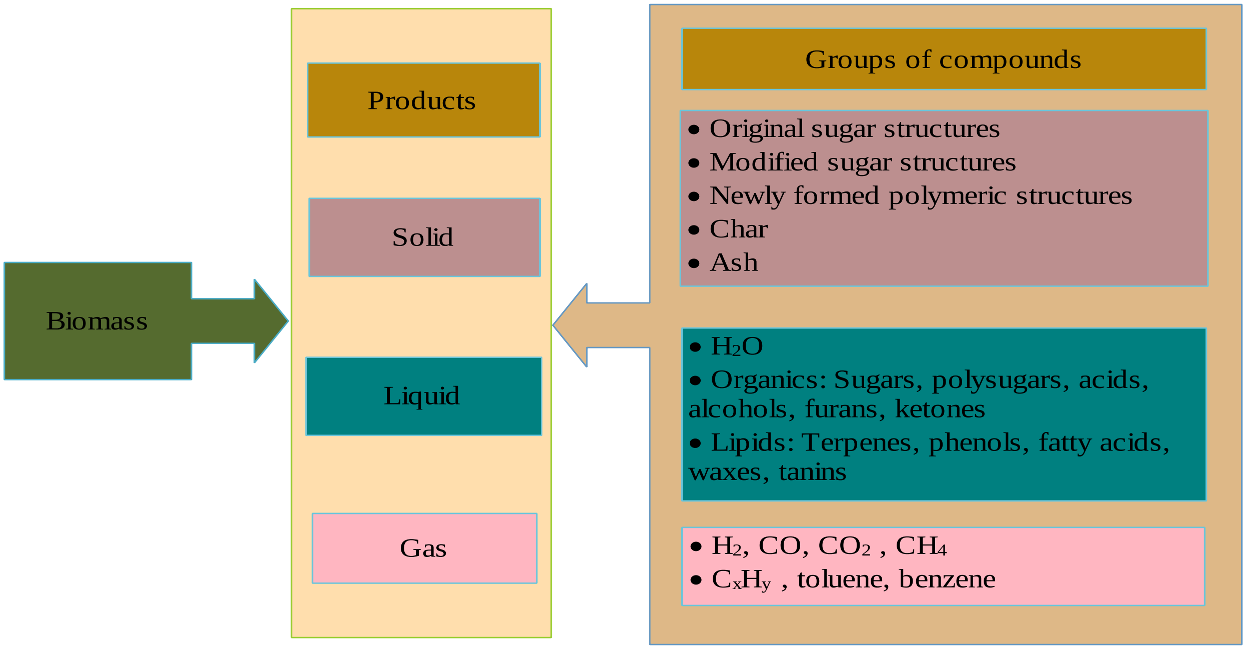


Figure 2. 2: Products formed during torrefaction of biomass

2.7.3. Properties of torrefied biomass

A. Moisture content

Moisture content is an important property of biomass fuels. According to Tumuluru et al., (2011), Feedstock moisture content ranges from 10–50%, but because torrefaction is a deep drying process, moisture content is reduced to 1–3% on a weight basis, depending on the torrefaction conditions. During torrefaction, the hydroxyl groups will be partly destroyed through dehydration. This prevents the formation of hydrogen bonding so that the torrefied biomass becomes hydrophobic. The lower saturated moisture content in torrefied biomass could also result from tar condensation inside the pores, obstructing the passage of moist air through the solid, and then avoiding the condensation of water vapor. The polar character of condensed tar on the solid also prevents the condensation of water vapor inside the pores (Chen et al., 2015).

Reduction in moisture during torrefaction provides three main benefits: (1) reduced moisture level for the conversion process, (2) reduced transportation costs associated with moving unwanted water, and (3) the prevention of biomass decomposition and moisture absorption during storage and transportation (Tumuluru et al., 2011).

B. Volatile matter, fixed carbon, and elemental contents

Apart from saturated moisture content, the proximate analysis of biomass also reveals the properties changes in the volatile matter (VM), fixed carbon (FC), and ash after torrefaction (Chen et al., 2015). Table 2.7 lists the VM and FC contents, the atomic oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios as well as the higher heating values (HHVs) of a variety of biomass species after torrefaction. As can be seen in the Table 2.7, the VM content of raw biomass is high, ranging from 70 to 88 wt%, while its FC content is low, ranging from 6 to 20 wt%. By virtue of the dehydration process of biomass from torrefaction, moisture and light volatiles are liberated from the materials. Therefore, VM in biomass is decreased, whereas FC is increased. The VM and FC contents of torrefied biomass are approximately in the ranges of 35–86 wt% and 13–42 wt%, respectively

The main elements in biomass include carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S). Carbon in a fuel is the major source of heat released from combustion. Hydrogen is also an important source of heat in combustion; however, more hydrogen contained in a fuel is usually accompanied by a lower content of carbon. Oxygen contained in biomass is conducive to fuel burning, but it reduces the calorific value of biomass. The higher the oxygen and ash contents in a fuel, the lower the biomass possess heating value. Compared to coal, carbon, nitrogen and sulfur contents in biomass are low, whereas its hydrogen and oxygen contents are high. Moreover, the moisture content in biomass is usually higher than that in coal. As a result, the calorific value of biomass is lower than that of coal (Chen et al., 2015).

As shown in Table 2.7, the atomic oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios in raw biomass are in the ranges of 0.715-1.032 and 0.121-0.148, respectively. After undergoing torrefaction, moisture and light volatiles, which contain more hydrogen and oxygen, are removed from biomass, whereas relatively more carbon is retained. This results in the slight or mild carbonization of biomass. As a consequence, the atomic O/C and H/C ratios are decreased to 0.183-0.937 and 0.065-0.137, respectively. Compared to coal, the sulfur and nitrogen content in biomass is much lower. Therefore, much less sulfur and nitrogen oxides are emitted into the atmosphere when biomass is burned.

Table 2. 7: Properties of various types of biomass before and after torrefaction

Biomass	T(^{o}C)	T (min)	VM (wt%)	FC (wt%)	O/C	H/C	HHV (MJkg^{-1})	Reference
Leucaena								(Wannapeera et al., 2011)
Raw			86.1	13.1	0.834	0.148	20.3	
Torrefied	200	30	85.3	14.0	0.783	0.137	21.0	
	225	30	84.3	14.9	0.76	0.135	21.2	
	250	30	82.2	16.9	0.753	0.12	21.2	
	275	30	73.8	24.9	0.638	0.096	22.8	
	250	2h	76.6	22.1	0.74	0.104	21.2	
	250	10h	69.8	28.9	0.601	0.089	23.3	
	250	15h	61.8	36.7	0.527	0.088	24.4	
Cotton stalk								(Chen et al., 2014)
Raw			74.96	15.80	0.833	0.140	18.31	
Torrefied	200	25	75.44	16.48	0.746	0.127	18.68	
	230	25	73.12	18.39	0.679	0.108	19.49	
	260	25	69.99	21.86	0.509	0.090	21.99	
	290	25	53.62	34.01	0.248	0.067	25.43	
Cornstalk								(Chen et al., 2014)
Raw			70.17	16.56	0.85	0.145	18.06	
Torrefied	200	25	69.32	18.41	0.743	0.113	18.26	
	230	25	64.77	21.47	0.614	0.097	19.19	
	260	25	54.53	28.32	0.441	0.085	20.73	
	290	25	35.30	41.19	0.183	0.065	23.61	
Sawdust								(Cai et al., 2017)
Raw			80.74	17.84	0.818	0.125	19.45	
Torrefied	200-220	1hr	83.17	14.75	0.823	0.125	19.20	
	240-260	1hr	75.43	22.78	0.779	0.115	19.60	
	280-300	1hr	68.53	28.44	0.651	0.106	21.10	
Rice Husk								(Cai et al., 2017)
Raw			78.66	6.57	0.884	0.132	15.85	
Torrefied	200-220	1hr	64.53	20.43	0.845	0.126	16.11	
	240-260	1hr	63.38	21.85	0.876	0.124	15.74	

Table 2. 7. (Continued)

Biomass	T(^{o}C)	T (min)	VM (wt%)	FC (wt%)	O/C	H/C	HHV (MJkg^{-1})	Reference
	280-300	1hr	56.06	26.00	0.647	0.107	17.59	(Cai et al., 2017)
Willow								(Bridgeman & Jones, 2008)
Raw			87.6	10.7	0.799	0.130	20.00	
Torrefied	230	30	82.1	16.1	0.779	0.122	20.2	
	250	30	79.8	18.4	0.749	0.118	20.6	
	270	30	79.3	18.6	0.697	0.114	21.4	
	290	30	77.2	20.5	0.665	0.110	21.9	
Wheat straw								(Bridgeman & Jones, 2008)
Raw			76.4	17.3	0.797	0.144	18.9	
Torrefied	250	30	77	15.6	0.718	0.123	19.8	
	270	30	65.2	26.5	0.639	0.114	20.7	
	290	30	51.8	38.0	0.489	0.099	22.	
Reed canary grass								(Bridgeman & Jones, 2008)
Raw			82.5	12.1	0.767	0.140	19.5	
Torrefied	250	30	80.3	13.3	0.736	0.125	20.0	
	270	30	76.6	16.1	0.715	0.115	20.8	
	290	30	70.5	21.3	0.669	0.112	21.8	
Cotton stalk								(Chen et al., 2015)
Raw			75.38	18.09	0.768	0.143	16.53	
Torrefied	220	30	74.25	18.56	0.655	0.115	17.09	
	250	30	69.76	20.32	0.492	0.097	18.85	
	280	30	56.23	32.49	0.268	0.075	20.31	
Wheat straw								(Bai et al., 2017)
Raw			75.6	19.09	1.032	0.121	17.88	
Torrefied	250	30	66.67	26.05	0.937	0.110	18.95	
	275	30	58.80	31.01	0.783	0.097	20.18	
	300	30	41.90	43.66	0.577	0.071	22.08	

C. Solid yield, energy density and energy yield

When biomass is torrefied, its dry matter is lost because of the thermal degradation. The solid yield is defined as the mass ratio of torrefied biomass and its parent biomass, with the value being less than unity (Chen et al., 2015). The solid yields and HHV so far a variety of raw and torrefied biomass materials at various operating conditions are listed in Table 2.8.

Table 2. 8: A list of solid yield, higher heating values, energy yield, and energy ratio of various types of biomass before and after torrefaction

Biomass	T (°C)	t (min)	Solid yield (%)	HHV (MJKg^{-1})	Energy yield	Energy ratio
Wheat straw						
Raw				18.90	1	
Torrefied	250	30	82.60	19.90	1.049	86.20
	270	30	71.50	20.70	1.095	78.20
	290	30	55.10	22.60	1.196	65.80
Rape stalk						
Raw				18.75	1	
Torrefied	200	30	63.29	19.50	1.040	65.82
	250	30	38.26	20.10	1.072	41.01
	300	30	25.30	21.59	1.151	299.13
Rice Husk						
Raw				14.32	1	
Torrefied	250	60	77.50	15.89	1.070	89.70
	270	60	74.25	16.07	1.120	83.33
	300	60	58.25	17.59	1.210	71.56
Coffee residue						
Raw				20.37	1	
Torrefied	240	30	89.41	21.78	1.069	95.60
	240	60	84.01	22.87	1.123	94.30
	270	30	74.13	25.34	1.244	92.20
	270	60	64.12	28.06	1.378	88.33
Wood						
Raw				20.70	1	
Torrefied	220	60	82.98	23.23	1.122	93.12
	250	60	54.73	27.52	1.329	72.76
	280	60	47.22	28.38	1.371	64.74

Source: (Chen et al., 2015)

Intensifying the calorific value or energy density of solid biomass fuel is the chief goal of torrefaction. The higher heating values (HHVs) of raw biomass and coal are generally in the ranges of 15–20 and 25–35 MJkg^{-1}, respectively (Chen et al., 2015). Consequently, it is essential to enhance the energy density of biomass if it is used as an alternative to coal. Table 2.7 and Table 2.8 indicate that the HHV of torrefied biomass is approximately between 15 and 29MJkg^{-1} which is closer to the HHV of coal.

D. **Grindability**

The energy required for grinding process of any materials could be defined as its grindability. The main limitations in the grinding of the raw biomass are fibrous and tenacious natures, which create difficulties in the grinding. Thus, the process that reduces fibrous and tenacious behavior of biomass enhances the overall performance of the size reduction equipment. After biomass is torrefied, the decomposition and the depolymerization of the macro-polymeric components to the micro-monomers, which decreases fiber length as well as increases porosity, increase the grindability of biomass. The improvement in the grindability reduces slenderness in the ground particles, producing a uniform particle size distribution suitable for co-firing power plants (Nhuchhen et al., 2014).

E. Particle size distribution, sphericity, and particle surface area

Particle-size distribution, sphericity, and surface area are important parameters for understanding flowability and combustion behavior during co-firing. According to Tumuluru et al. (2011) review, Many researchers observed that ground, torrefied biomass produced narrower, more uniform particle sizes compared to untreated biomass due to its brittle nature, which is similar to coal. In addition, it was observed that torrefaction results in increased sphericity and particle surface area.

2.8. Torrefaction and pelletizing

Torrefaction is a thermal pre-treatment method that improves the fuel properties of biomass and makes it more suitable for co-firing with coal (Nunes et al. , 2014). In combination with pelletization, the aim is to produce a durable bio-based fuel pellet of high energy density, with a high degree of homogeneity and hydrophobic characteristics that can, ideally, be handled and stored outdoors without weather (rain) protection. The brittleness and the reduced oxygen content of torrefied pellets make them an ideal candidate to replace coal with biomass in existing heat and power plants (Rudolfsson et al., 2015).

Table 2.9. compares the properties of woodchips, conventional wood pellets, torrefied biomass, TBP's, and bituminous coal. As shown, TBP's are a superior fuel compared to woodchips and wood pellets with regard to calorific value, energy density, moisture content, and degradability. TBP's properties approach those of bituminous coal. Combined torrefaction and pelletizing produce an energy dense biomass fuel with properties similar to those of bituminous coal. The high calorific value and high energy and bulk densities of TBP's may lead to significant cost savings in the biomass-to-energy chain when compared to state-of-the-art biofuel chains, especially in logistics, because the higher the energy density of a fuel is, the more energy a truck, train, or ship carrying that fuel can transport. At the same time, less storage space is required, also leading to cost savings. A high energy density also brings other benefits, such as improving the functionality and decreasing the energy use of conveyors and mills at the power plant.

Table 2. 9: Fuel properties of woodchips, wood pellets, torrefied biomass, TBPs and bituminous coal

	Wood chips	Wood pellets	Torrefied biomass	TBPs	Bituminous coal
Moisture content (%) ^{i}wt	30-60	7-10	2	1-5	5-10
Mass density (Kg/m^3)	250-400	600-650	230	750-850	800-1000
*LHV (MJ/kg)	6-13	16.2	19.9	19-22	>25
Calorific value (Mwh/t)	1.7-3.6	4.5	5.5	5.2-6.2	7
Energy density	0.7-0.9	3	1.3	4.2-5	5.6-7
Hygroscopic nature	Hygroscopic	Hygroscopic	Hydrophobic	Hydrophobic	Hydrophobic
Biological degradation	yes	yes	no	no	no

*Low heating value

Source: *(Nunes et al., 2014).*

In addition to the possible savings in logistics that can be achieved when switching from untreated biomass or conventional pellets to TBP's, higher grindability is one of the key properties that make torrefied biomass and TBP's so attractive for co-firing in existing coal-fired power plants. The low moisture content of TBP's facilitates storage, allowing longer storage periods than those of woodchips or wood pellets, for example, and is also expected to lead to reduced stack losses and a higher power plant efficiency compared to conventional co-firing. Despite their many good fuel properties, TBP's are still a new fuel, and, unlike the case of woodchips and wood pellets, there is not yet much experience of their large-scale handling and use.

Gaps in the literature retrieval

Reviewing past literatures concerning torrefaction indicate that many literature are reported on torrefaction of different biomass such as cotton stalk and corn stalk (Chen et al., 2014), bamboo, banyan and willow (Chen et al., 2011), corn stalk (Poudel & Oh, 2014), marula seeds and blue gum wood (Mamvura, Pahla, & Muzenda, 2018), Leucaena (Wannapeera et al., 2011), Sawdust and rice Husk (Cai et al., 2017), Willow, Wheat straw and Reed canary grass (Bridgeman & Jones, 2008). Few studies are reported on combined torrefaction and pelletization of biomass. However, to the best of the author's knowledge, none have so far studied in detail the fuel property of mixed torrefied coffee husk and cotton stalk pellet.

3. MATERIALS AND METHODS

3.1. Physiochemical and thermal characteristics of raw cotton stalk and coffee husk

The biomass that have been used in this study were collected as residue from large-scale farms at Upper Awash Agro Industry for the case of cotton stalk while coffee husk was collected from Gambella**.** The initial reduction in moisture content was made through sun drying for 6-7 days. Then, subsequent grinding and sieving of both residues were made to a particle size of (100-125µm), (125-250 µm) and (250-500 µm).

The experiments were conducted in four different institutes. Experiments such as proximate analysis, torrefaction and pelletization process were performed at the school of chemical and bioengineering and mechanical workshop, AAiT. Ultimate analysis and FT-IR analysis were conducted in AAU, science faculty. Moreover, calorific value and ash chemistry where determined at Dangote cement factory. Thermogravimetric analysis was conducted at the Leather industry development institute.

3.1.1. Proximate analysis

3.1.1.1. Material

The major equipment that were used was jaw crusher, grinder, centrifuge mill, sieve, electrostatic balance, platinum crucible, ceramic crucibles, drying oven, muffle furnace (0-1200℃) and desiccators

3.1.1.2. Method

The proximate analysis of cotton stalk and coffee husk was measured according to American society for testing and materials standard (ASTM E871-82, 2014) for moisture content, (ASTM, 2011) for volatile matter, (ASTM, 2007) for ash content and the fixed carbon was computed by subtracting the sum of the percentage of ash content, volatile matter and moisture content from 100. Detail procedure can be seen in appendix a.

3.1.2. Elemental Analysis (CHNS)

3.1.2.1. Material

The major equipment that was used Flash EA 1112 CHNS elemental analyzer.

3.1.2.2. Method

This is a standard method that was used to determine the amount carbon, hydrogen, nitrogen, and sulfur before and after thermal treatment of both raw cotton stalk and coffee husk by using Flash EA 1112 CHNS elemental analyzer. The samples were fed into the analyzer along with carrier gas (helium) flow rate of 120 ml/min, reference flow rate 100 ml/min, and excess supply of oxygen at a flow rate 250 ml/min. The reaction of oxygen with other elements (namely carbon, hydrogen, nitrogen, and sulfur) present in the sample produces carbon dioxide, water, nitrogen dioxide, and sulfur dioxide respectively. The combustion products were separated by a chromatographic column and are detected by the thermal conductivity detector (T C D), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent compositions of elements in the sample. From these results, the oxygen composition was determined by subtracting the sum of Carbon, Hydrogen, Nitrogen, and Sulphur compositions from 100.

3.1.3. Calorific value determination

3.1.3.1. Material

The major equipment used was XRY-1A oxygen Bomb calorimetry.

3.1.3.2. Method

According to the ASTM D 3286 standard, the heating values of raw cotton stalk and coffee husk samples were determined using bomb calorimeter (XRY-1A oxygen Bomb calorimetry). A 0.5 gram of dried and milled sample was taken in a clean crucible. The crucible was placed in the bomb by letting the nickel wire to be immersed in the fuel sample. Then it was filled with oxygen at 25 atmospheric pressure and placed in the calorimeter, which was filled by a known mass of water. With a continues stirring, the initial temperature was recorded. The sample was then ignited and heat was liberated. Uniform string was continued and the maximum temperature attained was recorded. The calorific value was then determined using the following formula:

$$\text{Calorific value} = \frac{\frac{\left(\left(T_f - T_i\right) * 14470\right) - 40}{m}}{4.185} \text{……………………….Equation 3.1}$$

Where; m=mass of the sample, 0.5g

T_f=final temperature

T_i= initial temperature

3.1.4. Ash composition of cotton stalk, coffee husk, mixed Pellet

3.1.4.1. Material

All chemicals that were used in the study was reagent grade and 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.

The major equipment that were used was Erlenmeyer flask, condenser, Volumetric flask, funnel, porcelain dish, spatula, pipette, burette, beaker, hot plate/Bunsen burner, electrostatic balance, metallic crucibles, drying oven, stove, plastic cup, muffle furnace (0-1200℃) and desiccators.

3.1.4.2. Method

Ash Chemistry of the raw cotton stalk 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. Determination of oxide each sample was done by measuring 0.5g of the sample which was dried at 105℃ and ashed at 650 ℃ for 30min. 6g of NaOH pellet was then added in the ash and placed in the muffle furnace at 650℃ for 20min. The crucible was cooled and the melted solution was placed into 300ml of the beaker and boiled with 100ml of water. The beaker was then removed from the stove and 25ml of concentrated HCl was added. While stirring, the crucible was washed with 1:5 HCl and added to solution till the crucible is free. 1 ml of nitric acid was then added in the solution. Determination of each oxide was done based on (ASTM, 2002) as shown in appendix E.

3.1.5. Thermogravimetric analysis (TGA)

3.1.5.1. Material

The major equipment used was thermogravimetric analyzer (TA instrument, model: SDT Q600).

3.1.5.2. Method

A thermogravimetric analyzer (TA instrument, model: SDT Q600) was used to determine the thermal behavior before and after thermal treatment of both raw cotton stalk and coffee husk samples using temperature programming from atmospheric temperature to 1000^{o}C at the heating rate of 20^{o}C/min. Testing was carried out under inert atmosphere (N_2) with a flow rate of 100ml/min to remove all corrosive gases and avoid thermoxidative degradation. The thermal degradation temperature with corresponding weight loss was recorded and analyzed.

3.1.6. Bulk density

3.1.6.1. Material

The major equipment that were used was electrostatic balance and baker.

3.1.6.2. Method

The bulk density of powdered cotton stalk and coffee husk was measured according to the method used by Zhang et al, (2012). Detail procedure is shown in appendix D.

3.2. Torrefaction and pelletization of cotton stalk and coffee husk

3.2.1. Torrefaction process

3.2.1.1. Material

The major equipment that were used was tubular furnace and nitrogen flow regulator.

3.2.1.2. Method

The process of torrefaction was undertaken in the tube furnace and both coffee husk and cotton stalk were torrefied at 200℃, 250℃ and 300℃ for one hour. As shown in fig 3.1, the reactor operated batch-wise and an inert gas (N_2) was used to purge the oxygen from the reactor.

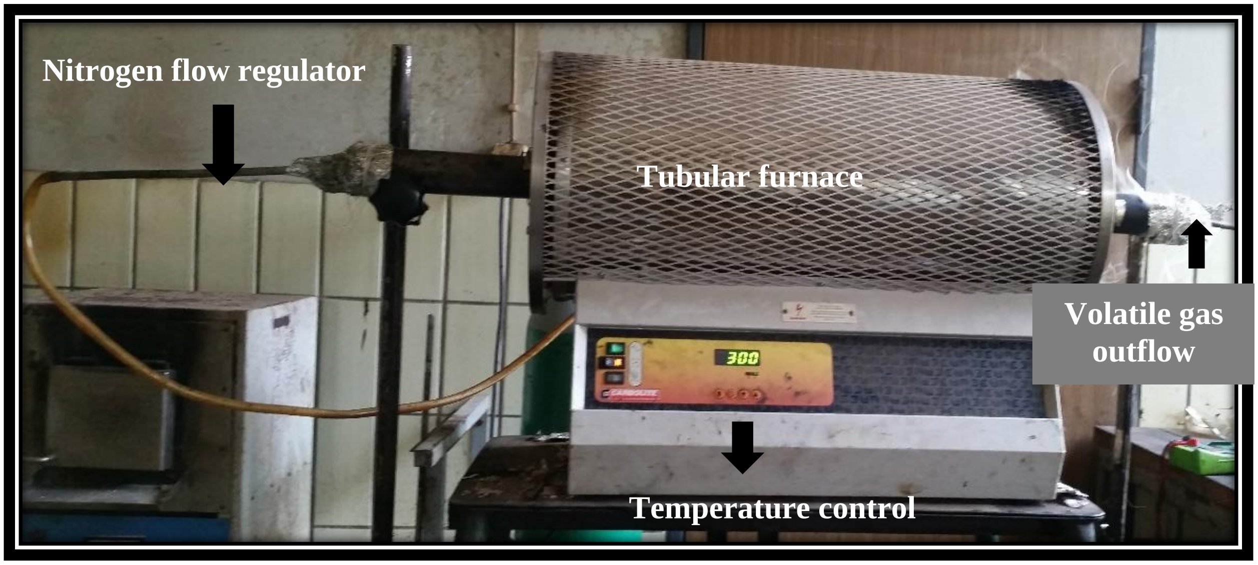


Figure 3.1: Laboratory tube furnace used for torrefaction of biomass

3.2.2. Pelletization process

3.2.2.1. Material

The major equipment that were used was self-made single pellet press with backstop and compressor.

3.2.2.2. Method

Pelletization of torrefied coffee husk and cotton stalk was undertaken using a single pellet press tool made in the laboratory. The experimental setup is shown in Figure 3.2. The pellet press tool contains a metal cylinder with a press channel and backstop (made of flat sheet metal). The die was made from hardened steel and the press channel had a diameter of 12 mm. To press the pellet, the press channel was closed with the backstop and the die was filled with 3g mixed torrefied coffee husk and cotton stalk then compressed into a pellet using press machine indicated in Figure 3.2. Once the pellet was pressed until 100pa was reached the pressure was held for 30min. then the backstop was removed and the pellet was pressed out.

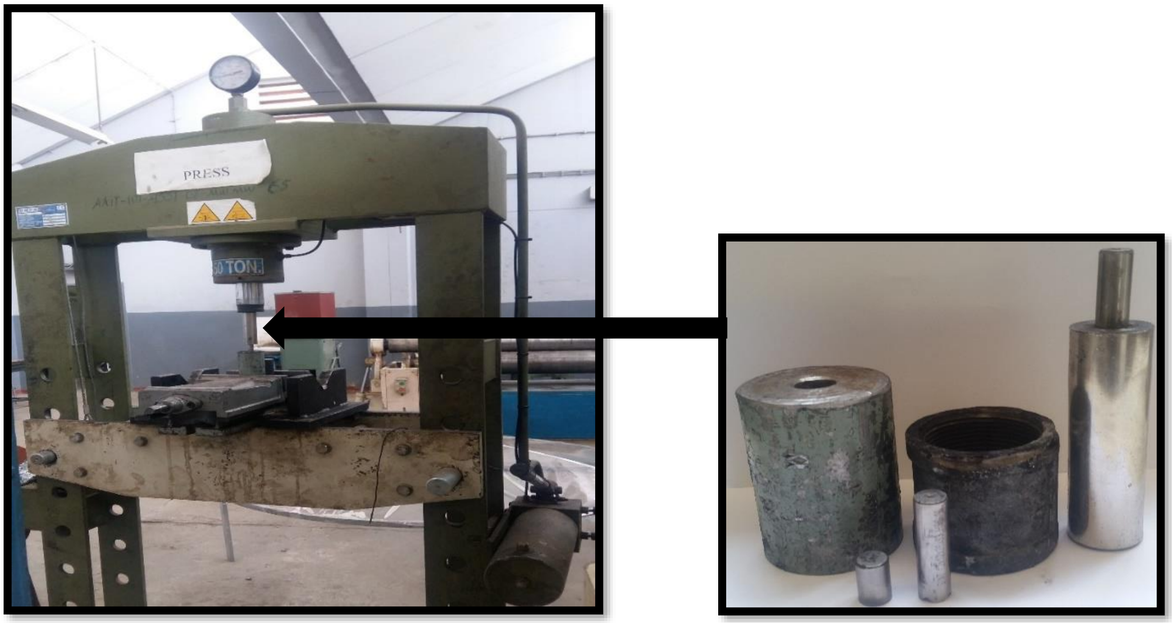


Figure 3. 2: Mechanical press and mold for laboratory scale pellet production

3.3. Experimental design and Statical analysis

3.3.1. Material

The statistical software package used for this study was Design-Expert version 7.0.0 (Stat –Ease, Inc.)

3.3.2. Method

The response surface method was applied to evaluate the effect of pelletization parameters and optimize conditions after studying the influence single and interaction effect. Box-Behnken experimental design with three numerical factors on three levels was used. This design consisted of twelve randomized runs with five replicates at the central point to minimize the error.

The level of particle size was chosen based on the particle size range used by (Piboon et al., 2017). According to them, they used a particle size range of 0.1-0.6mm (100µm-600µm) to study the densification of corncobs using algae as a binder. (Harun & Afzal, 2016; Serrano et al., 2011) also confirmd the the use of pellet made from lower particle size allow for higher density and mechanical resistance of pellets. Therefore, in this study a particle size range between 100 µm - 500 µm was used.

The level of mixing ratio was chosen based on preliminary study. The calorific value of both torrefied coffee husk and cotton stalk was determined and resulted as 22.49 MJ/kg and 19.85MJ/kg repectively. When this result was compaired with the calorific value at the mixing ratio of 0.33 and 0.67, the calorific value at mixing ratio of 0.33 (20.09 MJ/kg) is close to the calorific value of torrefied cotton stalk and the calorific value at mixing ratio of 0.67 (22.428 MJ/kg) is close to the calorific value of coffee husk. Therefore, there is no need for further investigation to go for mixing ratio below 0.33 and beyond 0.67.

Moreover, the level of torrefication temprature is chosen based on litrature. A torrefaction temperature range of 200℃-300℃ was recommended by many researchers like Tumuluru et al., (2011b), Wu & Lin, (2012), Darr & Potter, (2010) and many more.

Table 3. 1: Experimental factors and levels

Abbreviation	Independent Variables	Unit	Levels		
			-1 (Low)	0 (Medium)	+1 (High)
A	Particle size	µm	112.5	243.75	375
			100-125	125-250	250-500
B	Mixing ratio	g/g	0.33	0.5	0.67
C	Torrefaction temperature	℃	200	250	300

The experiments required to perform are evaluated according:

$N=2k(K-1)+C_p$……………………………………………………………………Equation 3.2

Where; N= number of experiments required to be performed

K=number of engine parameters and

C_p =number of central points

A second order polynomial equation was used to find the relationship between the independent variables and the response. For three chosen factors the equation can be written as:

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

………………………………………………………………………………………Equation 3.3

Where β_0 is a constant, A, B, and C are independent variables, β_is are the coefficients for liner interaction effect, $\beta_{ii}s$ are the coefficients for cross-products interaction effect, $\beta_{ij}s$ are the coefficients for quadratic interaction effects and ε is the random error. The regression analysis and estimation of these coefficients were performed by a statistical software package Design-Expert version 7.0.0 (Stat –Ease, Inc.). The adequacy of the model equations was evaluated using analysis of variance (ANOVA). Quality of fit of the model equations and their statistical significance were expressed using F-test, coefficient of determination(R^2), prediction coefficients of determination (Pred R^2), adjusted coefficients of determination (adj-R^2), and coefficients of variation (CV).

3.4. Physiochemical and thermal characteristics of optimum torrefied mixed pellet

3.4.1. Proximate analysis

3.4.1.1. Material

The major equipment that were used was jaw crusher, grinder, centrifuge mill, sieve, electrostatic balance, platinum crucible, ceramic crucibles, drying oven, muffle furnace (0-1200℃) and desiccators

3.4.1.2. Method

The proximate analysis of optimum torrefied mixed pellet was measured according to American society for testing and materials standard (ASTM E871-82, 2014) for moisture content, (ASTM, 2011) for volatile matter, (ASTM, 2007) for ash content and the fixed carbon was computed by subtracting the sum of the percentage of ash content, volatile matter and moisture content from 100. Detail procedure can be seen in appendix a.

3.4.2. Elemental Analysis (CHNS)

3.4.2.1. Material

The major equipment used was Flash EA 1112 CHNS elemental analyzer.

3.4.2.2. Method

This is a standard method that was used to determine the amount carbon, hydrogen, nitrogen, and sulfur before and after thermal treatment of optimum torrefied mixed pellet by using Flash EA 1112 CHNS elemental analyzer. The samples were fed into the analyzer along with carrier gas (helium) flow rate of 120 ml/min, reference flow rate 100 ml/min, and excess supply of oxygen at a flow rate 250 ml/min. The reaction of oxygen with other elements (namely carbon, hydrogen, nitrogen, and sulfur) present in the sample produces carbon dioxide, water, nitrogen dioxide, and sulfur dioxide respectively. The combustion products were separated by a chromatographic column and are detected by the thermal conductivity detector (T C D), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent compositions of elements in the sample. From these results, the oxygen composition was determined by subtracting the sum of Carbon, Hydrogen, Nitrogen, and Sulphur compositions from 100.

3.4.3. Calorific value determination

3.4.3.1. Material

The major equipment used was XRY-1A oxygen Bomb calorimetry.

3.4.3.2. Method

According to the ASTM D 3286 standard, the heating values of optimum torrefied mixed pellet sample was determined using bomb calorimeter (XRY-1A oxygen Bomb calorimetry). 0.5 gram of dried and milled sample was taken in a clean crucible. The crucible was placed in the bomb by letting the nickel wire to be immersed in the fuel sample. Then it was filled with oxygen at 25 atmospheric pressure and placed in the calorimeter, which was filled by a known mass of water. With a continues stirring, the initial temperature was recorded. The sample was then ignited and heat was liberated. Uniform string was continued and the maximum temperature attained was recorded. The calorific value was then determined using the following formula:

$$\text{Calorific value} = \frac{\frac{\left(\left(T_f - T_i\right)*14470\right)-40}{m}}{4.185} \text{……………………….Equation 3.1}$$

Where; m=mass of the sample, 0.5g

T_f=final temperature

T_i= initial temperature

3.4.4. Ash composition of optimum torrefied mixed pellet

3.4.4.1. Material

All chemicals that were used in the study was reagent grade and 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.

The major equipment that were used was Erlenmeyer flask, condenser, Volumetric flask, funnel, porcelain dish, spatula, pipette, burette, beaker, hot plate/Bunsen burner, electrostatic balance, metallic crucibles, drying oven, stove, plastic cup, muffle furnace (0-1200℃) and desiccators

3.4.4.2. Method

Ash Chemistry of optimum torrefied mixed pellet was performed in order to determine the percentage of different oxides such as SiO_2, Fe_2O_3, Al_2O_3, CaO and MgO. Determination of oxide was done by measuring 0.5g of the sample which was dried at 105℃ and ashed at 650 ℃ for 30min. 6g of NaOH pellet was then added in the ash and placed in the muffle furnace at 650℃ for 20min. The crucible was cooled and the melted solution was placed into 300ml of the beaker and boiled with 100ml of water. The beaker was then removed from the stove and 25ml of concentrated HCl was added. While stirring, the crucible was washed with 1:5 HCl and added to solution till the crucible is free. 1 ml of nitric acid was then added in the solution. Determination of each oxide was done based on (ASTM, 2002) as shown in appendix E.

3.4.5. Thermogravimetric analysis (TGA)

3.4.5.1. Material

The major equipment used was thermogravimetric analyzer (TA instrument, model: SDT Q600).

3.4.5.2. Method

A thermogravimetric analyzer (TA instrument, model: SDT Q600) was used to determine the thermal behavior before and after thermal treatment of optimum torrefied mixed pellet using temperature programming from atmospheric temperature to 1000^oC at the heating rate of

20^{o}C/min. Testing was carried out under inert atmosphere (N_2) with a flow rate of 100ml/min to remove all corrosive gases and avoid thermoxidative degradation. The thermal degradation temperature with corresponding weight loss was recorded and analyzed.

3.4.6. Fourier Transmission Infrared Spectroscopy analysis (FT-IR)

3.4.6.1. Material

The major equipment that were used was FTIR Spectrometer (Spectrum 65 FT-IR, PerkinElmer).

3.4.6.2. Method

FTIR analysis was carried out in order to identify the functional groups as a result of torrefaction. Optimum torrefied mixed pellet was subjected to this analysis using FTIR Spectrometer (Spectrum 65 FT-IR, PerkinElmer) at wave number range of 4000-400 cm-1. First, the sample was mixed with KBr particles to make it suitable for infrared analysis. The mixture was then pressed to a small thickness, slightly below 1 mm, required for FTIR analysis.

3.4.7. Bulk density

3.4.7.1. Material

The major equipment that were used was electrostatic balance and Verner caliper.

3.4.7.2. Method

The bulk density of optimum torrefied mixed pellet was measured by approximating the volume of the pellet to a cylindrical shape. Detail procedure is shown in appendix D.

4. RESULTS AND DISCUSSION

4.1. Physiochemical and thermal Characterization of cotton stalk and coffee husk

4.1.1. Proximate analysis

Proximate analysis in terms of moisture content, ash content, volatile matter and fixed carbon is determined and results are presented in Table 4.1, where an average of three replications of each sample.

A. Moisture content

The moisture content of fresh cotton stalk and coffee husk were 11.23% and 13.67% respectively. As it can be seen in Table 4.1, through sun drying the moisture content was reduced to 8.33% and 9.323% respectively. A similar result was reported by (Powar et al., 2014) and (Taylor et al., 2010) for the moisture content of cotton stalk (8.3%) and coffee husk (10 %) respectively. The comparative higher moisture content of both biomasses with respect to coal indicated that they have to dry so that they could easily bun off and used as a source of heat.

B. Ash content

Ash content of biomass is the non-combustible residue left after biomass is burnt. The ash content and its composition influence the design and operation of biomass delivery systems. It is a function of both the intrinsic properties of the biomass and the collection and handling systems (Akdeniz et al., 2004). As indicated in Table 4.1, the ash content of raw cotton stalk and coffee husk are 5.63 and 3.91 respectively. A similar observation was obtained by Yin (2001) and Mhilu (2014) for the ash content of raw cotton stalk and coffee husk to be 5.1% and 2.5% respectively.

C. Volatile content

The volatile content of a fuel is the condensable and non-condensable vapor released when the fuel is heated. As can be seen in Table 4.1, there is more volatiles in cotton stalk than coffee husk in which their respective values are 78.44 and 77.79. In contrast, Yin, (2011) reported a higher value of volatile to contain coffee husk than cotton stalk in which their value is 78.5% and 76% respectively. This can be justified by the environmental conditions in which these biomasses are grown. In general, the amount of biomass in fuel is higher compared to coal. This high content of volatiles leads to a fast vaporization of most of the biomass. The gases formed burn in homogenous gas phase reactions. The remaining charcoal burns relatively slowly in heterogeneous combustion reactions. This is why the volatiles has a strong impact on the thermal degradation and combustion behavior of the biomass.

D. Fixed carbon

Fixed carbon is a solid combustible residue that remains after a biomass particle is heated and the volatile matter is expelled. It is determined by subtracting the percentage of moisture, volatile matter, and ash from the sample. As indicated in Table 4.1, the fixed carbon of cotton stalk and coffee husk is 15.933% and 18.301% respectively.

4.1.2. Elemental analysis

Elemental analysis has been applied to present the composition of carbon, hydrogen, and oxygen in a sample. The level of these elements gives extensive information on the storability, energy content and the overall quality of the biomass. Their presence in the initial feedstock also affects the air required for combustion (Stephen Gent et al., 2017). The elemental analysis of the raw cotton stalk and coffee husk in Table 4.1 shows the content of carbon is low while the content of hydrogen and oxygen is high.

4.1.3. Calorific value

The term calorific value is used to refer to the energy contained in the fuel, determined by measuring the heat produced by the complete combustion of a specified quantity of it. The calorific value of biomass is an influential quality that ascribes for energy generation applications (Poudel et al., 2017). As presented in Table 4.1, the calorific value of cotton stalk and coffee husk is 16.57 and 18.26MJ/kg.

4.1.4. Ash composition

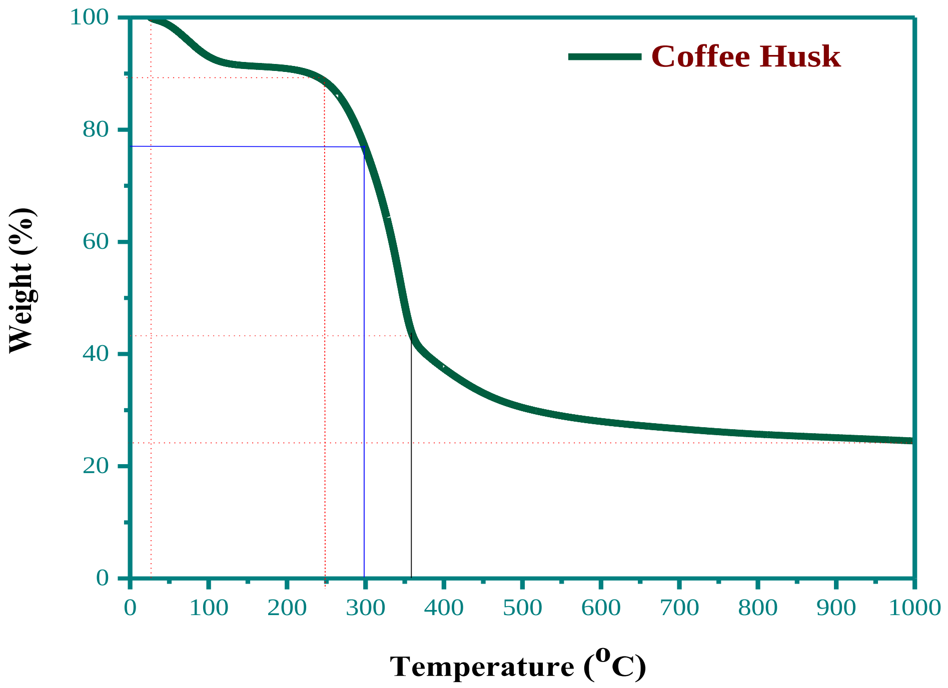
As summarized in Table 4.1, the ash composition of cotton stalk and coffee husk are given in terms of percentage of calcium oxide (27.51% and 20.12%), magnesium oxide (10.47% and 7.99%), iron oxide (6.74% and 1.06%), aluminum oxide (7.89% and 30.23%) and silicon oxide (22.47%, and 16.27%) respectively.

Table 4. 1: Composition and heating value of cotton stalk and coffee husk

Parameter	Cotton stalk	Coffee husk
Proximate analysis		
Moisture content (%)	8.33	9.323
Ash content (%)	5.63	3.91
Volatile Matter (%)	78.437	77.789
Fixed Carbon (%)	15.933	18.301
Elemental analysis		
Carbon (%)	44.418	47.382
Hydrogen (%)	5.787	6.566
Nitrogen (%)	-[a]	-[a]
Sulphur (%)	-[a]	-[a]
Oxygen (%)	49.795	46.052
H/C	0.1303	0.1386
O/C	1.121	0.9719
Elemental composition of ash (%)		
CaO	27.51	20.12
MgO	10.47	7.99
Fe_2O_3	6.74	1.06
Al_2O_3	7.89	30.23
SiO_2	22.47	16.29
Heating value MJ/kg		
Raw	16.57	18.26
Torrefied at 300℃	19.85	22.49

4.1.5. Thermogravimetric analysis

Figure 4.1. shows thermogravimetric analysis (TGA) of cotton stalk and coffee husk under an inert atmosphere at a heating rate of $10℃/min$. The results obtained from the thermal decomposition process indicate that both cotton stalk and coffee husk exhibit usual shape for lignocellulostic matereial.



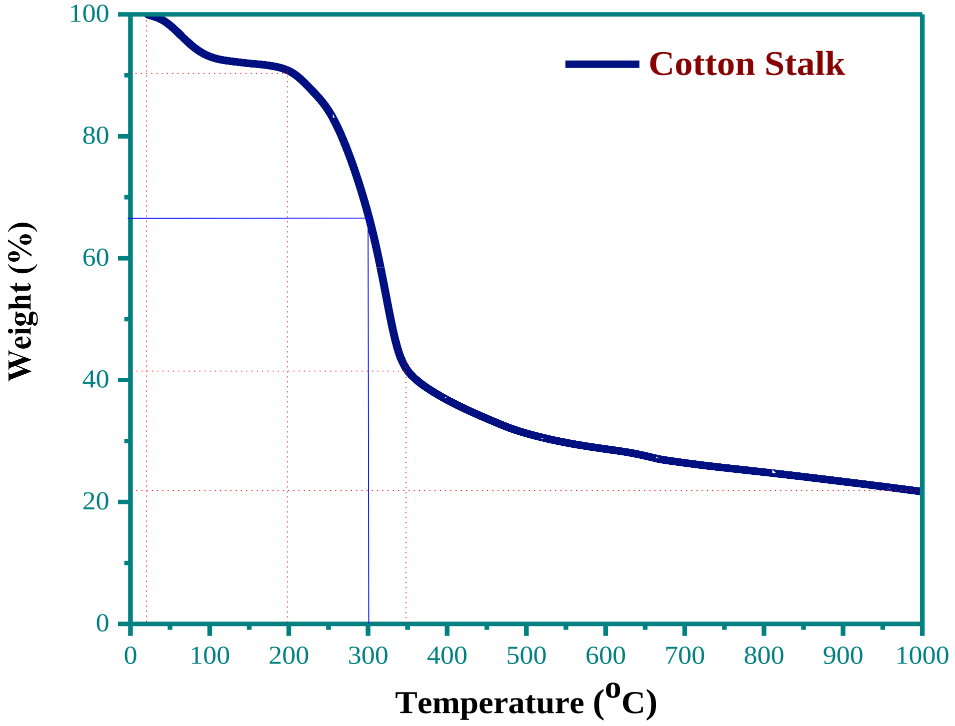


Figure 4. 1: TGA analysis of raw Cotton stalk and coffee husk

4.2. Experimental design and statistical analysis

As defined by Douglas C. Montogomory, (2001), Response surface methodology (RSM), is a collection of mathematical and statistical techniques useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. In this study, the response surface method was applied to evaluate the effect of pelletization parameters and optimize conditions after studying the influence of single and interaction effect. Box-Behnken experimental design with three numerical factors, i.e. particle size (100-125µm, 125-250µm, and 250-500µm), the Mixing ratio (0.33, 0.5 and 0.67) and torrefaction temperature (200℃, 250℃ and 300℃) with corresponding levels that affect the response variable (calorific value) was used. As indicated in Table 4.5, the design consisted twelve randomized runs with five replicates at the central point to minimize the error.

4.2.1. Analysis of variance (ANOVA)

The analysis of variance (ANOVA) (Table 4.2) showed that the model was extremely significant ($P<0.0001$). The model F-value was 112.79, which implies the model is significant. There was only a 0.01% chance that a “Model F-value” this large could occur due to noise. In the ANOVA table, Values of “Prob>F” less than 0.05 indicated model terms were significant while Value greater than 0.1 indicated the model terms were not significant. Accordingly, the model terms A, B, C, AB, AC, B^2 and C^2 were significant. Where A stands for particle size, B for mixing ratio and C for torrefaction temperature.

The lack of fit test measures the failure of the model to represent the data in the experimental domain at points which are not included in the regression (Miafo et al., 2015). As shown in Table 4.2, the F value and P value of lack of fit test were 1.06 and 0.459, respectively, which implies it was not significant and indicate that the model equation was adequate for predicting the calorific value of torrefied mixed pellet. There was a 45.9% chance that a “Lack of fit F-value” this large could occur due to noise.

Table 4. 2: Analysis of variance (ANOVA) of the response surface model for calorific value

Source	Sum of square	Df	Mean squire	F-value	P-value Prob>F	
Model	2.300E+006	9	2.556E+005	112.79	< 0.0001	Significant
A-Particle size	59783.63	1	59783.63	26.39	0.0013	
B-Mixing ratio	6.266E+005	1	6.266E+005	276.56	<0.0001	
C-Torrefaction temprature	1.219E+006	1	1.219E+006	538.01	<0.0001	
AB	15795.46	1	15795.46	6.97	0.0334	
AC	14569.70	1	14569.70	6.43	0.0389	
BC	3391.90	1	3391.90	1.5	0.2607	
A^2	732.48	1	732.48	0.32	0.5874	
B^2	3.099E+005	1	3.099E+005	136.78	< 0.0001	
C^2	34366.90	1	34366.90	15.17	0.0059	
Residual	15860.72	7	2265.82			
Lack of fit	7023.48	3	2341.16	1.06	0.4590	Not significant
Pure Error	8837.24	4	2209.31			
Cor total	2.316E+006	16				

4.2.2. Model fit summary

The model fit summary is given in Table 4.3 indicates that the quadratic model was suggested by design expert.

Table 4. 3: Sequantial model fitting for caloric value

Source	Sum of squares	df	Mean square	F-value	p-value prob> F	Remark
Mean Vs Total	3.915E+008	1	3.915E+008			
Linear vs mean	1.905E+006	3	6.352E+005	20.12	< 0.0001	
2FI vs Linear	33757.06	3	11252.35	0.30	0.8256	
Quadratic vs 2FI	3.608E+005	3	1.203E+005	53.08	< 0.0001	Suggested
Cubic vs quadratic	7023.48	3	2341.16	1.06	0.4590	Aliased
Residual	8837.24	4	2209.31			
Total	3.938E+008	17	2.316E+007			

From the lack of fit test, it is clear that the second-order quadratic model subjected by design expert was suitable because the lack of fit was insignificant (prob>F is 0.6799). The insignificant lack of fit is desirable for the model to fit the experimental data properly. The coefficient of determination (R^2) shows in Table 4.3 for a regression model of calorific was 99.32% which implies that the model accounted for 99.32% variability in the data.

Table 4. 4: Model summary statistical

Source	**Std. dev.**	**CV**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**Press**	**Remark**
Linear vs mean	177.69		0.8228	0.7819	0.6975	7.006E+005	
2FI vs Linear	194.08		0.8373	0.7398	0.4489	1.276E+006	
Quadratic vs 2FI	47.60	0.99	0.9932	0.9843	0.9455	1.262E+005	Suggested
Cubic vs quadratic	47.00		0.9962	0.9847			Aliased

Furthermore, the "pred R-squared" of 0.94550 is in reasonable agreement with the "Adj R-squired " of 0.9843. "adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 36.717 indicates an adequate signal. This model can be used to navigate the design space. The model predicted value are given in Table 4.4 as follows in comparison with the actual experiment values. For a good model, the values of R squared and adjusted R-squared should be close to each other and they should be close to 1. In this case, the predicted R-squared and adjusted Required values are close to each other and they are close to 1.

4.2.3. Regression model equation

The model equation that correlates the response (calorific value) to the pelletization process variables in terms of actual value after excluding the insignificant model terms is given in equation

$$Calorific\ value = +319.730 - (3.542 * Particle\ size) + (4411.121 * Mixing\ ratio) + (22.470 * Torrefaction\ temprature) + (1.915 * particle\ size * mixing\ ratio) + (9.197E - 0.03 * particle\ size * torrefaction\ temprature) - (4340.833 * maxing\ ratio^2) - (0.036\ torrefaction\ temprature^2) \ldots\ldots \text{Equation 4.1}$$

Table 4. 5: The 17 experimental runs which are arranged according to BBD

Standard Order	A[1]	B[2]	C[3]	Actual Value	Predicted Value
1	112.50 (-1)	0.33 (-1)	250.00 (0)	4567.68	4559.94125
2	375.00 (+1)	0.33 (-1)	250.00 (0)	4280.32	4261.36875
3	112.50 (-1)	0.67 (+1)	250.00 (0)	4975.06	4994.01125
4	375.00 (+1)	0.67 (+1)	250.00 (0)	4939.06	4946.79875
5	112.50 (-1)	0.50 (0)	200.00 (-1)	4607.68	4627.9275
6	375.00 (+1)	0.50 (0)	200.00 (-1)	4302.87	4334.33
7	112.50(-1)	0.50 (0)	300.00 (+1)	5319.4	5287.94
8	375.00 (+1)	0.50 (0)	300.00 (+1)	5256	5235.7525
9	243.75 (0)	0.33 (-1)	200.00 (-1)	3984.77	3972.26125
10	243.75 (0)	0.67 (+1)	200.00 (-1)	4512.97	4473.77125
11	243.75 (0)	0.33 (-1)	300.00 (+1)	4655.54	4694.73875
12	243.75 (0)	0.67 (+1)	300.00 (+1)	5300.22	5312.72875
13	243.75 (0)	0.5 (0)	250.00 (0)	5001.3	4975.0216
14	243.75 (0)	0.5 (0)	250.00 (0)	4925.23	4975.0216
15	243.75 (0)	0.5 (0)	250.00 (0)	5042.79	4975.0216
16	243.75 (0)	0.5 (0)	250.00 (0)	4945.978	4975.0216
17	243.75 (0)	0.5 (0)	250.00 (0)	4959.81	4975.0216

[1] Partcle size [2] Mixing ratio [3] Torrrefaction temperature

4.2.4. Diagnostic Plots

The adequacy of the model was checked by constructing different diagnostic plots are shown in Figure 4.2, in order to find whether the derived model would give sufficient approximation value to the actual values. The normal % probability plot of residuals for response was normally distributed, as lie reasonably close to the straight line and shows no deviation of the variance (Figure 4.2.A). Internally studentized residuals plot was constructed to facilitate the satisfactory fit of the developed model and the plot. Figure 4.2 B shows that all the data points lie within the limits (±3). The predicted values obtained from the developed model were quite close to the experimental values and lie reasonably close to the straight line and indicate the adequate agreement with real data (Figure 4.2 C). The results suggest that the model used in the study is able to predict the optimum conditions for the production of higher calorific value torrefied pellet.

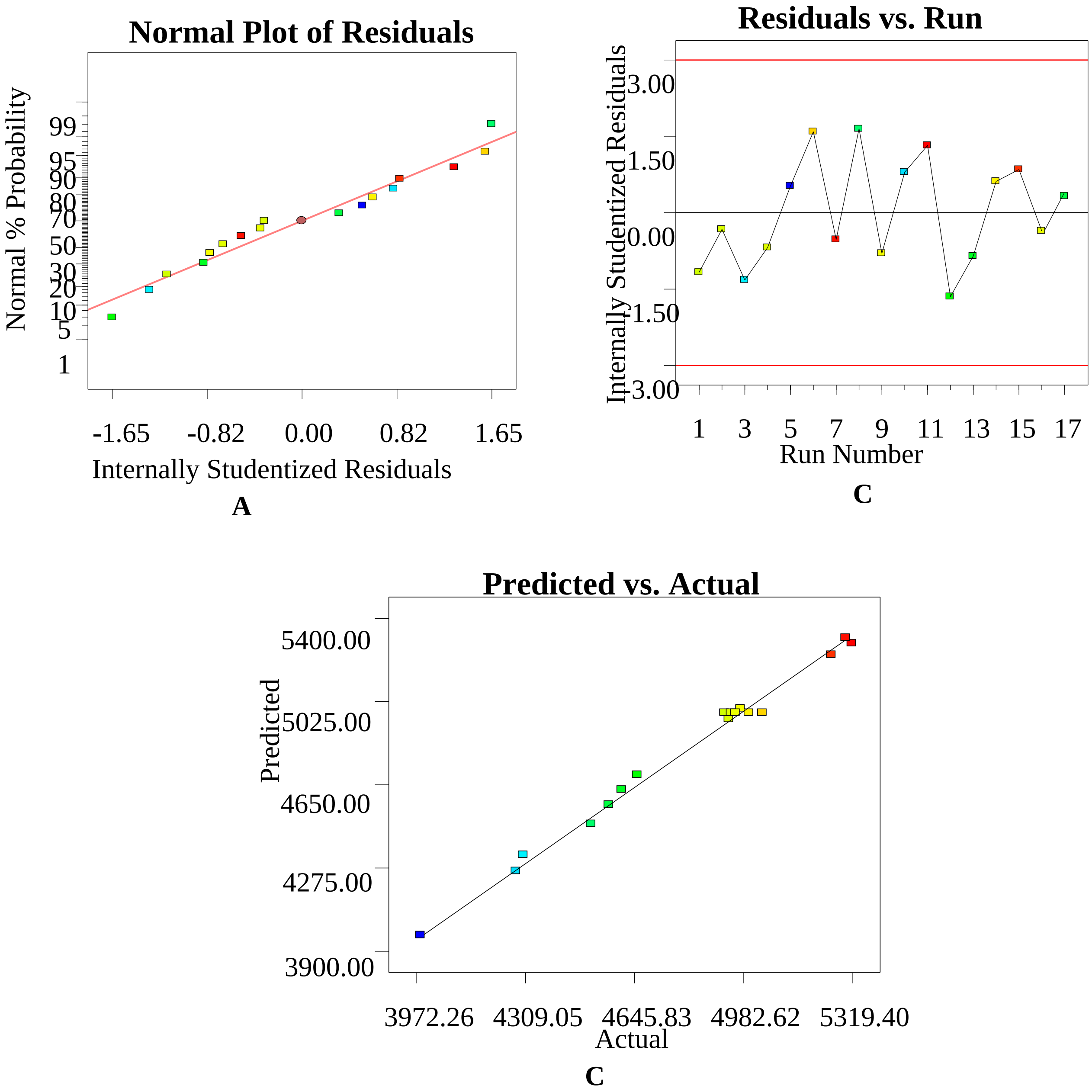


Figure 4. 2: Diagnostic plots for adequacy of the proposed model

4.2.5. Effect of process variable on calorific value

In this study, three factors at three levels of BBD were applied, to investigate the influence of the process variables such as particle size, mixing ratio, and torrefaction temperature. The effect of main process variables was depicted as shown in Figure 4.3. The interaction between the independent variable and the dependent variable was also plotted in the form of three dimensional (3D) response surface and contour plots (Figure 4.4). 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.

A. The main effect of the process variable

- **Effect of particle size on calorific value**

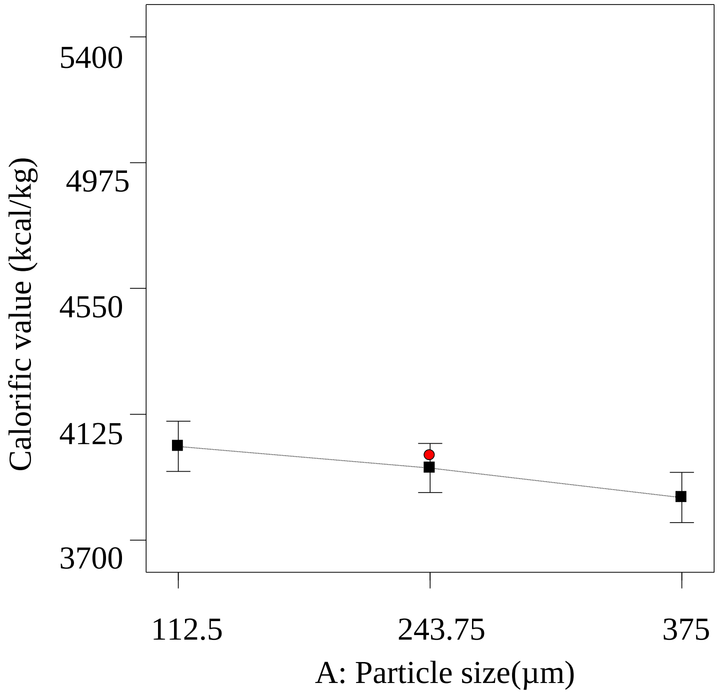
The effect of particle size, mixing ratio and torrefaction temperature on calorific value was illustrated in Figure 4.3. To determine the effect particle size on calorific value, mixing ratio and torrefaction temprature were fixed at 0.33 and 200℃ respectively. Upon such condition, It was observed that as a particle size increased from 112.5µm (µm) to 375 µm (µm), the calorific value of the pellet was decreased. This is may be due to the fact that the amount of heat required depends on the size, shape and biomass properties. These parameters affect the rate of both convective and conductive heat transfer from the reactor to the biomass and within the biomass, respectively. A small piece of biomass will have more surface area per unit mass and vice-versa. Therefore, smaller particle size has a better heat transfer rate and results in the removal of moisture and some of the volatiles.

- **Effect of mixing ratio on calorific value**

The effect of mixing ration on calorifc value was determibed by fixing the particle size and torrefaction temprature at 112.5µm and 200℃ respectively. As depicted in Figure 4.3 (b), until the mixing value reached a ratio of 0.5 the calorific value was increased considerably. This is may be due to the higher calorific value of torrefied coffee husk than the torrefied cotton stalk. Therefore as the proportion of torrefied coffee husk in the mix increases the calorific value of the pellet also increases. However, there is a very small increase in calorific value between 0.5 to 0.67. This may be due to, beyond 0.5 ratios, the proportion of torrefied cotton stalk was decreased and the calorific value of coffee husk was dominated the overall calorific value of the pellet.

Effect of torrefaction temperature on calorific value

The effect of torrefation temperature on calorific value was determined by fixing the effect of particle size and mixing ration at 112.5 µm and 0.33% respectively. As shown in Figure 4.3 (c), when the temperature was increased from 200℃ to 300℃ the calorific value was significantly increased. A similar result was observed by Bevan et al., (2015) while they were studying torrefaction of pelletized oil palm empty fruit bunches. Based on their observation the heating value of EFB briquettes increased from 17.57 MJ/kg to 26.24 MJ/kg after torrefication from 250℃ to 300℃. This is primarily because of the increase in carbon, fixed carbon content as well as the decrease in oxygen content as it can be similarly observed in Table 4.6. Therefore, we can infer that the increase in torrefaction temperature significantly improved the heating value by 34.6% with respect to raw cotton stalk and by 22.15% with respect to the raw coffee husk.



a

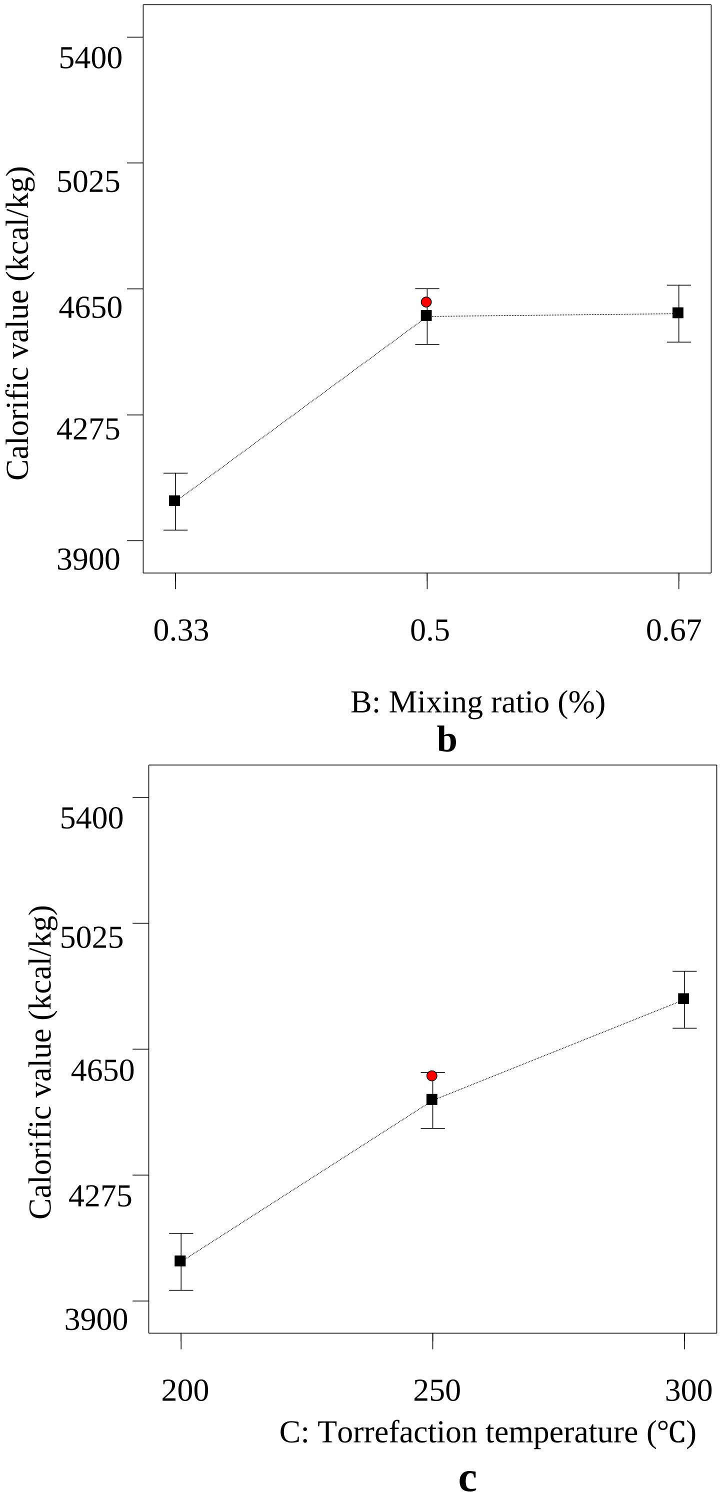
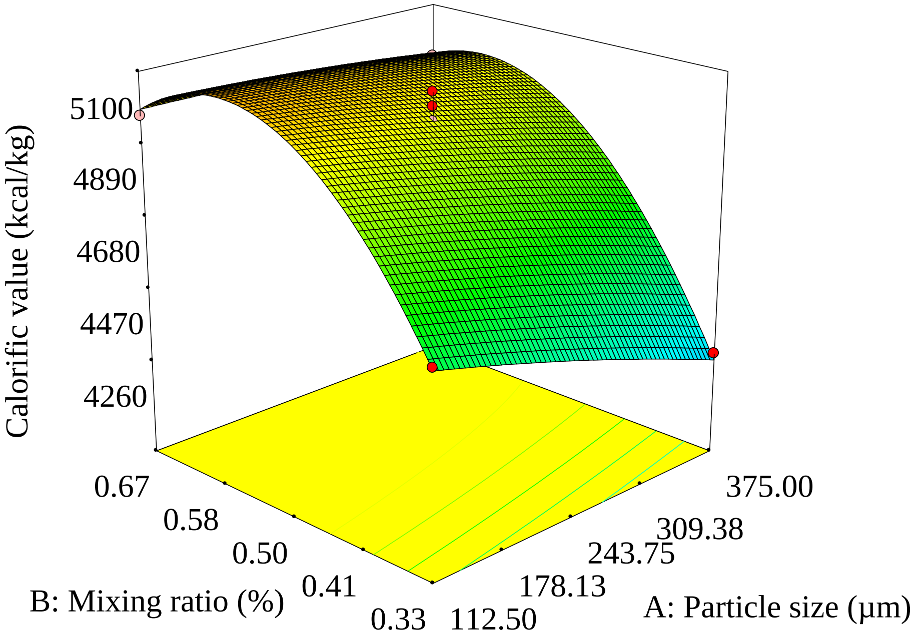


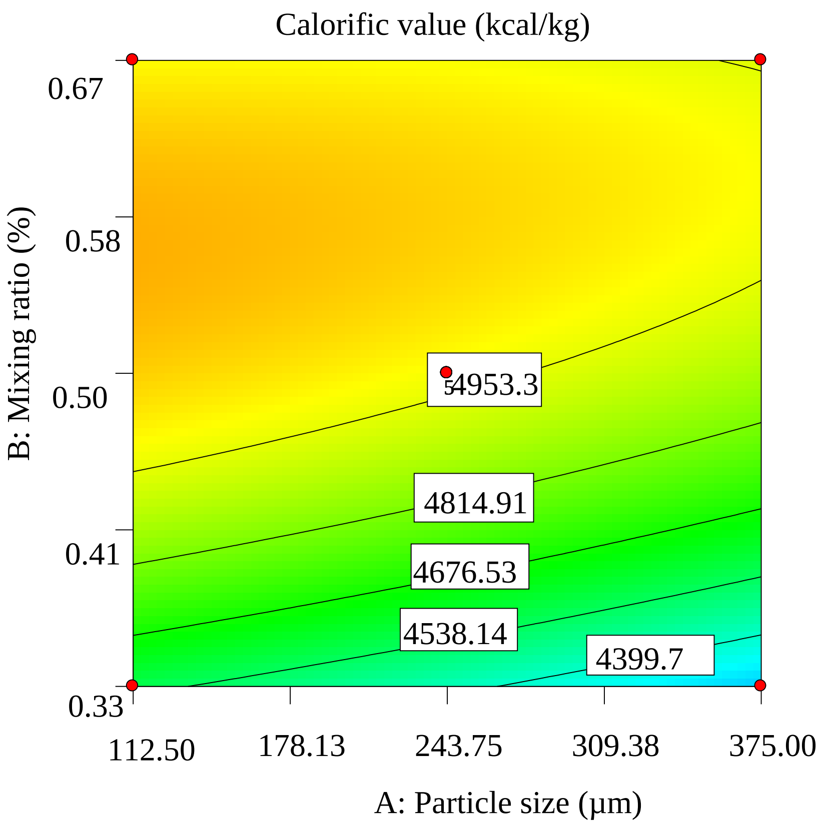
Figure 4. 3: One-factor plot for the main effects (a) Effect of particle size on calorific value (b) Effect of mixing ratio on calorific value (c) Effect of temperature on calorific value

B. The interaction effect of the process variable

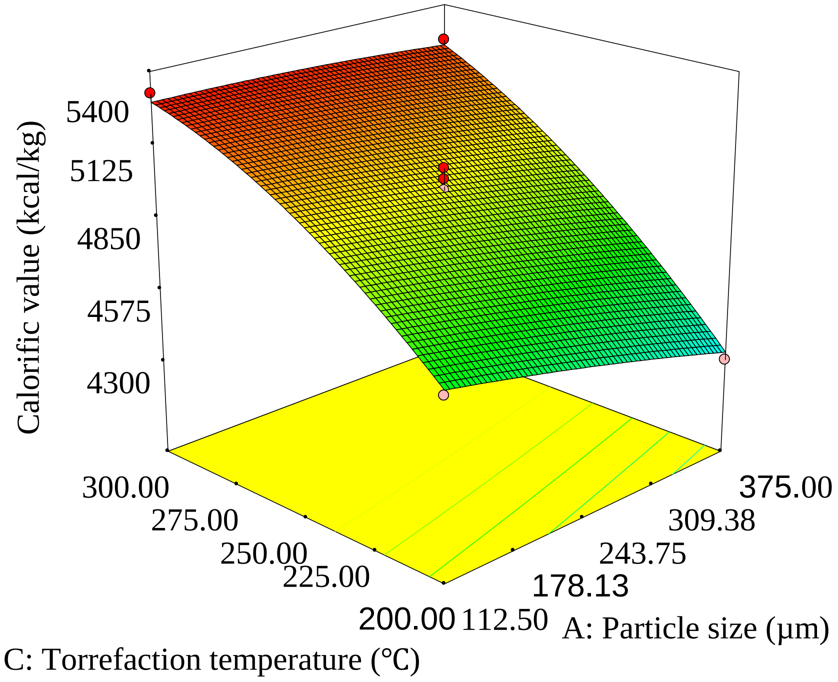
The result of ANOVA revealed that process variables interaction could affect the calorific value at a significant level. Particularly, particle size with mixing ratio and particle size with temperature interactions were the process interaction variables that affect the process significantly. The interaction between the independent variable and the dependent variable was plotted in the form of three dimensional (3D) response surface and contour plots (Figure 4.4). 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 4.4 (1 a & b), The increase in calorific value was observed at lower particle size 112.5µm (100-125 µm) and 0.63 of mixing ratio. However, the decrease in calorific value was observed at higher particle size 375 µm (250-500 µm) and the lower mixing ratio (0.33). In Figure 4.4 (2 a & b), The increase in calorific value was observed at lower particle size 112.5µm (100-125 µm) and at higher temperature 300℃. However, the decreased in calorific value was observed at particle size 375 µm (250-500 µm) and lower temperature. This may be due to, at a higher temperature, smaller particle size has a better heat transfer rate and results in the removal of more moisture and some of the volatiles than larger particle size.



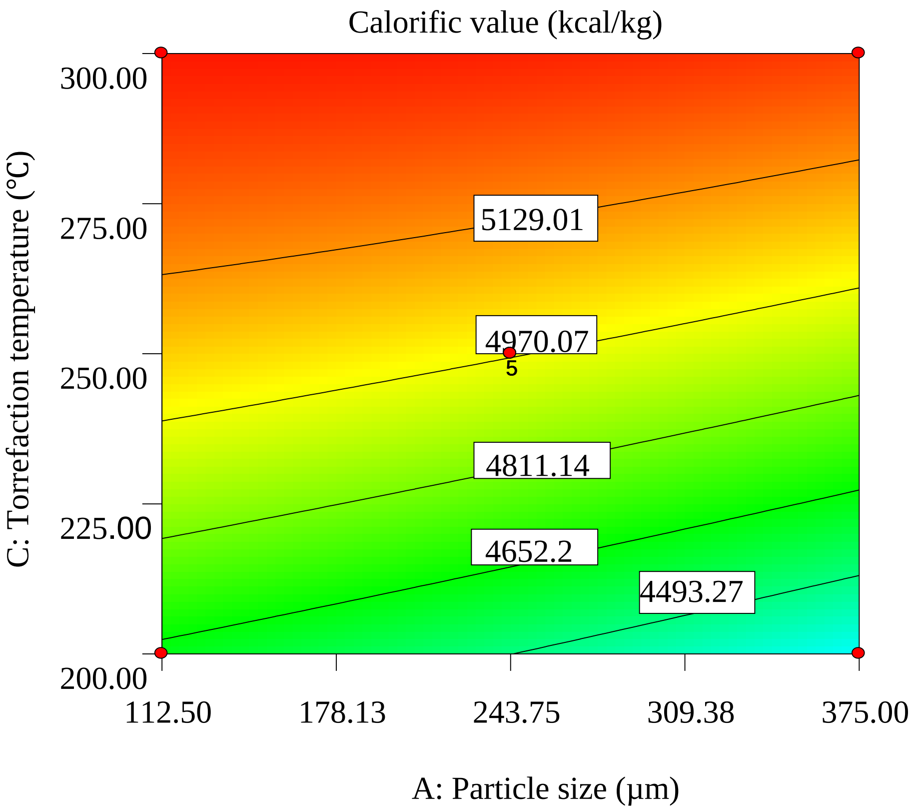
1a (@ 250 torrefaction temperature)



1b (@ 250 torrefaction temperature)



2a (@ mixing ratio of 0.5%)



2b (@ mixing ratio of 0.5%)

Figure 4. 4: Response surface plots (a) Effect of mixing ratio and particle size on calorific value (b) Effect of torrefaction temperature and particle size on calorific value

4.2.6. Optimization of the process parameters and validation

According to the Box–Behnken design, combined with the numerical optimization technique, the optimal condition to obtain maximal calorific value was calculated by Derringer's desired function methodology. Therefore, the particle size was set to minimum, the mixing ratio was set within the studied range and the temperature was set to maximum value. The optimum values of the influencing factors for maximum calorific value under these circumstances are particle size between 100-125μm, 0.63 mixing ratio and 300℃ torrefaction temprature which gives 5320.72 kcal/kg. Based on the optimal values, a desirability ramp was developed using numerical optimization techniques (Figure 4.5). The experiments were performed at optimal values in triplicates, and the results were compared with the predicted values from the model equation. The average value of three replicate of calorific value under the optimum condition was obtained 5322.31 kcal/kg. The good correlation between the predicted values and the experimental values indicates that the derived Box–Behnken combined desirability method could be effectively applied to optimize the heating value of torrefied pellet.

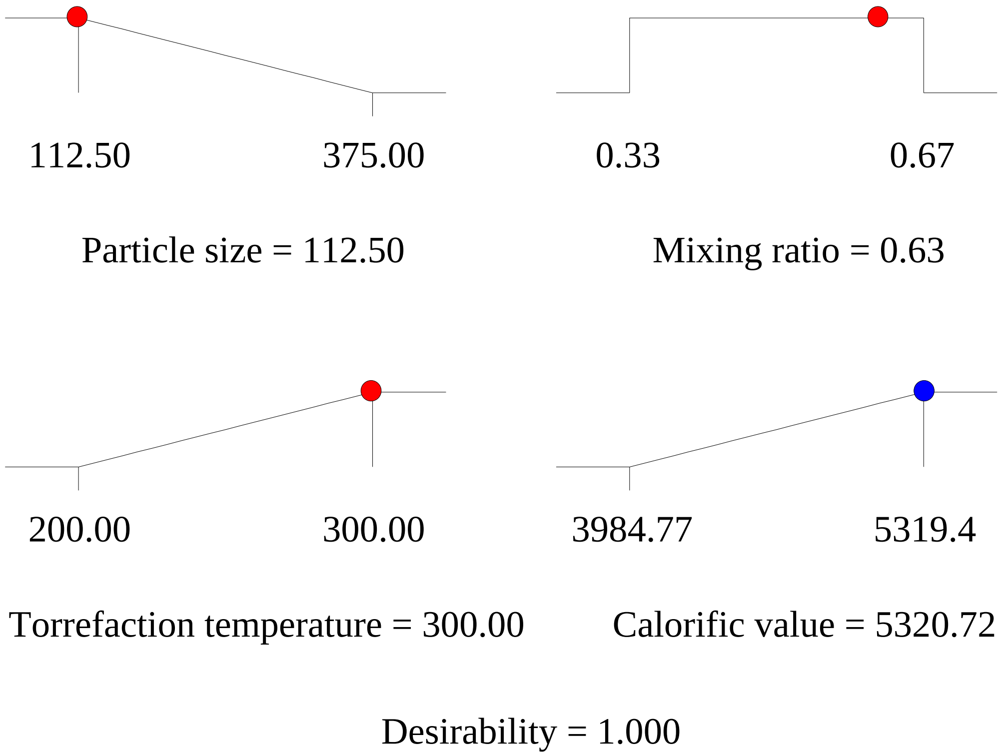


Figure 4. 5: Desirability ramp for numerical optimization for four selected goals.

4.3. Characterization of optimum torrefied mixed pellet

4.3.1. Proximate analysis

Proximate analysis in terms of moisture content, ash content, volatile matter and fixed carbon was determined for mixed pellet and results were presented in Table 4.7, where an average of three replications of each sample.

A. Moisture content

The moisture content of optimum torrefied mixed pellet was decreased to 1.669% as a result of thermal treatment at 300℃ for one hour. This finding is similar to the review of Tumuluru et al. (2011), which suggests the reduction of moisture content to 1-3% depending on the torrefaction condition. The reduction in moisture content implies the higher thermal efficiency during thermal combustion of the torrefied pellet. It also prevents decomposition and moisture absorption during storage and transportation. According to Miranda et al., (2015) explanation, Lower moisture contents allow higher flame temperatures (with a better temperature gradient and heat transfer, and enabling the completion of combustion), and shorter residence times in the combustion chamber. When the result of the moisture content of optimum torrefied mixed pellet is compared with commercial coal stated in Table 4.6, it is within an acceptable limit.

B. Ash content

The fraction of ash, the inert and non-combustible material, contained in the optimum torrefied mixed pellet increased to 12.41%, because none of it is driven away during torrefaction (Nhuchhen et al. 2014). Upon thermal treatment at 290ºC, an increment in ash content of bamboo from 1.03-2.00% to about 3.5-4.5% was reported by Wu & Lin, (2012). Bridgeman & Jones, (2008) also reported an increment in ash content while they were studying about torrefaction of reed canary grass, wheat straw, and willow to enhance solid fuel qualities and combustion properties.

As shown in Table 4.6, the ash content of optimum torrefied mixed pellet is lower than the South African coal which is 13%. As a result, there is an overall reduction in fly ash production with associated particulate reduction when some optimum torrefied mixed pellets replace coal in cement industry.

C. Volatile content

The Torrefaction drives away the volatile matter from both biomasses due to the decomposition and the de-volatilization reactions. As indicated in Table 4.7, the volatile content of optimum torrefied mixed pellet reduced to 50.45%. As a result, the burnout rate of biomass decreases because of the low volatile content in the torrefied biomass. Compared to that of the raw biomass the burning of the torrefied biomass takes longer time for the above reason. This effect is more prominent in the torrefied biomass at higher temperatures because of the higher volatile reduction potential. The burn out time is, however, shorter than that of coal, which has a volatile content of

23-24%, because of its more porous structure and remaining volatile matter (Nhuchhen et al., 2014)

D. Fixed carbon

During torrefaction, some amount of fixed carbon drives way from both cotton stalk and coffee husk due to decomposition reaction. Although the absolute amount of fixed carbon decreases after torrefaction, the fraction of fixed carbon in the optimum torrefied mixed pellet was increased to 35.47%. Bridgeman & Jones (2008), in their study on torrefaction of reed canary grass, wheat straw, and willow, made a similar observation, where increase in temperature from 503K (230^{o}C) to 563K (290^{o}C) the fixed carbon was increased from 12.1%, 17.3% and 10.7% to 21.3%, 38%, and 20.5% respectively.

4.3.2. Elemental analysis

The elemental analysis of torrefied mixed pellet in Table 4.7 shows the content of carbon increased as a result of torrefaction while the content of hydrogen and oxygen were decreased. Bridgeman & Jones (2008), in their study on torrefaction of reed canary grass, wheat straw, and willow, made a similar observation, where the effect of torrefaction on elemental analysis of each biomass between the temperature of from 503K (230^{o}C) to 563K (290^{o}C) was investigated. In their study, they showed that the carbon content is increased while the hydrogen and oxygen content is decreased.

As the result of a change in chemical composition, the atomic ratio of O/C and H/C of the torrefied mixed pellet is low in comparison to raw cotton stalk and coffee husk. This is due to the release of volatile-rich in hydrogen and oxygen, such as water, carbon mono oxide, and carbon dioxide during torrefaction. This change in chemical composition of biomass will improve its quality as an energy source through an increase in energy density since more oxygen than carbon is lost in form of volatiles (Darr & Potter, 2010). This study complies with the research carried out by Poudel et al., (2017).

There is no nitrogen and Sulphur detected in torrefied mixed pellet, 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 4. 6: Specification and terms for grade a South Africa thermal coal

Parameters	Accepted	Rejected
Calorific value	6000-6200 kCal/kg	5850 kCal/kg
Volatile matter	24-23%	24%
Ash content	13%	15%
Total moisture	<6%	9%
Total Sulphur	<0.76%	1%

Source: http://southafricancoal.blogspot.com/

4.3.3. Calorific value

As presented in Table 4.7, the calorific value of torrefied pellet is higher than that of cotton stalk and coffee husk. This is because, during torrefaction, biomass loses relatively more oxygen and hydrogen, which increases the calorific value of the product to 22.277MJ/kg.

Wu & Lin, (2012), also observed a similar result while they were studying the property of torrefied biomass from six major Bamboos in Taiwan. The results of the heating value of torrefied bamboo, torrefied under 290 °C, were increased 6%, 16%, 11%, 13%, and 8% for Makino bamboo, Ma bamboo, Green bamboo, Thorny bamboo, Long-shoot bamboo, respectively. Poudel et al., (2017) also confirm that HHV increases with increase in torrefaction temperature in their report.

4.3.4. Ash composition

As summarized in Table 4.7, the ash composition of mixed torrefied pellet was founded in terms of percentage of calcium oxide (30.26%), magnesium oxide (3.64%), iron oxide (5.02%), aluminum oxide (33.9%) and silicon oxide (20.247%) respectively. When this result is compared with the ash composition of South Africa coal reported by Odunayo et al., (2016), the mixed torrefied pellet ash would have a higher amount of calcium oxide, magnesium oxide, aluminum oxide and lower amount of silicate oxide while the iron oxide content is almost similar.

Table 4. 7: Composition and heating value of mixed pellet and South Africa coal

Parameter	Optimum torrefied mixed pellet	South Africa Coal (Odunayo et al., 2016)
	Proximate analysis	
Moisture content (%)	1.67	0.78
Ash content (%)	12.41	9.44
Volatile Matter (%)	50.45	5.58
Fixed Carbon (%)	37.14	
	Elemental analysis	
Carbon (%)	68.1195	45.8
Hydrogen (%)	3.0005	3.5
Nitrogen (%)	-[a]	1.16
Sulphur (%)	-[a]	-[b]
Oxygen (%)	28.8816	40.10
H/C	0.044	0.076
O/C	0.4239	0.8755
	Elemental composition of ash (%)	
CaO	30.26	5.62
MgO	3.64	1.41
Fe_2O_3	5.02	5.07
Al_2O_3	33.9	23.8
SiO_2	20.247	52.3
Heating value (MJ/kg)	22.277	20.526

4.3.5. Thermogravimetric analysis

Figure 4.6 shows thermogravimetric analysis (TGA) of torrefied pellet under an inert atmosphere at a heating rate of $10℃/min$. The results obtained from the thermal decomposition process indicate that the torified mixed pellet sample differed from raw biomass in its thermogravimetric profile. This is because of the fact that at higher tempreture of torrefaction much of hemicellulose and some of the cellulose would decompose and the portion of the lignin in the overall mass increases. As a result, the biomass would exhibit similar property with that of lignin. This result is similar with the TGA graph shape of lignin reported by Basu, (2013).

In order to understand the decomposition reaction of the samples, it is important to look for the composition of the biomass. As is well known, biomass is mainly composed of hemicelluloses, cellulose, and lignin which decompose at a temperature range of 200-300℃, 240-250℃, and 280-500℃ respectively (Carrier et al., 2011; Tumuluru et al., 2011). These components in the biomass perform unique functions within the plant structure and interact differently depending on thermal treatment time and temperature. Therefore, exposure of biomass to elevated temperature results in thermal degradation of its structure, which often is accompanied by loss of mass.

Figure 4.l and 4.6 reveals that the first weight loss occurs between 23-105℃, 22-105℃, and 22-105℃ respectively. This weight loss is associated with loss of moisture and biomass shrinkage. This also results in reduced porosity in biomass, though the biomass may still have the ability to retain its structure if rewetted. This region is known as the nonreactive drying zone, where most of the chemical constitutes of biomass remain intact (Tumuluru et al., 2011). Above 105℃, a slight weight loss due to the loss of light volatiles occurs. For the case of the cotton stalk and coffee husk, a huge mass loss is observed between a temperature of 250-350℃ due to decomposition reaction of hemicellulose and cellulose. However, for the case of torrefied pellet, there is a small change in weight due to each of the hemicellulose and cellulose content was removed during the process of torrefaction. At the end of this decomposition step, a continuous slight depolarization is observed. This is attributed to the slow degradation of thermally stable structures and char formation.

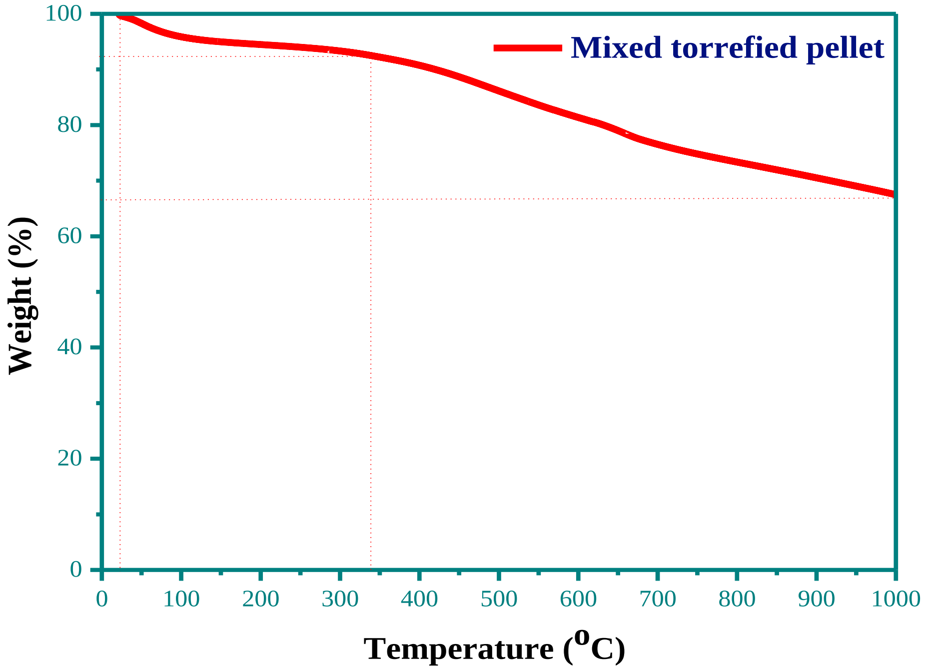


Figure 4. 6: TGA analysis of optimum torrefied mixed pellet

4.3.6. Fourier Transmission Infrared Spectroscopy analysis (FT-IR)

Fourier transform infrared spectroscopy was used to investigate changes in the chemical structure of mixed torrefied pellet at the optimum condition with respect to raw coffee husk and cotton stalk. This change is largely due to reduced oxygen-containing functional groups as a result of thermal decomposition of organic groups (especially hemicellulose).

The broadband in the OH stretching vibration region at about 3460-3412cm^{-1} is due to intra and intermolecular hydrogen bonds and bands characteristics of crystalline cellulose. This hydroxyl group, which can form ions and attract water molecules, is responsible for the hydrophilic behavior of biomass. As shown in Figure 4.7, the intensity of this band is decreased as the result of thermal treatment at 300°C. This indicates that torrefaction reduces the hydroxyl groups and decreases the hydrophilic nature of biomass. The removal of the hydroxyl group also decreases the capability of forming hydrogen bonds that in turn reduces the moisture-absorbing capacity of biomass. This effect leads to the transformation of polar molecules to non-polar unsaturated molecules and produces a hydrophobic product (Nhuchhen et al., 2014)

As studied by Chen 2015, The C=O peak (1738-1709 and 1675-1655) is due to the carboxyl group in cellulose and hemicellulose. At higher torrefaction temperature, the transmittance of the C=O peak was increased due to the de-carbonization reaction, breakage of glycosidic and cyclic C=O bonds. Subsequently, less oxygenated compounds (such as acid, alcohols, aldehydes, and ethers) and non-condensable gas like CO_2 and CO were produced. During torrefaction, oxygen-containing compounds were gradually broken down and eliminated, this results in simplification of organic content in torrefied mixed pellet and lower the oxygen content. This result is consistency with the result of the ultimate analysis.

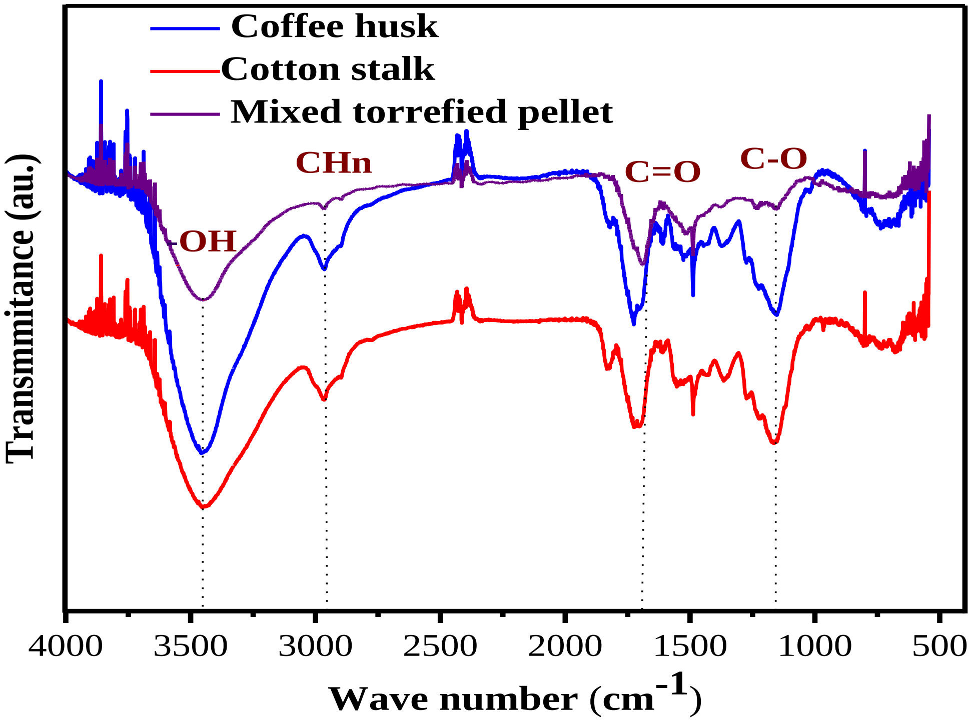
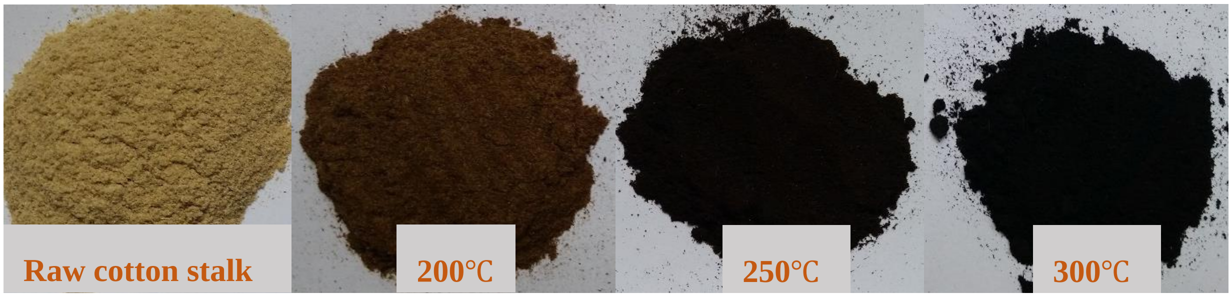


Figure 4. 7: FT-IR analysis of raw Cotton stalk, coffee husk, and mixed torrefied pellet

4.3.7. The appearance of torrefaction products

As can be observed from Figure 4.8 a and b, with an increase in torrefaction temperature from 200℃ to 300℃, the color of both cotton stalk and coffee husk turned from brownish to dark. This color change in the torrefied biomass samples is a good indicator of the chemical changes that occur within the cell structure during torrefaction. An increase in reaction temperature causes chemical changes within the biomass and a subsequent color change between untreated and torrefied biomass. At low temperatures and residence times, biomass becomes slightly darker due to drying. Under severe conditions, biomass turns nearly black due to intense devolatization and an increase in carbon content. Although color change is biomass specific, it can be a quick indicator of the degree of torrefaction (Bevan et al., 2015; Stephen et al., 2017).

Similarly, Mamvura et al., (2018) observed a color change in marula seed sample before and after torrefaction. A similar trend was also reported by Bevan et al., (2015).



a) Cotton stalk

b) Coffee husk

Figure 4. 8: Color change during torrefaction process at a different temperature a) cotton stalk b) coffee husk

4.3.8. Strength

As shown in Figure 4.9, the strength of the torrefied pellet is lower than the raw biomass (cotton stalk and coffee husk pellet). As the torrefaction temperature increases from 200 ℃ to 300℃ the pellet exhibit many defects. Similarly, Shang et al. (2012) noted that the strength of pellets from Scot Pine torrefied at 250 °C was significantly reduced, and the pellets are brittle, uneven, and non-uniform in the physical appearance. Stelte et al. (2011) also reported the negative impact of torrefaction on pelletization process and pellet properties as torrefaction results higher friction in the press chanal and low compression strength of the pellet. This is because of the reduction in hydrogen bonding site as the result of thermal degradation of hemicellulose and lignin during torreffecation (Stelte et al., 2011).

Furthermore, the amount of hydrogen binding site reduces with torrefication temperature and the torrefied pellet contains less moisture. This may reduce the inter-diffusion of the wood-polymer between the adjacent particle and thus the formation of solid bridges between them. The resulting pellets are brittle and less stable than the pellet made by raw biomass. Meanwhile, the intermediate product formed from decomposition reaction of hemicellulose, cellulose, and lignin, including sugar, acid, and charcoal, were released and coated on the surface of biomass, resulting in decrease plasticity. The decrease of particle plasticity increased the energy consumption in the extrusion process.

As explained by Stelte et al., (2011), it is probably that Van der Waals forces and fiber interlocking remain as the major forces keeping a pellet together. Since these forces are weak compared to covalent bonds and hydrogen bonds this could be an explanation for the reduced pelletization property of torrefied mixed pellet.

The instrument used for pelletization in this study could be another cause for the lower pelletizing property at higher torrefaction temperature. The press used by Rudolfsson et al.,(2015) was equipped with thermocouples to preheat the die until the temperature set point. In their study, they used a temperature range of 125℃-180℃ as a pelletization temperature and spruce was pressed until 300MPa. Stelte et al., (2011) also used a die preheated at a temperature of 100℃ and pressed both spruce and torrefied spruce particles until 200MPa was reached.

As explained by Stephen et al., (2017), the pelletization quality increases with an increase in lignin content. This enhancement is illuminated by the increased lignin active sites opened during torrefaction due to the breakdown of the hemicellulose matrix and formation of fatty unsaturated structures, making lignin an excellent natural binding agent. In order for the lignin to act as a binding agent, it must be softened by heating to 50-150°C (Stephen et al., 2017). As used by Rudolfsson et al.,(2015) and Stelte et al., (2011) the preheating of the die prior to pelletization resulted in a better pelletization property.

Futhermore, Tumuluru et al., (2010) stated that the application of high compression pressures during biomass densification can result in crushing the biomass particles, thus opening up the cell structure and exposing the protein and pectin that act as natural binders. If the pelletization was made by preheating the dye at softening temperature of lignin and at higher pelletization pressure, a better fuel with enhanced pellet property would be obtained.

However, the goal of pelletization is to produce durable pellet that can be stored outdoors and can withstand rain. This means, at the moment, there are no clear guidelines for required pellet strength, but most probably this will be similar to that for wood pellets. Though, if pellet strength is too pronounced in the pelletizing then this may influence downstream processes, e.g. increased energy consumption when milled to a powder prior to co-firing (Rudolfsson et al., 2015).

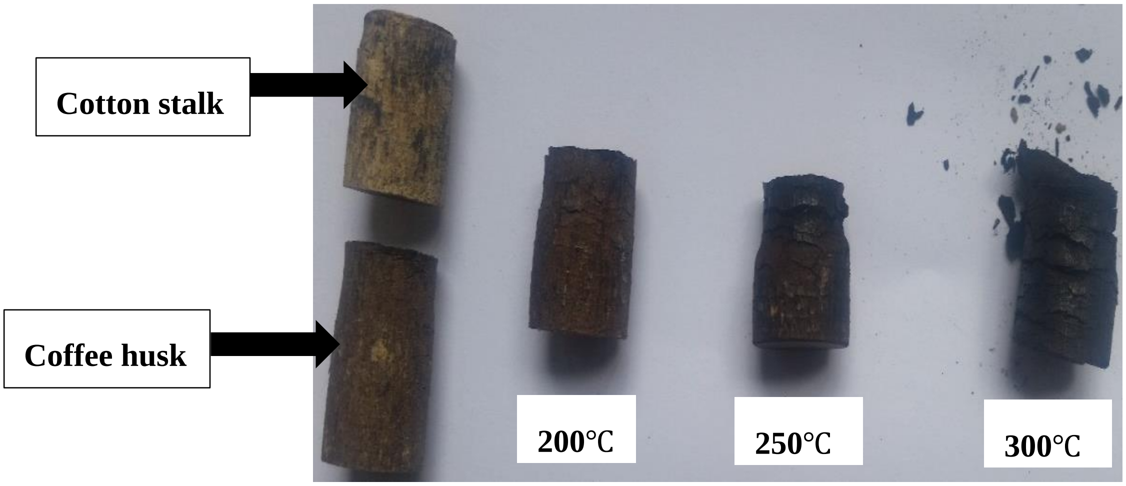


Figure 4. 9: Raw cotton stalk, coffee husk and Mixed torrefied pellet at a different temperature

4.3.9. Bulk density

The other property regarding pellet characteristic is bulk density. The bulk density of powdered coffee husk, powdered cotton stalk and mixed torrefied pellet obtained was 331.125 Kg/m^3, 581.125 Kg/m^3 and 782.7Kg/m^3 respectively. Therefore, the bulk density of the mixed torrefied pellet is significantly improved from that of powdered coffee husk and cotton stalk. The result of bulk density obtained for mixed torrefied pellet lies between the rage of the bulk density of torrefied pellet reported by Nunes et al.(2014).

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this research, mixed torrefied pellets were investigated as a source of alternative energy source and optimized using the BBD, RSM. Process parameters that affect the calorific value such as particle size (100-125μm, 125-250 μm and, 250-500 μm), mixing ratio (0.33, 0.5 and 0.67) and torrefaction temperature (200℃, 250℃ and 300℃) were optimized. The optimal conditions were (particle size=100-125μm, mixing ratio=0.63 and torrefaction temperature of 300℃), with a maximum calorific value of 5327.62kcal/kg.

Torrefaction of both biomasses at 300℃ change chemical compositions associated with extensive devolatilization and carbonization resulting in the formation of water, CO and CO_2 and influence the hydrogen, oxygen and carbon content of the biomass. As the result, the mixed torrefied pellet showed a decrease in moisture content (1.67%), volatile content (50.45%), H/C (0.044) and O/C (0.4239) while the fixed carbon (37.14), elemental carbon and calorific value (22.304 MJ/Kg) increased considerably. As shown in the FT-IR analysis, loss of - OH groups result in decrease hydrogen-bonding capacity and the mixed torrefied pellet is a more hydrophobic solid. The TGA analysis showed that the lignin content in the higher torrefaction temperature is higher which is responsible for the higher heating value of mixed torrefied pellet. The pellet from the mixed torrefied pellet needs more caring, as it is easily breakable. For a better pelletization property preheating the pelletizer die is required.

Considering the result obtained in this study, the proposed mixed torrefied pellet has a potential to be used as a source of alternative energy for cement industries.

5.2. Recommendation

Considering the very promising results obtained in this thesis, the following recommendations are suggested for future works.

- The economic feasibility of this research should be investigated
- The structural composition of lignin, cellulose, hemicellulose before and after torrefaction should be further investigated
- More advanced physiochemical characterization technique such as SEM, TEM, XRD analysis and compression test of the pellet should be undertaken.
- Pellet press with preheating die should be designed with appropriate compression pressure.
- The fouling and slugging behavior of mixed coal and biomass pellet ash should be studied in the future.

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APPENDICES

Appendix A: Proximate analysis

A. Moisture content

The moisture content of cotton stalk, coffee husk, and the mixed pellet was measured according to standard (ASTM E871-82, 2014). One gram of sun-dried powder was dripped out with a spoon or spatula from the sample bottle and measured (to the nearest ±0.1mg). Then the weighted sample was put in the crucibles and dried in the oven at 105±5 ^{o}C for 24 hrs. After 24 hours, the sample was withdrawn, cooled and weighted to the nearest ±0.1mg. The percentage of moisture content was determined by using the following equation.

$$\text{Moisture in the analysis sample} = \frac{\mathrm{W_i} - \mathrm{W_f}}{\mathrm{W_i} - \mathrm{W_c}} * 100$$

Where; W_c = container weight, g,

Wi= initial weight, g, and

W_f = final weight, g

B. Volatile matter

The percentage of volatile matter was determined by using ASTM standard method (ASTM, 2011). The volatile matter was determined by establishing the loss in weight resulting from heating the solid fuel under rigidly controlled condition. The measured weight loss, correlated for moisture as determined in test method E 871 establishes the volatile matter content. The volatile matter of each agricultural residue was determined by using the following equation.

First, the weight loss percentage was obtained by:

$$weight\ loss, \% = 100 * \frac{W_i - W_f}{W_i - W_c}$$

Where; W_c = container weight, g,

Wi= initial weight, g, and

W_f = final weight, g

Then the volatile matter percent in the samples was obtained by:

$$Volatile\ matter\ in\ the\ analysis\ sample, \% = A - B$$

Where: A= weight loss %, and

B= moisture, %, as determined using Method E 871

C. Ash content

This test method covers the determination of inorganic residue of the solid fuel. According to the standard method (ASTM, 2007), one gram of dried sample was weighted to the nearest 0.1mg and was burned at 600℃.

$$Ash, \% = \left(\frac{W_1}{W_2}\right) * 100$$

Where: W_1= weight of ash, and

The W_2= weight of oven- dry sample

D. Fixed carbon

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

$$\%FC = 100 - (\%AC - \%VM + \%MC)$$

Where; FC= Fixed carbon

AC= Ash content

VM= Volatile matter

MC= Moisture content

Proximate analysis

Parameter (%)	Run 1	Run 2	Run 3	Average
		Coffee husk		
Moisture content	9.42	9.42	9.13	9.323
Volatile matter	76.597	78.53	78.24	77.789
Ash content	3.87	3.95	3.91	3.91
Fixed carbon	18.94	17.52	17.85	18.301
		Cotton stalk		
Moisture content	8.62	8.06	8.31	8.33
Volatile matter	79.02	78.33	77.96	78.437
Ash content	5.56	5.69	5.64	5.63
Fixed carbon	15.42	15.98	16.4	15.933
		Mixed torrefied pellet		
Moisture content	1.65	1.67	1.69	1.67
Volatile matter	12.2	12.9	12.13	12.41
Ash content	49.63	52.51	49.21	50.45
Fixed carbon	38.17	34.59	38.66	37.14

Appendix B: Ultimate analysis

Parameter (%)	Run 1	Run 2	Average
	Coffee husk		
Carbon	47.654	47.110	47.382
Hydrogen	6.226	6.906	6.566
Nitrogen	-	-	-
Sulfur	-	-	-
Oxygen	46.12	45.984	46.052
	Cotton stalk		
Carbon	44.747	44.089	44.418
Hydrogen	5.668	5.906	5.787
Nitrogen	-	-	-
Sulfur	-	-	-
Oxygen	49.585	50.005	49.795
	Mixed torrefied pellet		
Carbon	67.903	68.333	68.118
Hydrogen	2.943	3.058	3.0005
Nitrogen	-	-	-
Sulfur	-	-	-
Oxygen	29.154	28.609	28.8815

Appendix C: Determination of calorific value

No	Mass	Initial temperature (℃)	Final temperature (℃)	Change in temperature (℃)	Calorific value (Kcal/kg)
17	0.5	24.183	24.846294	0.663294	4567.68
10	0.5	24.711	25.332739	0.621739	4280.32
9	0.5	25.213	25.935205	0.722205	4975.06
2	0.5	25.633	26.349999	0.716999	4939.06
13	0.5	24.097	24.766078	0.669078	4607.68
3	0.5	24.257	24.882000	0.625000	4302.87
11	0.5	24.765	25.537000	0.772000	5319.40
15	0.5	25.261	26.023832	0.762832	5256.00
5	0.5	25.146	25.725000	0.579000	3984.77
8	0.5	25.642	26.297383	0.655383	4512.97
12	0.5	26.320	26.996000	0.676000	4655.54
7	0.5	26.033	26.802227	0.769227	5300.22
14	0.5	26.531	27.257000	0.726000	5001.30
1	0.5	26.760	27.474999	0.714999	4925.23
6	0.5	27.155	27.887000	0.732000	5042.79
4	0.5	26.426	27.144000	0.718000	4945.98
16	0.5	26.94	27.66000	0.720000	4959.81

$$\text{Calorific value} = \frac{\frac{\left(\left(T_f - T_i\right) * 14470\right) - 40}{0.5}}{4.185}$$

Where; m=mass of the sample

ΔT= temperature change between final and initial temperature

Example: Run 17

$$\text{Calorific value} = \frac{\frac{\left((24.846294 - 24.183) * 14470\right) - 40}{0.5}}{4.185} = 4567.68\ \text{Kcal/kg}$$

Appendix D: Determination of bulk density

A. Bulk density for powdered coffee husk and cotton stalk

An empty container (4mL) was weighed using a digital balance to the nearest 0.0001g. The container was filled with the sample and the material will be slightly compacted to ensure the absence of large void spaces. The container and the sample were then weighed. Three replicates were carried out. The wet bulk density of the sample was then calculated from the following equation (Zhang et al, 2012):

$$\rho_b = \frac{(W_2 - W_1)}{V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \mathit{Equation}\ 3.2$$

Where: $\rho_{b=}$ The bulk density of the sample (g/ml)

W_2= The weight of the container and sample (g)

W_1= The weight of the container (g)

V= The volume of the container (ml)

- **For cotton stalk:**
  - ✓ Mass 1=36.581g
  - ✓ Mass 2=37.9055g
  - ✓ Volume= 4ml

$$\rho = \frac{M_2 - M_1}{V} = \frac{37.9055g - 36.581g}{4ml} = \frac{1.3245g}{4ml} = 331.125\,{}^{kg}/_{M^3}$$

- **For coffee husk:**
  - ✓ Mass 1=36.581g
  - ✓ Mass 2=38.9055g
  - ✓ Volume= 4ml

$$\rho = \frac{M_2 - M_1}{V} = \frac{38.9055g - 36.581g}{4ml} = \frac{2.3245g}{4ml} = 581.125\,{}^{kg}/_{M^3}$$

A. Bulk density for mixed torrefied pellet

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

$V = \pi r^2 h$, $\rho = \frac{M}{V}$ Where: V= volume of the pellet

R= radius of the pellet

- **For mixed torrefied pellet:**
  - ✓ The diameter of the pellet=14mm
  - ✓ The height of the pellet= 18mm
  - ✓ Mass of the pellet= 0.7827g

$$V = \pi r^2 h$$

$$V = 3.14 * 7^2 * 18 = 2{,}769.48mm^3 = 2.76948ml$$

$$\rho = \frac{M}{V} = \frac{2.1678}{2.76948} = \frac{0.7827g}{ml} = 782.7\, {}^{kg}/_{M^3}$$

Appendix E: Determination of oxide

ASTM procedure for each oxide are stated as below:

A. Determination of Fe_2O_3 in the solution

25 ml of solution was diluted up to 150ml with distilled water in 300 ml beaker. drops of NH_3OH (1 gm/l) was added to the solution and pH adjusted to 2 and heated. Then, endpoint determination was obtained by adding 10 drops of Sulfosalicylic acid indicators. The reddish color of the solution changed in to colorless when it was titrated with EDTA.

The formula which was used to determine Fe_2O_3

$$\%Fe_2O_3 = \frac{T_{Fe_2O_3} * V_{EDTA}}{M}$$

Where: M= Mass of ash

V_{EDTA}= Volume of EDTA added

T_{Fe2O3} = 0.7840

B. Determination of SiO_2 in the solution

50 ml of the above-mentioned solution was measured in to 250ml plastic cup.15 ml of concentrated HNO_3 was added and the solution was cooled in cold water bath for 15 min. After this,10ml of KF (150 g/l) was added to maximize the SiO_2 content and 3 spatulas solid KCl, was added until it gets saturated then Wait for the solution to be dissolved for 15 min. The solution was then filtered using filter paper and the paper was rinsed 3 times by KCl (150g/l) (10,10,5 ml) in to previous plastic beaker and 10 ml of ($KCl+CH_3CH_2OH$) and 8 drops of phenolphthalein were added to the solution Until pink color appear titrates by NaOH (0.15 g/l) then, hot water was added up to mark of 200 ml and also 3 drops of 0.1 g /NaOH ,1 drop of phenolphthalein were added to the solution and further titrated by NaOH (0.15 g/l) until colorless was changed in to light pink in to yellow when it was titrated by EDTA (0.015 mol/l).

After all these experimental procedures were done, determine of SiO_2 was obtained by

$$\%SiO_2 = \frac{V_{NaOH} * T_{SiO_2} * 0.5}{M}$$

Where: M=mass of the ash

V=Volume of the NaOH solution

T_{SiO_2}= 2.04

C. Determination of Al_2O_3 in the solution

After the Fe_2O_3 was finished 15 ml EDTA was added to the solution and pH was adjusted to 4.3 and heated. While stirring, 10 drops of PAN indicator was added to the solution which was titrated by $CuSO_4$ (0.015 mol/l). Finally, endpoint determination was obtained when the yellow color of the solution changed in to violet.

The formula which was used to determine Al_2O_3

$$\%\mathrm{Al_2O_3} = \frac{\frac{20}{15}\left(\mathrm{K} * \mathrm{V_{CuSO_4}}\right) * \mathrm{T_{Al_2O_3}}}{\mathrm{M}}$$

Where; K= Excess EDTA + Consumption of $CuSO_4$

$T_{Al_2O_3}$=0.7355

M= Mass of ash

D. Determination of CaO in the solution

A Filtrate of 25ml was pipetted into a 300ml beaker. After 10ml of KF (20g/l) was added to the solution and kept for 5 min, the solution was diluted up to 200ml. In order to deactivate Fe_2O_3 and Al_2O_3, 5ml of TEA (triethanolamine) and 5 drops of CMP indicator was added. Then 20ml of KOH (200g/1) was added to the solution in order to adjust the pH of the solution to 10.2. Lastly, the green color of the solution was changed into a red color when it was titrated by EDTA. The formula which was used to determine CaO was;

$$\%CaO = \frac{V_{EDTA} * T_{Cao}}{M}$$

Where; M= Mass of ash

$V_{EDTA=}$ Volume of EDTA added

T_{Cao}= 0.7840

E. Determination of MgO in the solution

A Filtrate of 25ml was pipetted into a 300ml beaker. After 10ml of KF (20g/l) was added to the solution and kept for 5 min, the solution was diluted up to 200ml. Then, 1 ml of potassium sodium tartrate, 5 ml of TEA, 20ml of ammonia hydroxide (pH adjusted to 12. 5) and 6 drops of KB indicator were added. The brown color of the solution changed into a blue color when it was titrated by EDTA.

The formula which used to determine MgO was;

$$\%MgO = \frac{(V_{MgO} * V_{CaO}) * T_{MgO}}{M}$$

Where: M= Mass of ash

V_{MgO}= Volume of MgO

V_{CaO}= Volume of CaO

T_{MgO}= 0.5816

i. For cotton stalk

- **Determination of CaO**

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

Where; M= Mass of ash

$\mathrm{V_{EDTA=}}$ Volume of EDTA added

$\mathrm{T_{Cao}}$= 0.8091

$$\%\mathrm{CaO} = \frac{17 * 0.8091}{0.5} = 27.51\%$$

- **Determination of MgO**

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

Where: M= Mass of ash

$\mathrm{V_{MgO}}$= Volume of MgO

$\mathrm{T_{MgO}}$= 0.5816

$\mathrm{T_{Cao}}$= 0.7840

$$\%\mathrm{MgO} = \frac{(0.7840 - 0.5816) * 26}{0.5} = 10.52\%$$

- **Determination of Fe_2O_3**

$$\%Fe_2O_3 = \frac{T_{Fe_2O_3} * V_{EDTA}}{M}$$

Where: M= Mass of ash

$\mathrm{V_{EDTA=}}$ Volume of EDTA added

$\mathrm{T_{Fe2O3}}$ = 0.7840

$$\%Fe_2O_3 = \frac{0.7840 * 4.3}{0.5} = 6.74\%$$

- **Determination of Al_2O_3**

$$\%\mathrm{Al_2O_3} = \frac{\frac{20}{15}\left(\mathrm{K} * \mathrm{V_{CuSO_4}}\right) * \mathrm{T_{Al_2O_3}}}{\mathrm{M}}$$

Where; K= Excess EDTA + Consumption of $CuSO_4$

$\mathrm{T_{Al_2O_3}}$=0.7355

M= Mass of ash

$$\%\mathrm{Al_2O_3} = \frac{30 - (1.0490 * 23.5) * 0.7355}{0.5} = 7.89$$

- **Determination of SiO_2**

$$\%SiO_2 = \frac{V_{NaOH} * T_{SiO_2} * 0.5}{M}$$

Where: M=mass of the ash

V=Volume of the NaOH solution

T_{SiO_2}= 2.04

$$\%SiO_2 = \frac{11 * 2.0427 * 0.5}{0.5} = 22.47\%$$

ii. **For Coffee husk**

- **Determination of CaO**

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

Where; M= Mass of ash

V_{EDTA}= Volume of EDTA added

$\mathrm{T_{Cao}}$= 0.8091

$$\%\mathrm{CaO} = \frac{12.434 * 0.8091}{0.5} = 20.12\%$$

- **Determination of MgO**

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

Where: M= Mass of ash

V_{MgO}= Volume of MgO

T_{MgO}= 0.5816

T_{Cao}= 0.8091

$$\%\mathrm{MgO} = \frac{(0.8091 - 0.5816) * 17.56}{0.5} = 7.99\%$$

- **Determination of Fe_2O_3**

$$\%Fe_2O_3 = \frac{T_{Fe_2O_3} * V_{EDTA}}{M}$$

Where: M= Mass of ash

V_{EDTA}= Volume of EDTA added

T_{Fe2O3} = 0.7840

$$\%Fe_2O_3 = \frac{0.7840 * 0.676}{0.5} = 1.06$$

- **Determination of Al_2O_3**

$$\%\mathrm{Al_2O_3} = \frac{\frac{20}{15}\left(\mathrm{K} * \mathrm{V_{CuSO_4}}\right) * \mathrm{T_{Al_2O_3}}}{\mathrm{M}}$$

Where; K= Excess EDTA + Consumption of $CuSO_4$

$T_{Al_2O_3}$=0.7355

M= Mass of ash

$$\%\mathrm{Al_2O_3} = \frac{30 - (1.0490 * 9.008) * 0.7355}{0.5} = 30.23$$

- **Determination of SiO_2**

$$\%SiO_2 = \frac{V_{NaOH} * T_{SiO_2} * 0.5}{M}$$

Where: M=mass of the ash

V=Volume of the NaOH solution

T_{SiO_2}= 2.04

$$\%SiO_2 = \frac{7.97 * 2.04 * 0.5}{0.5} = 16.26$$

iii. For mixed torrefied pellet

- **Determination of CaO**

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

Where; M= Mass of ash

$V_{EDTA=}$ Volume of EDTA added

T_{Cao}= 0.8091

$$\%\mathrm{CaO} = \frac{18.7 * 0.8091}{0.5} = 30.26\%$$

- **Determination of MgO**

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

Where: M= Mass of ash

V_{MgO}= Volume of MgO

T_{MgO}= 0.5816

T_{Cao}= 0.8091

$$\%\mathrm{MgO} = \frac{(0.8091 - 0.5816) * 8}{0.5} = 3.64\%$$

- **Determination of Fe_2O_3**

$$\%Fe_2O_3 = \frac{T_{Fe_2O_3} * V_{EDTA}}{M}$$

Where: M= Mass of ash

V_{EDTA}= Volume of EDTA added

T_{Fe2O3} = 0.7840

$$\%Fe_2O_3 = \frac{0.7840 * 3.2}{0.5} = 5.02\%$$

- **Determination of Al_2O_3**

$$\%\mathrm{Al_2O_3} = \frac{\frac{20}{15}\left(\mathrm{K} * \mathrm{V_{CuSO_4}}\right) * \mathrm{T_{Al_2O_3}}}{\mathrm{M}}$$

Where; K= Excess EDTA + Consumption of $CuSO_4$

$\mathrm{T_{Al_2O_3}}$=0.7355

M= Mass of ash

$$\%\mathrm{Al_2O_3} = \frac{30 - (1.0490 * 23.8) * 0.7355}{0.5} = 7.405\%$$

- **Determination of SiO_2**

$$\%SiO_2 = \frac{V_{NaOH} * T_{SiO_2} * 0.5}{M}$$

Where: M=mass of the ash

V=Volume of the NaOH solution

T_{SiO_2}= 2.04

$$\%SiO_2 = \frac{10.1 * 2.04 * 0.5}{0.5} = 20.247\%$$

Appendix F: Correlation table of FT-IR

Range of maxima wavenumber (cm^{-1})	Band assignment
3460-3412	O-H stretching
3000-2842	C-H stretch in methyl and methylene group
1738-1709	C=O stretch in unconjugated ketone, carbonyl and ester group
1675-1655	C=O stretch in conjugated p-subst, aryl ketones
1605-1593	Aromatic skeleton vibrations plus C-;O stretching; S>G: Gcondensed>Getherified
1515-1505	Aromatic skeleton vibrations (G > S)
1470-1445	C-H deformations (asym in -CH_3 and -CH_2-)
1430-1422	Aromatic skeleton vibrations combined with C-H in plane deformations
1370-1365	Aliphatic C H stretching in CH_3 and phen. OH
1330-1325	Condensed S and G ring (G ring bound via position 5)
1270-1266	G ring plus C + O stretching
1233-1214	C-C + C-O + C=O stretching (Gcondensed>Getherified)
1166	Typical for HGS lignins; C-O in ester groups (conj.)
1140	Aromatic C H in-plane deformation (typical of G unit; Gcondensed > Getherified)
1120-1125	Typical of S unit; also secondary alcohol and C-O strt.
1110	Aromatic C-H deformation of S units
1086	C-O deformation in sec. alcohol and aliphatic ether
1035-1030	Aromatic C-H in-plane deformation (G > S) plus C-O deform. in primary alcohols plus C-H stretching (unconjugated
990-966	-HC-CH- out-of-plane deform (trans)
925-915	C-H out of plane (aromatic ring)
895-885	C-H deformation vibration; CH_2 wagging
858-853	C-H out of plane in positions 2, 5 and 6 (G units)
835-834	C-H out of plane in positions 2 and 6 (S units)
832-817	C–H out of plane in positions 2, 5 and 6 (G units)

G: Guaiacyl unit; S: syringyl units; H:P-hydroxyphenyl unit

Source: (Chen et al., 2015)

Appendix G: Laboratory work pictures

Coffee husk

Cotton stalk

Raw material preparation (Size reduction and sieve analysis of cotton and coffee husk)

Torrefaction

Pelletization

Raw and mixed torrefied pellets

Bomb calorimeter for determining calorific value

TGA Instrument FT-IR Instrument

Preparation of solution for oxide determination

Chemicals and Indicator used for determination of oxides

Color change of solution during oxide determination
