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The Assessment of Peanut shell and Chat stem as Alternative Energy Source for Cement Industries

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Abstract

Cement industries are one of the major energy-intensive industries and heavy polluting process. To reduce the energy cost and environmental impact, cement producers are currently using alternative fuels. This study analyzed the assessment of peanut shell and chat stem as alternative energy source for cement industries. The main objective of this study was to carbonized mixed of a peanut shell and chat stem. The parameters of carbonization process, which affect the calorific value such as temperature (350, 450 and, 450^{o}C), time (60, 90 and 120min) and mixing ratio (25, 50 and 75%) were optimized via Central Composite Design (CCD).

*All the necessary analysis that included physiochemical characteristics of peanut shell and chat stem, mixed carbonized and mixed carbonized pellet, then the results were compared with commercial coal. In addition, thermogravimetric analysis were examined the thermal property of peanut shell and chat stem. Based on the result, the optimal conditions were (temperature at 450^{o}C, time for 60min and mixed ratio 75%) with a maximum calorific value of 6552.6 Cal/g. However, the energy content of sample was comparable with coal, but it needs pellet for suitable storage, handling, transporting. Then the optimum mixed carbonized pellet with 10% of molasses, the calorie develop to 6838.19cal/g. The optimum mixed carbonized pellet showed a decrease in moisture content (2.87%), volatile content (30.75%), Hydrogen (2.95%) and Oxygen (26.19%) while the fixed carbon (57.57%), and carbon (*70.86%*) increased considerably. Therefore, in this study shows that the mixed carbonized pellet has potential replaced coal as an alternative energy source for cement production due to their calorific value at optimum carbonation condition.*

***Keywords**: Peanut shell, Chat stem, Carbonization, Pelletization, Calorific value*

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Acronyms

AC	Ash content
ANOVA	Analysis of variance
ASTM	American Society of Testing and material
BTU	British thermal unit
Cal/g	Calorie per gram
CCD	Central Compost Design
EDTA	Ethylenediaminetetraacetic acid
FC	Fixed carbon
MC	Moisture content
NOx	Nitrogen Oxides
RSM	Response surface methodology
SOx	Sulfur Oxides
SA	South Africa
TGA	Thermogravimetric analysis
VM	Volatile mater

1 INTRODUCTION

1.1 Background

Cement is the most important raw material for building and civil engineering construction activity, it mixed with sand and water is known as concrete. Portland cement is the most widely used cement in concrete construction, was patented in 1824. Cement industry plays a crucial role in the infrastructural development of the country and directly related to the state of the construction business in general and therefore tracks the overall economic situation closely. World cement production has grown steadily since 1950, with increased production in developing countries (Reference Document on Best Available Techniques in Cement , Lime and Magnesium Oxide Manufacturing Industries 2010).

The cement industries are one of the major energy-intensive industries (Richards et al. 2008), with about 200 kg of coal used per tonne of cement. Also, the cement industry generates about 5% of global greenhouse gases (GHG) (Zhang 2013). Being an energy-intensive industry, fuel consumption accounts for 30%–40% of the total cement production costs (Cortada et al. 2015). Cement production includes the isolation and preparation of the raw materials typically (limestone and clay or shale), and drying, burning of the raw material mixture to form cement clinker. Clinker is the main component of cement and it is formed in rotary kilns. Rotary kilns are huge furnaces where the cement clinker is made. The raw materials fed into the top of the kiln and move down toward the tube where coal dust, oil, or gas flame is burning at the bottom of the tube. Near the flame, in the sintering or clinkering zone of the rotary kiln with a gas temperature of 1800-2000℃, the temperature of the material being burnt reaches 1450-1500℃, which is necessary for the formation of clinker (Kaddatz et al. 2013). The clinker is subsequently ground together with gypsum and other additives to produce cement.

The energy sources of cement production are fossil fuels in a greater amount which means it needs a persistent supply of energy resource. Fossil fuels such as coal, petroleum and natural gas provide most of the energy needs of the world today. Coal have been used as primary energy sources in the cement manufacturing industry.

These fossil fuels besides their high energy content, they influence on cost consumption and negative effect on the environment especially in increasing concentration of greenhouse gases in the atmosphere, particularly carbon dioxide. Therefore, these fuels switching to alternative energy sources are becoming more attractive for cement industries to reduce the environmental impact and gain economic advantages by reducing fuel costs. The replacement of fossil fuel by carbon dioxide neutral fuels will reduce net carbon dioxide emissions to the atmosphere (Albino et al. 2011), while letting the manufacturer

There are different types of alternative fuels and alternative sources of energy in the world such as biomass, waste-derived fuels, wind energy; hydroelectric power and solar energy. Among different renewable sources of energy, biomass is considered to be a very good option. Biomasses are sources of environmental and social sustainable which represent a vast and large untapped renewable energy source for the countries of sub-Saharan Africa such as wood chips, sawdust, cotton stack and coffee husk. These biomass has high availability and strongly dependent on regional conditions (Demirbas 2010). In addition, sulfur and trace metals are typically much lower in biomass fuels than in fossil fuels.

National energy balance of Ethiopia has been so far predominated by energy resources of biomass. Ethiopia has sufficient and diverse biomass residue resources presenting opportunities to harness for renewable biomass fuels (Guta 2017). Since agricultural residues such as peanut shell and chat stem are indigenous resources generated in large scale, thus, are largely available and rather inexpensive, these materials are considered as potential renewable and economically safe way of providing energy. According to the CSA report on area and production of crops, more than 352,077 private peasant holding households have grown groundnut in close to 80,000 hectares of land in the 2013/14 cropping season leading to a total production of well over 0.11 million tons (CSA, 2014) (Nega et al. 2015). In our country, after harvesting the peanuts, they are transported to a processing facility where they are dried and stored. At this point, they are sent to a Sheller, where the shell or hull is separated from the nut. These peanut shells account for approximately 20% of the dried peanut pod by weight, meaning there is a substantial amount of shell residual left after peanut processing (Bharthare et al. 2014).

On the other hand, chat is among the most important cash crops grown and consumed in Ethiopia, particularly in the eastern and southern parts of the country. It is also one of the major crops exported to neighboring countries, earning significant amounts of foreign currency for the country. Total land under chat in 2004/05 was over 120,000 hectares, up by 8% on preceding years (CSA, 2005). In Ethiopia yield of chat crop about 6,608 tonnes/year (Guta 2017). Despite its availability, large amounts of chat residue/chat stem are left on the roads or piled up in the fields of many cities for lack of alternative uses.

Generally, the benefits of using biomass fuels to displace fossil fuels used in the energy-intensive industries are financially lower unit cost thermal energy than the fossil fuels and environmental friend due to the less amount of CO_2 and sulfur emissions compared to fossil fuels. However, the potential of these biomass residues are large, but inefficient for cement production as a fuel because of their less energy, heterogeneity, non-uniform physical property and high moisture content. Therefore, they must be improved by carbonization and pelletization process before as energy application in cement industries.

1.2 Statement of problem

Ethiopia's economic development and brought significant changes and improvements particularly in areas of agricultural productivity, industrial development, and expansion of infrastructure. Ethiopia's Growth and Transformation Plan (GTP) is a five-year plan to propel the country toward a climate resilient middle income status by 2015 (Seboka et al. 2016). Therefore, Ethiopia is becoming more cement industrialized in the near future, due to this, the demand of energy for cement production is increasing a time to time. The source of energy in cement industries is conventional fossil fuel. However, the conventional fossil is not producing in Ethiopia, it's imported from abroad. The cost consumptions of fossil fuels are increasing through the time constantly as a consequence of limited energy sources because of their depletion, non-renewability and also it is not sufficiently available in the world.

The major contribution to global warming with a high emission of CO_2 and other pollutants to the environment (NOx and SOx) in cement production. The needs for energy to comply with environmental regulation will grow at a faster rate. The local cement industries will require looking forward to an alternative renewable energy source in order to substitute the conventional fossil fuels.

In Ethiopia; there are a lot of possibilities of renewable resources which can be a shift from conventional fossil fuel to alternative fuels such as biomass (peanut shell and chat stem). Peanut is generated and some private cultivators active in Babile. After cultivation, they accumulate the residues in large volume and mostly they use it for household fuel and the rest residue they burnt as waste so that it affects the environment. On the other hand, Chat is largely produced, marketed and consumed in Awoday. Mostly The residue of chat (chat stem) dumped on the marketplace, recreational centers, on access roads along on waste water drainage, and other available spaces. Due to the chat stem disposed of in open urban sewer sit can block the drainage, it leads to overflows on the environment. Therefore, it causes environmental degradation and health problems because of its unpleasant odor and also affect the feature of the city.

Therefore, the above aforementioned critical limitations of conventional fossil fuels and the above-mentioned gaps to utilize residue (peanut shell and chat stem) as alternative energy source for cement industries are drives me to study this research, for the reason that utilizing such alternative fuels for meeting energy requirement is a sustainable initiative which can be help to save of fossil fuel cost and mitigate greenhouse gas (GHG) emissions.

Despite all its advantages, biomass has some shortcomings that often create difficulties in its wide-scale use as an energy source. A different study showed that when compared to other fossil fuels like coal, biomass has higher moisture and oxygen content, lower calorific value, bulk density and carbon content. Thus biomass faces some technical challenges in energy conversion systems. A low bulk density of raw biomass causes storage and handling problems. It also reduces the energy density of biomass that in turn increases the volume of biomass feed into a conversion system to produce a given amount of power. Higher oxygen content reduces the heating value and thereby makes it a lower-grade fuel. Therefore, biomass pyrolysis and pellet have emerged as a promising technology to fulfill the aforementioned problems of biomass raw materials as well as to reduce the volume of biomass residue and to increase calorific value for balancing with commercial coal. This research develops a carbonization process by mixed a peanut shell and chat stem to improve physiochemical characteristics.

1.3 Objective

1.3.1 General Objective

The aim of this research is to assess Peanut shell and Chat stem as an alternative energy source for cement industries.

1.3.2 Specific Objectives

The specific objectives of this research are;

- To investigate the physiochemical characteristics of peanut shell and chat stem.
- To examine the effects of carbonization time, temperature and mixed ratio on calorific value of mixed peanut shell and chat stem.
- To determine the optimum parameters of carbonization process by using response surface methodology
- To examine the effect of pelletization on calorific value of optimum mixed carbonized sample with molasses.
- To investigate the physiochemical characteristics of mixed carbonized pellet and compare with commercial available coal.

1.4 Significance of Research

This research has a great role for the Ethiopian cement industries by substituting non-renewable resources under strictly controlled conditions and a safe sound solution for the environment and society. The significant advantage of alternative fuel substitution is the utilization and preservation of non-renewable energy sources and conservation of the environment. Replacement of some conventional fuels with alternative fuels brings both environmental and economic benefits. Alternative fuels are cheaper than the fossil fuels which lead the cement industries to use them in optimal proportion because of their availability as an industry that is especially suitable for the application of such fuels, from the technological and environmental points of view. Alternative fuels are used in many cement plants throughout the world.

There has been increasing positive environmental impact on human industrial activities beyond the cost cutting benefits which can save foreign currency by replacing imported fuel, these fuels can also contribute greatly to the environmentally sound disposal of residue and the mitigation of green gas house emission.

2 LITRATURE REVIEW

The literature review included in this chapter contains available information (studies) related to the use of alternative energy sources in cement manufacturing. Most materials contain some energy which can be utilized as a fuel for cement production should be meet the requirement of the thermal energy. Many researches and case studies were reviewed and analyzed on alternative sources. In particular, studies related to the environmental, health, social and economic costs and benefits of the use of alternative sources compared to the fossil fuels.

2.1 Review on Overall Cement Production

Cement is a basic material for all types of construction and building, including housing, roads, schools, hospitals, dams and ports, and may even be used in decorative items such as tables and bookcases. It is a finely ground, non-metallic, inorganic powder, which, when mixed with water, forms a paste that sets and hardens. It’s most important use is in the production of concrete, acting as the binder gluing the other key ingredients of concrete sand and gravel.

The basic chemistry of the cement manufacturing process begins with calcinations, the decomposition of calcium carbonate ($CaCO_3$) at about 900°C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO_2). This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically 1400–1500°C) with silica, alumina and ferrous oxide to form the silicates, aluminates and ferrites of calcium which comprise the clinker. The clinker is subsequently ground together with gypsum and other additives to produce cement.

The cement manufacturing processes pollute the environment, particularly in terms of greenhouse gas emissions. Cement-related greenhouse gas emissions originate from fossil fuel combustion, 5% of the annual carbon dioxide output, half of these emissions originate from the burning of fuel and half from the calcinations reactions. At its operation about 40% of the industry’s emissions; transport activities (5%) and the combustion of fossil fuels about (50%) originate from the manufacturing process that converts limestone ($CaCO_3$) to calcium oxide (CaO), the primary precursor to cement. It is chemically impossible without generating CO_2 to convert $CaCO_3$ to CaO, and then cement clinker, This CO_2 is currently emitted to the atmosphere

(Richards et al. 2008). Due to the unique nature of the product it manufactures, the cement industry currently emits 0.73 to 0.99 kilograms of CO_2 for every kilogram of cement produced (Y. Wang et al. 2014). At any emission rate within this range, current proposals to curb CO_2 emissions will profoundly affect the activities and finances of the industry.

The mining activity (quarrying) starts with preparing an access road to the target site, removing the over burden, preparing bench to have good and step wise blasting. Depending on the characteristics, the raw materials are quarried by blasting. Limestone deposits vary from soft, water dispersible chalks and marls to the hardness of minerals. Much of lime stone used is hard and it must be mined or quarried using explosive to break up the deposits. Cement raw materials blasted in the quarry requires size reduction before further processing. The quarried material is reduced in size by processing through a series of crushers and after primary and secondary size reduction, the raw materials are further grinded in raw mill and proportioned so that the resulting mixture has the desired fineness and chemical composition for delivery to the pyro-processing systems. The ground raw material, fed into the top of the kiln, moves down the tube counter current to the flow of gases and toward the flame-end of the rotary kiln, where the raw meal is dried, calcined, and enters into the sintering zone at $1450^{o}C$ (Rahman et al. 2015). Once the clinker is formed in the rotary kiln, it is cooled rapidly to minimize the formation of a glass phase and ensure the maximum yield of alite (tricalcium silicate) formation, an important component for the hardening properties of cement. After cooling, the clinker can be stored in the clinker dome, silos, bins, or outside. The material handling equipment used to transport clinker from the clinker coolers to storage and then to the finish mill is similar to that used to transport raw materials. To produce powdered cement, the nodules of cement clinker are ground to the consistency of face powder. Grinding of cement clinker, together with additions 3-5% gypsum to control the setting properties of the cement can be done in ball mills, ball mills in combination with roller presses, roller mills, or roller presses.

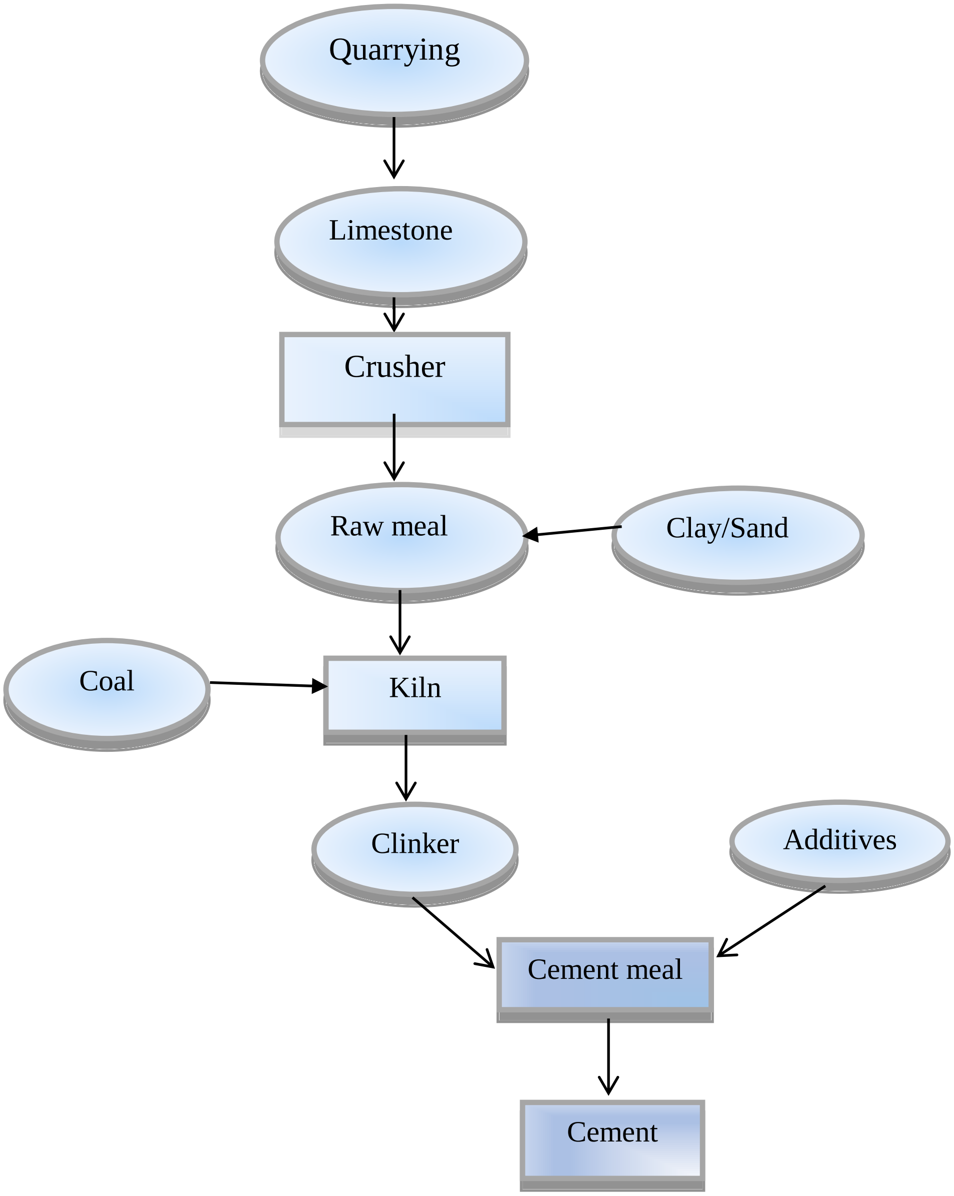


Figure 2.1 Flow sheet of cement production

Cement production is an energy-intensive process consuming thermal energy of the order of 3.3 GJ/tonne of clinker produced, which accounts for 30 to 40 percent of production costs (Psomopoulos and Themelis 2014). In 2005, the global cement industry consumed about 9 exajoules (EJ) of fuels and electricity for cement production (Murray & Price, 2008).

Table 2-1 Categories of fuels

Category	Fuels
Gaseous fuels	Refinery waste gas, landfill gas, pyrolysis gas, natural gas
Liquid fuels	Tar, chemical wastes, distillation residues, waste solvents, used oils, wax suspensions, petrochemical waste, asphalt slurry, paint waste, oil sludge
Solid fuels	Petroleum coke (petcoke), paper waste, rubber residues, pulp sludge, sewage sludge, used tyres, battery cases, plastics residues, wood waste, domestic refuse, rice husks, refuse derived fuel, nut shells, oil-bearing soils, diapers, etc.

Historically, these energy sources have been treated as competing energy resources for which economics and environmental constraints determine which energy source are used, such as cement, glass, and ceramics and so on.

2.1.1 Cement Industry in Ethiopia

The Ethiopian cement industry has endured through three major milestones, i.e., the beginning of cement production and modernizations till 1984, construction boom in 2004 followed by acute shortage and aggressive expansion of the sector in 2012 onwards resulting in inflaming excess capacity.

The first cement factory in Ethiopia was established in 1936 in the city of Dire-Dawa. In 1964 in Addis Ababa was established respectively with capacity of 70,000 tons each per year. Since then cement sector growth had remained sluggish for decades. In 1984 with establishment of Mugher cement, the industry had revived. As cement demand growth prospect appeared promising in 2001, Messebo cement becomes operational with initial 600,000-ton clinker capacity. In the subsequent years Messebo had expanded its capacity to its current level.

In the period 2003-08, the government increased its infrastructure spending threefold mainly in road, waterworks, public building and Dams. Since 2004 sustained shortage of cement supply resulted in price hike. In 2007 the government responded to the price hike by allowing the private sector to import cement. However, this intervention did not succeed since most importers lack foreign currency. As a result of sustained acute shortage and continued growth in demand. Accordingly, from 2008-2011 due to drastic growth of the construction sector, overall growing economy, as well as frequent power interruption among others; cement supply significantly found short of meeting demand from domestic production sources (Ethiopian cement focus n.d.)

Table 2-2 Profile of Ethiopian cement companies

Company name	**Production capacity**	
	Clinker ton/year	**Cement ton/year**
Muger cement	1.5 mil	2.2 mil
Derba Cement	1.8 mil	2.5 mil
Messebo cement	1.5 mil	2.2 mil
National Cement Share Company	0.9 mil	1.2 mil
Habesha	0.95 mil	1.4 mil
Debresina Business	72,000	75,000
Inchinni Bedrock	200,000	300,000
Pioneer Cement	257,737	9625.2
Ethio Cement	540,000	771,429

2.2 Review on Conventional Fossil Fuels

Fossil fuels, coal, petroleum coke (petcock), oil, and natural gas, which are the major fossil fuels, have been used as stand-alone fuels or in various combinations since the industrial revolution in the cement industry. Coal and pet coke, the most carbon-intensive fossil fuels, are the most widely used fuels in the cement industry. Fossil fuels are non-renewable sources, and their usage has a significant environmental impact. Burning fossil fuels generates NOx, which leads to acid rain and air contamination, and CO_2, which contributes to intensify the greenhouse effect (Cortada et al., 2015).

Coal is a combustible carbonaceous rock that contains varying amounts of carbon, hydrogen, nitrogen, oxygen, sulphur and mineral matter and nearly 8 gigatonnes per year of coal is produced globally. It is an important energy resource, an organic rock that is composed of minerals and its reserves are abundant fuels necessarily needed to meet the demands of electricity. The combustion of lignite, sub-bituminous, bituminous coal, and anthracite for power generation produces a range of coal combustion residues, also known as coal ash. The growing interest in mineral matter and trace elements in coal and coal fly ash largely stems from environmental standards required for power generation (Odunayo et al. 2016). Historically, the primary fuel used in cement industry is coal. Coal used to energy for firing cement-making kilns, either on their own or in various combinations consumed in cement plants worldwide because of its physiochemical characteristics.

Table 2.2 Proximate analysis of fossil fuel (Cortada et al., 2015)

Fuel	**Proximate Analysis [wt% dry]**			
	Volatile matter	**Fixed carbon**	**Ash content**	**Lower heating value [MJ/kg]**
Anthracite coal	1.7-11	67-98	3.8-20	30.2-34.9
Bituminous coal	14-40	33-86	3.7-12	19.7-34.9
Lignite coal	26-47	29-40	4.2-18	9.3-19.3
Pet coke	9-13	71-95	0.2-3	29.5-34
Crude oil	Not available	Not available	~0	39-42.7
Natural gas	100	0	0	46.8-53.8

Petcock fuel is used for cement production, coke refined from either coal or petroleum. As shown in table 2.2, this has high calorific value 29.5 to 34MJ/kg, low ash content and low volatile matter. The drawback of using petcock fuel in cement production is has higher level of sulphur content (condensation of sulphate and chlorides in preheater section resulting in jamming of process flows), has nitrogen content (NOx emission), low hard groove index (difficult to grind) and low volatility (due to its volatiles petcock) has to be ground very finely, in order to enable it to burn completely (Hoenig 2012).

Based on the data obtained from Cortada et al., 2015, the composition of different coals used to fire cement kilns can vary considerable, as illustrated in table 2.2 which shows typical proximate analyses and heating values of different fossil fuels. According to the data, the highest volatile matter is found in natural gas which shows its matter content to obtain a definite content of unburned carbon in ash. It is described on the document that the volatile content is important for the combustion characteristics and the fuel reactivity. Solid fuels are normally pulverized before use, and required fuel fineness is needed according to the volatile content of the fuel in order to enable good combustion in the kiln and calciner. Fossil fuels are typically introduced with a particle sieve residue of 2%–20% on a 90 μm sieve. There exists an empirical rule, which relates the required coal fineness to the proximate of volatile matter content to obtain a definite content of unburned carbon in ash.

Worldwide, coal is the predominant fuel burned in cement kilns. Cement production consumes approximately 120 kg of coal per tonne of cement. In the European Union about 25 million tonnes of coal is required annually by the Cembureau members to service the demand of cement in Europe.

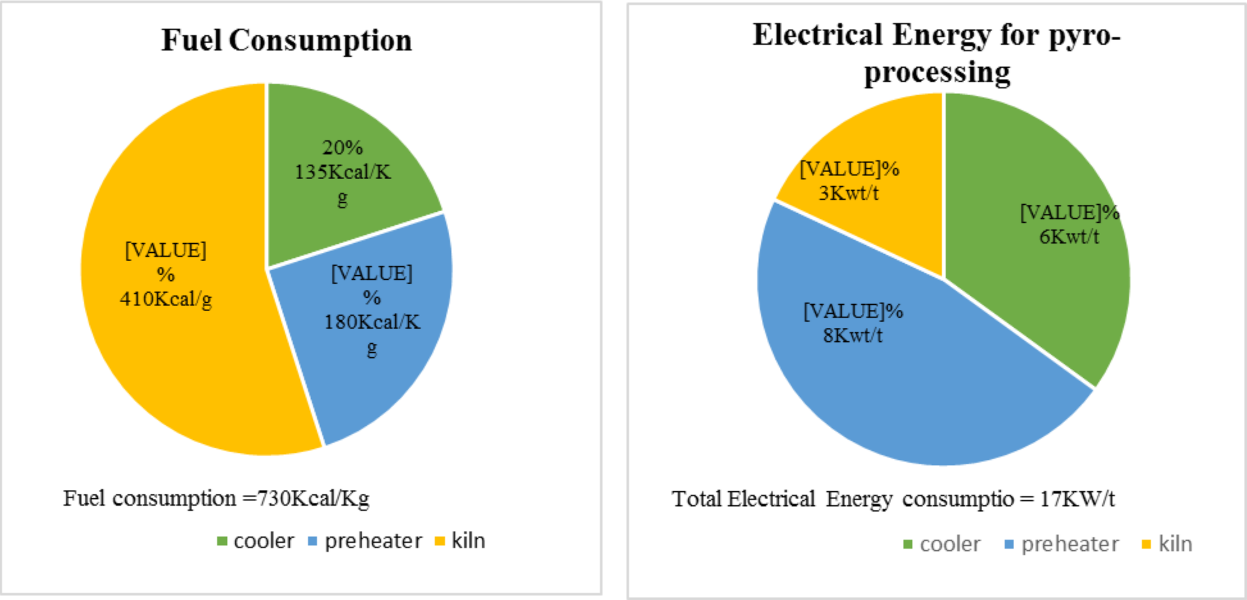


Figure 2.2 Fuel consumption and Electrical energy for pyro-processing

2.2.1 Deposit of Coal in Ethiopia

Exploration of coal in Ethiopia was started in the year 1935 at Nejo and Wuchale (Ahmed 2008) Ethiopia is known to have some coal deposits in the Dilbi-Moye basin in the southwest of the country. Deposits are estimated about 14,016,730 tonnes (MME, 2009). Other areas with coal deposits include the Geba basin (250,000,000 tonnes), Chilga basin (19,000,000 tonnes) and Chida Waka (9.38 million tonnes) (MME, 2009). These coals classified under low-medium ash content, medium volatile matter, moderate calorific values lignite to bituminous coal (Ahmed 2008).

Table 2-3 Proximate analysis and calorific value of coal deposits in different basins (Ahmed 2008)

Resource	**Moisture (%)**	**Volatile matter (%)**	**Ash content (%)**	**Calorific value (Kcal/Kg)**
Delbi-Moye coal	4-8	25-29	11-25	2948-5190
Chilga coal	5-10	21-31	16-41	3072-4560
Mush valley	21	31-40	19-27	2824-3568
Nejo	14-16	30-35	19-23	3400-3987
Wuchale	10-12	18-29	35-48	3700-5445
Yayu coal	8-20	28-46	25-42	3795- 5930

2.3 Review on Alternative Fuels

Alternative fuels are another source of energy used by cement producers around the world. These fuels are usually derived from the mixtures of industrial, municipal and hazardous wastes, biomass, tire, meat bone meal, tyre and sewage sludge. But which are less implemented. The use of alternative fuels for cement clinker production is certainly of high importance for the cement manufacturer as well as for the environment. Alternative fuels have been increase now and are gaining an increasing share in the global energy market (Alnino et al. 2011).

The Carbon War Room estimates that substituting coal with lower-carbon fuels offers the greatest short-term potential to reduce CO_2 emissions in the industry. Most alternative fuels have lower carbon intensity than fossil fuel. According to the International Energy Association, these mixed fuels can be 20 to 25% less carbon-intensive than traditional fossil fuels (Patil and Khond

2014). Using alternatives to replace the coal and pet coke as replacement fuels in a cement kiln can significantly reduce greenhouse gas emissions and in some cases other air pollutants.

In cement plants less than 15% of the energy consumed from alternative fuels. The alternative fuels are highly adopted in countries with more restrictive environmental standard which has high positive impact on emission and energy cost. Between 2000 and 2010, average alternative fuel consumption in the 27 nations of the present European Union quadrupled to roughly 20% (Alnino et al. 2011).

Fuels in various countries have been prepared from mixed types of waste in order to ensure the better use of the chemical energy contained in waste. It is now established that processed waste with energy content can be utilized as an energy source. Belgium 18%, France 52.4%, Italy 4.1%, Portugal 1.3%, Spain 1%, Sweden 2%, Switzerland 25%, Czech Republic 9.7%, Great Britain 20%, Germany 15%, Poland 1.4% (Patil and Khond 2014).

In the United States, approximately 5 percent of fuel used in the cement industry comes from renewable and non-renewable waste fuels such as wood, tires and other nonhazardous and hazardous materials. Various sources suggest the availability of millions of tons of wood that could be used in cement factories to reduce greenhouse gas emissions and minimize forest fires (Alnino et al. 2011).

A study by Walker et al., (2009) reported the use of waste wood in cement kilns reduces the amount of fossil fuel required by industry, the ashes resulting from the combustion of waste wood are mixed with raw material in the clinker, thus reducing the requirements for new input materials.

In UK: Cemex cement factory in Rugby uses alternative fuels such as tyres and ‘climafuel’, which is derived from household and commercial wastes. The ‘climafuel’ can contain at least 50 percent biomass, displacing nearly 180,000 tones of fossil fuel CO_2 (Cemex, 2009; Cement News, January 2009). According to Cement World, October 2008 the Lafarge plant at Hope uses bone meal (MBM) which is expected to reduce 30,000 tons of CO_2 emissions per year.

The UK's Committee on the Medical Effects of Air Pollution, has stated that the burning of waste-derived fuels in cement kilns results in no changes in emissions that would be of significance to human health. Its latest (2008) report on Meat and Bone Meal, processed Sewage Pellets, and Refuse Derived Fuel extended the 2005 review of waste tyres and substitute liquid fuels, and indicated that these findings were relevant to any combination of these fuels.

In addition to these Austria's cement factories were amongst the earliest to start burning tyres since the 1980s, and have been burning solid waste such as plastics, paper, textile and composite materials since 1993. All nine cement plants in Austria use solid waste to various degrees (European Cement Association, 2009). One of the factories Wietersdorfer & Peggauer cement plant, claims to have used alternative fuels substituting up to 70 percent of fossil fuels (Zieri, 2007).

In Brazil, a waste management joint venture, Eco-Process, supplies plants with substitute fuels. In some cement plants in Brazil, 42% of the fuel used comes from biomass or waste, which reduced emissions of 156,000 tonnes of CO_2 in 2007 (Lafarge, 2008) and also Cimpor, 2008 states that Hazardous waste can be used as an alternative fuel in cement kilns, which also realizes the complete destruction of such waste. The combustion of hazardous waste in cement kilns reduces the fossil fuel requirements of plants and also reduces CO_2 emissions. Chlorinated organic compound emissions, for example, are expected to decrease compared to the use of fossil fuels.

A cement firm operating in Kenya and Uganda claims to have cut its annual carbon dioxide emission by reducing its use of fossil fuels in cement making by 20 percent. The company, which is partly owned by Lafarge Cement, plans to reduce its use of coal by using wood from its own plantations as well as coffee, rice, and cashew nut husks. It is targeting a reduction of 132,000 tonnes of CO_2 per annum by 2010 (Reuters, March 11, 2008; Lafarge, 2007).

In Ethiopia, Messebo cement factory is working to replace partially its fuel consumption with biomass (sesame husk), which have been considered as waste and ignited at farmlands in woreda kafta Humera. Currently the plant installed all the machinery and equipment designed for 40% heat required (Messebo Biomass Project n.d.). Assuming the average specific energy consumption of Messebo cement factory for the pyro processing system to be 750 k.cal/Kg of clinker and the heating value of imported coal to be 6000 kcal/Kg of coal, hourly fuel consumption of Messebo cement factory, with a production capacity of 125 tons of clinker per hour, is estimated at 15.63 ton/hour of imported coal. Replacing 40% this imported coal with sesame husk, would require about 9.26 ton/hour of sesame husk fuel (assuming a heating value of 4050 K.cal/Kg) (Gebreslassie et al. 2018). This is a considerable amount of fuel to handle on hourly basis. Sesame husk is considered to be carbon-neutral or green energy because the crop grown to replace the combusted sesame husk is considered to absorb CO_2 from the atmosphere while growing, thereby in effect 'canceling out' the CO_2 emissions associated with the combustion of the cultivated crop each year, the net effect on the atmospheric carbon balance is zero.

2.3.1 Criteria of Alternative Fuel for Cement Production

Solid alternative fuels are may differ significantly in physical and chemical properties compared to traditional solid fossil fuels. From the process point of view, considering a modern kiln system for cement production and the use of alternative fuels mainly influences: kiln process stability (may accelerate build-up of blockages preventing gas and/or solids flow), cement clinker quality, emissions and decreased production capacity. Kiln process stability in particular is influenced by insufficient carbon burnout in the calcine system, which results in reducing conditions in the material inlet of the rotary kiln and consequently an increased tendency to form deposits induced by sticky eutectic melts. Clinker quality is mainly affected by minor components from the fuel ashes or from carbon dropping into the material charge of the rotary kiln. Their main components consider with respect to clinker chemistry. The emissions seem not to have been affected by the alternative fuels used up until now (Boberg et al. 2007).

The following properties should be examined before the burning of alternative fuels: Physical state of the fuel (solid, liquid, gaseous), Content of circulating elements (Na, K, Cl, S), Toxicity (organic compounds, heavy metals), Composition and content of ash, Content volatiles, Calorific value, Physical properties (scrap size, density, homogeneity), Grinding properties, Humidity content and Proportioning technology

As a mixture of various wastes, alternative fuels may be produced in conformity with certain rules as follows: (Patil and 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 being 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.

The specifications of criteria for the as-received alternative fuels listed below were targeted by this particular cement plant during this study (Schindler et al. 2012).

- Energy value ≥ 5,000 BTU/lb,
- Chlorine content ≤ 0.2 %,
- Sulfur content ≤ 2.0 %
- Nitrogen content ≤ 1.4 %,
- Moisture content ≤ 14%, and
- Ash content ≤ 18 %.

2.3.2 Review on Biomass

Biomass can replace a portion of the traditional fuel uses. Biomass-based energies are basically derived from three sources: agricultural residues, forestry residues and energy crop There is a wide range in the calorific values reported in the literature for biomass categorically, as well as for individual types. The range in lower heating values 12 (LHV) of biomass is 14 and 21 MJ/kg. Because of less heating value compare to fossil fuel, the quantity of agricultural biomass residues should be replacing one tone of coal depends on the fuel's energy value (Alnino et al., 2011). Although, it's recommended to replace ratio of biomass in an amount not exceeding 20% for maintain a stable combustion process, quality of the clinker and did not significantly affect the pollution emissions in the combustion tests (Borowski 2013).

Biomass can be used in cement plants through two major modes, namely direct combustion and transformation into producer gas. Direct combustion of biomass in pre-heaters / pre- calciners and in the kiln by part-replacing the fossil fuel used in raising the temperature of the raw meal. This can happen in two ways: first, by mixing crushed and pulverized biomass with coal or petcock for use in the kiln, and secondly, by direct feeding of biomass in solid lump form (such as pellets and briquettes) into the rotary kiln and / or pre-heater/pre-calciner combustion chamber. The biomass can also be transformed into producer gas (also known as 'synthesis 'synthesis gas' or 'syngas') and co-firing it in the kilns using a gas burner (Mikul 2016).

According to Demirbas (2010), the importance of biomass varies significantly across regions. In Europe, North America and the Middle East, the share of biomass averages to 2–3% of total final energy consumption, whereas in Africa, Asia and Latin America, which together account for three-quarters of the world's population, biomass provides a substantial share of the energy needs: a third on average, but as much as 80–90% in some of the poorest countries of Africa and Asia (e. g., Angola, Ethiopia, Mozambique, Tanzania, Democratic Republic of Congo, Nepal, and Myanmar). In the study the elemental analysis of typical fuels samples is included.

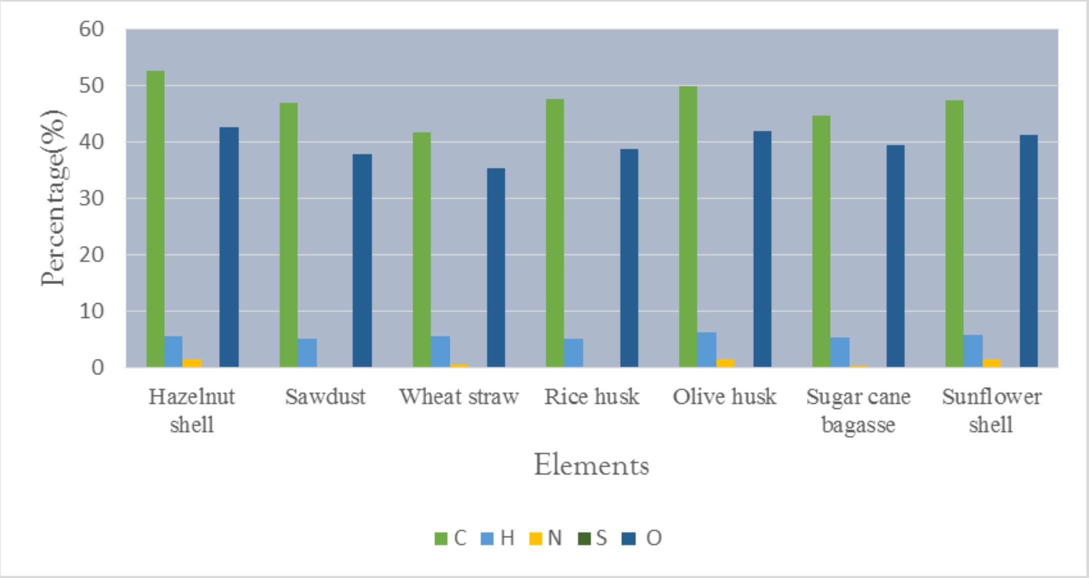


Figure 2.3 Elemental analysis of biomass fuels (Demirbas 2010)

A study conducted by (Rahman et al. 2015), stated that co-firing biomass fuels with coal has the capability of reducing both NOx and SOx levels. Different biomasses have higher nitrogen content than those in coal or petroleum. Most of the nitrogen in biomass is converted to ammonia, which promotes the conversion of NOx to gaseous nitrogen; these emissions of NOx can also be reduced. On the other hand, calcium (Ca) and potassium (K) are important components in biomass. Because an increase in the potassium oxide (K_2O) content decreases the melting point of the ashes, enhancing agglomeration problems in the combustion chambers, therefore co-combustion of biomass with coal or pet coke, which have lower calcium contents, is recommended. These mixtures produce ashes with a higher melting point and operational problems are thus avoided. Moreover, the alkaline base and chlorine contents are also important, especially at high levels because they can cause deposition, slag fusion, or corrosion problems (Mikul, 2016).

A paper by Mckendry (2002) conducted research on energy production from biomass. Ultimate (elemental) analysis of typical biomass materials are examined and compared with bituminous coal and lignite as shown in the table 2.2.

Table 2.3 Ultimate analyses for typical biomass materials (Mckendry 2002)

Material	**C**	**H**	**O**	**N**	**S**	**Ash**
Cypress	55.0	6.5	38.1	-	-	0.4
Ash	49.7	6.9	43.0	-	-	0.3
Beech	51.6	6.3	41.4	-	-	-
Wood(average)	51.6	6.3	41.5	0	0.1	1
Miscanthus	48.1	5.4	42.2	0.5	<0.1	2.8
Wheat straw	48.5	5.5	3.9	0.3	0.1	4
Barley straw	45.7	6.1	38.3	0.4	0.1	6
Rice straw	41.4	5	39.9	0.7	0.1	-
Bituminuous coal	73.1	5.5	8.7	1.4	1.7	9
Lignite	56.4	4.2	18.4	1.6[a]	-	5

In addition, fuel properties of selected biomass materials like (higher heating value, fixed carbon content, volatile content, ash content, alkali metal content) together with bituminous coal are also examined and summarized in the study. The following table 2.4 shows the results of fuel properties of the different biomass.

Table 2.4 Properties of different biomass materials (Mckendry 2002)

Material	**MC (%)**	**HHV (MJ/kg)**	**FC (%)**	**VM (%)**	**AC (%)**	**Alkai metal (Na and K oxides) (%)**
Fir	6.5	21	17.2	82.0	0.8	-
Danish pine	8.0	21.2	19.0	71.6	1.6	4.8
Willow	60	20.0	-	-	1.6	15.8
Poplar	45	18.5	-	-	2.1	16
Cereal straw	6	17.3	10.7	79.0	4.3	11.8
Miscanthus	11.5	18.5	15.9	66.8	2.8	-
Bagasse	45-50	19.4	-	-	3.5	4.4
Switch grass	13-15	17.4	-	-	4.5	14
Bituminous coal	8-12	26-2	57	35	8	-

2.3.3 Biomass Fuel Resource Potential in Ethiopia

Ethiopia has a huge biomass energy potential with estimates putting the national woody biomass stock at 1,149 million tonnes with annual yields of 50 million tonnes in the year 2000 (Seboka et al. 2016). In Ethiopia, driven by massive population growth and rural poverty, biomass is expected to source significant energy requirement. With the aid of appropriate strategies biomass resources can provide renewable energy. According to the report, in the year 2008 alone 92% of Ethiopia's energy demand was met from biomass source (Guta 2017). The estimated total amount of biomass resource available for energy in Ethiopia in 2014–2015 is 1120 million tons with the annual energy potential of 46.91 million tons of coal equivalent and the annually exploitable agro-wastes account for 18 million tons (Berhanu, Jabasingh, and Kifile 2017). These shows the extent to which national energy balance of the county is predominated by biomass resources.

Firewood was the major biomass type consumed in Ethiopia. The country is the number one producer in its share to world's charcoal and woody fuel wood as compared to other African countries. Evidences indicate that 99% of households, 70% of industries and 94% of service enterprises use biomass as energy source (Guta 2017). Agro-processing industries, such as processing sugar-cane bagasse, cotton stalk, coffee hull and oil- seed shells, present an opportunity for biomass energy. But currently, there are no grid-connected biomass power plants (Seboka et al.2016).

Table 2-4 Ethiopian biomass residues energy resource potential and uses (Guta 2017)

Biomass residues	**Amount**	**Uses**
Coffee Residues	214,299 tonnes/year	Production of briquettes charcoal
Cotton Stalk residue	89,000 tonnes/year	Charcoal production or directly used
Chat (cash crop)	6,608 tonnes/year	Directly used
Crop residues	24.23 billion tonnes	Multiple uses (fertilizer, fodder, building material, etc.)
Sawmill residue	25,000tonnes per year	Production of substitutable fuel industries
Energy plants (Jatropha, Castor bean, palm tree	land for Jatropha investment 23.3million ha	Suited to agro ecology
Woody biomass resources	Forest coverage 12.2 million ha	Charcoal production or directly used

2.3.3.1 Potential of Chat in Ethiopia

Chat (Catha edulis) is now one of the largest crops grown and consumed in Ethiopia, particularly in the eastern and southern parts of the country. The major production area of chat in Ethiopia is the Hararghe, located in eastern Ethiopia. It is an essential source of income for millions of Ethiopian farmers and also one of the major crops exported to neighboring countries, earning significant amounts of foreign currency for the country.

In Ethiopia, total land under chat in 2004/05 was over 120,000 hectares, up by 8% on preceding years (CSA, 2005). Only 1.2 percent of total area cultivated is used for chat production, however, its share in area cultivated grew with 6.1 percent per year in 2003/04-2008/09 (Taffesse et al. 2011). The yield of chat crop about 6,608 tonnes /year in the area ranges from 1500–1800 kg/ha through monoculture (Guta 2017). Despite its availability, large amounts of chat residue/chat stem are left on the roads or piled up in the fields of many cities for lack of alternative uses.

2.3.3.2 Potential of Groundnut /Peanut in Ethiopia

Groundnuts (Arachis hypogaea), also known as peanuts or monkey nuts, are the edible seeds of a legume plant that grow to maturity in the ground. Groundnut was introduced in the early 1920s and are becoming increasingly important in Ethiopian agriculture and domestic demand has been on a steady increase. They can be consumed directly (roasted and salted), processed into oil or cake/meal, or further processed into confectionary products or snack food.

In Ethiopia, groundnut is the second important lowland oilseed of warm climate next to sesame. It is mainly grown in eastern Harerghe, with immense potential in Gamogofa, Illubabor, West Gojam, North Shoa, North and South Wello, East and West Wellega, and Western Tigray (CSA 2010) (Nega et al. 2015). According to the CSA report on area and production of crops, more than 352,077 private peasant holding households have grown groundnut in close to 80,000 hectares of land in the 2013/14 cropping season leading to a total production of well over 0.11 million tons (CSA, 2014). Table 2.4 shows trends in production, area cultivated and productivity of groundnut in Ethiopia. One of the significant features emerged from the data presented in the table 2.4 is the increasing trend in area and productivity of groundnut.

Table 2-5 Production and productivity of groundnut in Ethiopia

Year	Area (ha)	Production (tons)	Yield (ton/ha)
2013/14	79947	112089	1.40
2012/13	90156	124419	1.38
2011/12	64477	103479	1.60
2010/11	49603	71607	1.44
2009/10	41579	46425	1.12
2008/09	41761	46887	1.12
2007/08	40198	44685	1.11
2006/07	37126	51080	1.38
2005/06	35462	34150	0.96
2004/05	27084	29053	1.07
Growth	12.8%	16.2%	3%

Source: CSA (2004 – 2014)

In our country, after harvesting the peanuts, they are transported to a processing facility where they are dried and stored. At this point, they are sent to a Sheller, where the shell or hull is separated from the nut. These peanut shells account for approximately 25–30% of the total weight of the dried peanut pod (Manzano-agugliaro 2018), meaning there is a substantial amount of shell residual left after peanut processing.

- **Peanut Shells for Energy**

The peanut industry is one of the main generators of agro industrial waste (shells). This residual biomass has a high energy content that is worth exploring. Different prediction models of the HHV value proposed by scientists for different types of biomass have been analysed and the one that best fits the calculation for the peanut shell has been determined. The CO_2 reduction that would result from the use of peanut shells as an energy source has been evaluated in all production countries (Manzano-agugliaro 2018).

Table 2-6 Quality parameters data of peanut shell samples (Manzano-agugliaro 2018).

Parameters	**Standard value**	**Minimum value**	**Maximum value**
Proximate Analysis (%)			
Moisture content	5.79	5.79	5.79
Ash content	4.26	4.11	4.41
Volatile matter	84.90	83.81	85.99
Fixed carbon	13.40		
Calorific value(MJ/kg)			
HHV	18.547	18.522	18.572
LHV	17.111	17.100	17.122
Ultimate Analysis(%)			
Carbon	46.42	46.413	46.427
Hydrogen	6.61	6.594	6.626
Nitrogen	0.50	0.488	0.512
Sulphur	0.54	0.53	0.55
Oxygen	41.77	39.317	44.223
Chlorine	0.07	0.069	0.071

2.3.4 Advantage of Substituting Conventional Fossil Fuel

Besides the environmental pollution from the combustion of fossil fuel is a serious concern of the world at this time. Thus, a search for alternative sources of energy appears to be an imperative option. For this purpose, the renewable sources of energy are considered to be the most suitable option. Like wind, solar and other renewable energy sources, biomass can make a positive impact on the atmosphere by reducing the dependence on climate change-inducing fossil fuels.

Biomass is now considered to be a contributor of bio-fuels alternative to fossil fuel providing clean energy and value-added products. Biomass has high carbon content; low ash content and it is renewable in nature. Biomass can easily be obtained from agricultural residues or green waste.

Woods and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main renewable energy resources available. Biomass solid wastes are available abundantly in most parts of the world. Mostly these are either unused or underutilized. The disposal of the large amount of the wastes is a problem as well. Thus, biomass is a promising eco-friendly alternative source of renewable energy in the context of current scenario. From the characterization studies of biomass solid wastes, it is found that these wastes have good prospects to be used as feedstock for better energy recovery in the form of solid bio-char, liquid oil and gaseous products. Besides value added products can be obtained from the liquid pyrolysis oil. Also, the char has its potential to be used as fuel (Z. Wang and Li 2017).

The use of agricultural biomass residues in cement manufacturing is less common in industrialized countries and appears to be concentrated in more rural developing regions such as India, Thailand, and Malaysia. The type of biomass utilized by cement plants is highly variable because of its diversity and volume of locally grown. For example, rice husk, corn Stover, hazelnut shells, coconut husks, coffee pods, and palm nut shells are among the many varieties of biomass currently being burned in cement kilns (Chinyama 1998).

Which are a CO_2 neutral fuel as it consumes CO_2 from the atmosphere during its growth which is almost same with the amount of CO_2 released during its combustion (Hyung, Chul, and Jin 2014). Biomass fuels contain between 5-10times less sulphur than fossil fuels. A large difference in sulphur content between fossil fuel exist (Cortada et al. 2014) and it may be required adjust the excess air and burner design. Sometime to make high dense fuel from low-density biomass, high pressure and temperature need to be applied (Rahman et al. 2015) and also, because of rising energy costs, concerns over greenhouse gas emissions and non-renewable nature of fossil fuels have prompted significant research into the conversion of biomass into biofuels by using carbonation due to thermochemical characteristics of selected biomass.

2.4 Thermochemical Conversion

Thermochemical conversion is one of the major technologies used for lignocelluloses biomass. Its technologies for the sustainable integration biomass mainly include gasification, pyrolysis, torrefaction and combustion. Gasification, pyrolysis, and torrefaction are performed in the absence of oxygen or with significantly less oxygen than what is required for complete combustion. The operating conditions (temperature, heating rate, and oxygen supply) and the yield of products varies between these three processes Gasification, pyrolysis, and torrefaction cannot be defined as completely separated processes because, for instance, pyrolysis can be considered as an incomplete gasification process and torrefaction an initial stage of gasification and pyrolysis (Matsakas et al. 2017). Torrefaction is a process where raw biomass is heated under an inert atmosphere within a temperature range of 200-300oC and where the hydroxyl groups are removed (Magdziarz 2017). Whereas, Combustion is naturally also a thermochemical conversion process, completely oxidation of the fuel and while releasing heating or transferred into heat. In thermochemical conversion, High temperature pyrolysis (order of 1000°C) maximizes the production of gas (gasification) while lower temperature pyrolysis processes (<600°C) have been used for the production of charcoal (carbonization).

2.4.1 Thermogravimetric Analyzer

Thermogravimetric analyzer (TGA)is used to study the pyrolysis and kinetics characteristics of biomass in different experimental conditions (Cai, Wang, and Wang 2015). Its technique used to determine the weight loss of a material in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere(Antero 2006). The output data from TGA are normally used to construct a thermogravimetric (TG) curve, from which the mass losses versus temperature or time can be observed.

2.4.2 Pyrolysis

Pyrolysis is the basic thermochemical process to convert biomass into more convenient products. Conventional pyrolysis involves heating the original material in the absence of oxygen at moderate temperature (350 - 600°C), until the volatile matters has been driven off (Truong, My, and Le 2015).

During the pyrolysis process, the lignocelluloses (cellulose, hemicelluloses and lignin) biomass is pyrolysis at different rates by different mechanisms and pathways. Lignin decomposes over a wider temperature range compared to cellulose and hemicelluloses which rapidly degrade over narrower temperature ranges. Hence there is an apparent thermal stability of lignin during pyrolysis. Additionally, each component of the natural polymeric constituents and long chains of carbon, hydrogen and oxygen compounds in biomass thermally break down into smaller molecules in the form of gases, condensable vapours (tars and oils) and solid charcoal under pyrolysis conditions (Jahirul et al. 2012).Depending on the reaction temperature, heating rate and residence time, pyrolysis can be classified into fast pyrolysis, slow pyrolysis (carbonization) and hydrothermal carbonization(Lin, Yan, and Sheng 2016).

➢ Fast Pyrolysis:

Fast pyrolysis used to produce Bio-Oil and Gas, the basic characteristics of the fast pyrolysis process is, biomass is rapidly heated (1000-10,000 ºC/s) at elevated temperature around 650 to 1,000ºC very short vapour residence time for 2s, rapid cooling of vapours and for high bio-oil yield and precision control of reaction temperature. a commonly used spiral quenching heat exchanger with electrostatic precipitator was applied to condense volatile gases issuing from the reactor (Choi, Choi, and Park 2012). Which is used to get 75 wt.% bio oil, 15 wt.% solid, and 10 wt.% gases (Sohaib et al. 2017).

➢ Hydrothermal carbonization

Hydrothermal carbonization (HTC) is a pressurized, low temperature thermal conversion. Water is used to crack biomass in order to produce bio-oil with reduced oxygen content because the hydrogen molecules bind to the decomposed hydrocarbons in a manner that increases the volatile (gaseous) yield of light hydrocarbons. There is currently a project that is using this process to convert biomass into hydrocarbons for fuel production. The solids content of the biomass feedstock is recommended between 5 and 35% wt. because of the ease of mixing and the flow of material (Malảák and Dlabaja 2015).

➢ Slow Pyrolysis

Slow pyrolysis primarily to produce Char through Carbonization. It is thermal decomposition of the carbohydrate structure of the biomass into carbonaceous solid residue (biochar), and condensable and non-condensable vapours of various molecular weight compounds (Burnette et al. 2010). This process is divided into four stages. The first stage is to heat biomass at the temperature of 180° C. The second stage involves the removal of volatiles by heating biomass at the temperature ranging from 180 to 280°C. When the temperature reaches 280°C, the full decomposition of hemicelluloses occurs. Third stage, the biomass that has been derived is then converted into charcoal. This stage needs temperature ranging from approximately 280 to 400°C which enables self-decomposition biomass through exothermic reaction. Celluloses in the biomass rapidly decompose at 280°C, and this stage results in white and yellow yield with pungent smell. This yield gives high quality wood vinegar if condensed. Moreover, in this stage, lignin decomposes at approximate temperatures of 310 to 400°C over a long period of time to maximize char formation. At the temperature higher than 400°C, biomass is entirely converted into charcoal. Finally, removing tar which is performed at the last stage will improve the quality of charcoal. Tar lowers the quality of charcoal, and if burned, it changes into two carcinogenic substances, those are, benzopyrene and dibenzanthracene. Therefore, charcoal is dried at 450°C to 600°C for a certain period of time in order to remove tar (Saptoadi and Wibisono 2016). Depending on the feedstock, heating rate and temperature, different distributions and yields of the aforementioned fractions can be obtained (Rosse et al. 2013).

2.4.2.1 Effects of Operating Parameters on Carbonization

In the conversion of biomass to char, it has been discovered that types of feedstock the operating conditions such as the heating rate, the pyrolysis temperature, and the pyrolysis time influence char yield.

- **Biomass Type**

Major constituents of Biomass are: Cellulose, Hemi-cellulose and Lignin. Cellulose at 150 to 350°C turns into condensable vapour (tar), Hemi-cellulose at 275 to 350°C yields primarily non-condensable vapour and Lignin at 250 to 500°C degrades slowly into char and liquid yield.

Chemical Properties and proximate analyses for all samples were performed in duplicate, following American Society for Testing and Materials (ASTM) method by using a thermogravimetric analyzer (Yan 2011) to investigate weight loss. After the determination of moisture, ash, and volatile matter, the fixed carbon content was calculated by difference.

- **Heating Rate**

Rapid heating to a moderate temperature (400-600ºC) will produce higher volatiles and increased oil production.

- **Pyrolysis Temperature/Residence Time**

The yield of biochar will decrease with increasing temperature. The individual products have complex relationship between the residence time and temperature. However, the proportion of weight loss is different in biochar produced from different sources of biomass, which is related to the contents of hemicellulose, cellulose, and lignin. Therefore, the yield of biochar is negatively correlated with pyrolysis temperature and residence time (Cao, Chen, and Meng 2018).

2.4.3 Process Technology of Pyrolysis Biomass Production

The established large scale technology which is suitable for heat production in cement kilns. It is currently the highest volume bio energy market worldwide. All pyrolysis reactors have definite feedstock size limitations for effective heat transfer and smooth operation. size. Therefore, biomass has to be prepared to the desired size by cutting and grinding operations. In addition to sizing, the biomass materials need to be dried to moisture content, after drying and grinding, the biomass is fed into the reactor and the carbonation process takes place.

The process description of the below schematic flow diagram in figure 2.4 is described as follows. Preceding to carbonization, biomass residues have to undergo a number of stages including collection, storage, cleaning, drying, and size reduction. Depending on the residue, each of the below stages will require a certain expenditure on equipment, materials and labor.

- **Feed Preparation**

The collection or reception of the raw material can be a major component of the carbonation process. The selected biomass residue tends to be widely spread in the fields and must be collected and transported to a location where it will be further processed for pyrolysis.

Cleaning/screening Cleaning is the same as screening for foreign materials such as stones and metal. The raw materials have to be screened for stones and pieces of metals that could reduce the quality of product.

High water content in biomass has an adverse effect on the pyrolysis process and on the calorific value. In general, a proper pyrolysis process needs moisture content below <14 wt% (Schindler et al. 2012). Therefore, biomass should undergo a thorough drying process to reduce the water content to suitable size reduction before carbonation is carried out. In contrast, high temperature during the drying process could be a critical issue for the possibility of producing thermal-oxidative reactions, causing a higher thermal stability of the biomass complex. (Jahirul et al. 2012) conducted an investigation on the effect of the biomass drying process temperature and duration on the properties, chemical composition and yield of pyrolysis product. The method of drying will depend on several factors, including environmental conditions, the initial moisture content of the material, the level of throughput, the size of the material, etc. The results of their study showed that the increase of drying temperature influenced the yield of pyrolysis products, while the increase in the drying time did not affect it. The biomass is then ground to 2–6 mm particle size to yield sufficiently small particles, ensuring rapid reaction in the pyrolysis reactor. Feedstock size reduction is usually achieved with a hammer mill and cutter as the properties of residue.

- **Carbonization Process**

The process of pyrolysis of organic matter is very complex and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. In this process; thermal decomposition of organic components in biomass starts at 350 °C–550 °C and goes up to 700 °C–800 °C in the absence of air/oxygen. The long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the form of gases, condensable vapours (tars and oils) and solid charcoal under pyrolysis conditions. Rate and extent of decomposition of each of these components depends on the process parameters of the reactor (pyrolysis) temperature, biomass heating rate, pressure, reactor configuration and feedstock. Relative proportions of the end products after pyrolysis of biomass at a range of temperatures and residence time. However, pyrolysis processes cannot be limited to a single reaction path because of widely varying structure and compositional properties of biomass.

Cooling carbonized material, as they leave the reactor, are quite hot. Therefore, they must be cooled before they are ready for use. Finally, storage the carbonized raw material should be stored in a good place. The type of storage required will depend on the environmental conditions it is subjected to. Usually, the carbonized raw material will be stored in an open-air heap, a shed, a bin or within retaining walls or fences. closed or sheltered storage is necessary to prevent the material from getting wet.

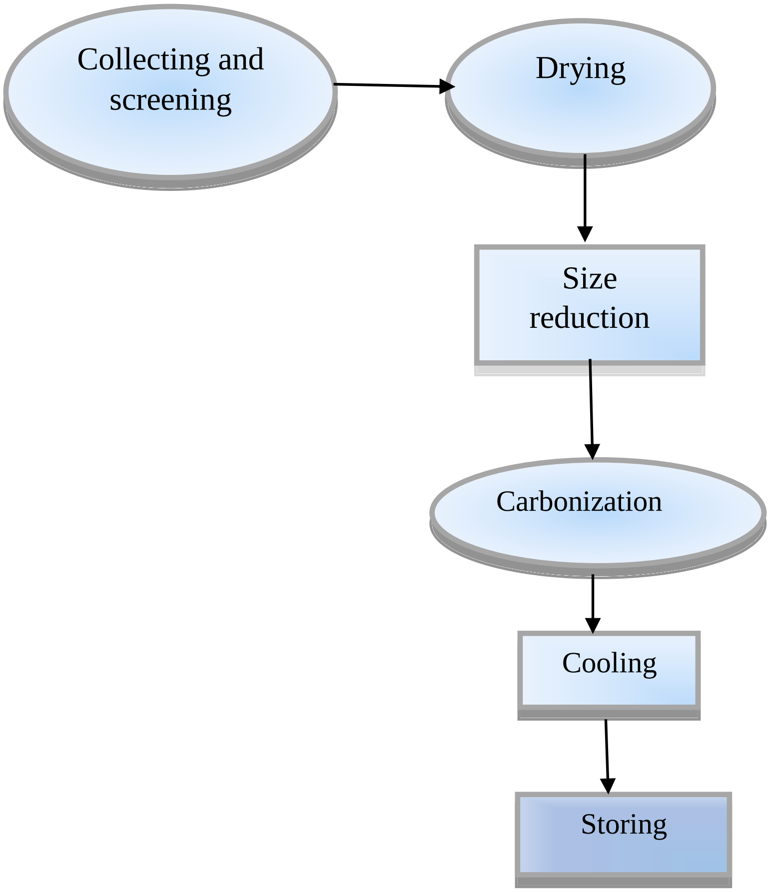


Figure 2.3 Schematic Process flow diagram of carbonization

2.5 Gap on Literature Retrieval

The Institutional documents, the social and economic impact of the use of alternative energy sources in cement manufacturing were not recognized. In addition, none of the institutional documents that were retrieved analyzed the social impact of using alternative fuels, some document dealing with social impacts was found among the institutional reports repossessed and little information was found in practitioner reports, but this was considered insufficient for a comprehensive knowledge of the topic.

More specifics about the costs related to the use of alternative fuels in cement kilns are required. Sustainability reports from practitioners provided detailed data about emissions. However, these reports averaged data based on all the cement plants belonging to a specific organization; as such, it is difficult to understand, in detail, the contribution made by alternative fuels to the reduction or increase of emissions. In addition, studies on life cycle assessment of alternative fuels and case study in cement industries are not identified which implies that more studies on life cycle assessment of alternative fuels have to be researched in different countries.

Typically, certain kinds of biomass (namely waste from industrial or agricultural processes) are less costly than fossil fuels, and therefore reduce fuel costs. In cement plants less than 15 to 20% of the energy consumed from alternative fuels recommended, although the causes of these measures are not clearly detailed.

For the other alternative fuels considered, the documents retrieved made a comparison among a subset of the possible end-of-life options, highlighting another gap in the literature. Researchers findings about the physiochemical properties related to the use of different alternative fuels are available especially calorific value and chemical properties but a gap on chemical property (ultimate analysis) and feeding position of these alternative fuels in cement kilns were noticed. Therefore, more researches on mechanisms of feeding these alternative fuels and their effects on gas emissions in the kiln must also be investigated in order to increase the consistency of findings and to give a knowledge and confirmation.

3 MATERIALS AND METHODS

3.1 Materials

The residue of peanut and chat (peanut shell and chat stem) that have been used in this study were found in the eastern part of Ethiopia. The peanut shell was collected from farmers of Babile while chat stem was collected from the market place of Awoday on street in plastic bags. Molasses was also obtained from Mojo Sugar factory for use as binding agent in formation of mixed charcoals of peanut shell and chat stem and transported to Addis Abeba. The experimental work was began in December 2017 and ended in Juley 2018.

The equipment used during sample preparation and experimentation were jaw crusher, grinder, sieves, volumetric flask, funnel, porcelain dish, pipette, burette, beakers, hot plate or Bunsen burner, electronic balance, ceramic and silver crucibles, drying oven, muffle furnace, desiccators, 5E Automatic proximate analyzer, thermogravimetric analyzer, stainless steel tubular reactor (carbonizer), pelletizer, elemental analyzer (EA 1112 Flash CHNS/O- analyzer) and oxygen bomb calorimeter (IKAC®5000 Calorimeter System).

Chemicals and reagents used during experiments were sodium hydroxide, hydrochloric acid, nitric acid, potassium fluoride, potassium chloride, potassium bromide, phenolphthalein, copper sulfate, triethanolamine(TEA), ethylenediaminetetraacetic acid (EDTA), distilled water, ethanol and ammonium hydroxide. All chemicals were analytical reagent grades and obtained from National Cement Share Company and Geological Survey.

3.2 Methods

3.2.1 Raw Sample Preparation

The collected raw materials were first cleaned from dust and leaf and then dried by the sun. The cleaned materials were then ground by crusher and disc grinder into small particles in the range of required size prepared for each type of characterization.

Experiments were conducted in different laboratory institutions. Proximate analysis to know the characteristics and property of the raw materials in relation to their energy content, carbonization process and pelletization were done at the School of Chemical and Bio engineering laboratory (AAiT), Calorific value and ash chemistry were conducted at Geological Survey and National Cement Share Company, located in Dire Dawa in order to examine the heating value and the contents of useful minerals such as calcium, silica, alumina, magnesia and iron oxides which can be used as a supplementary material. Elemental analysis was done at Addis Ababa College of Natural Science (AACNS) in order to know the elemental composition of the materials. Thermo gravimetric analysis of Peanut shell and chat stem samples were done at Leather Industry Development Institute in order to examine the combustion characteristics and weight loss of the product with increasing temperature.

3.2.2 Characterizations of samples

I. Proximate analysis

Proximate analysis was conducted per ASTM procedure for the determination of the parameters ash content, moisture content, volatile matter and fixed carbon of peanut shell, chat stem, their mixed carbonized sample and pellet. ASTM standards are chosen because of their instrumentality in specifying the standard dimensions and make use of the various instruments.

Moisture content may be present as adsorbed water on the external surface of samples. That content obtained by a method of (ASTM E871-82, 1998). Ash content is the inorganic solid residue left after the fuel is completely burned. Its primary ingredients are silica, aluminum, iron, and calcium; small amounts of magnesium, titanium, sodium, and potassium may also be present, it was determined by (ASTM D1102-84, 2001). And also volatile matter consists mainly of the combustible gases such as hydrogen, carbon monoxide, and hydrocarbon, as well as incombustible gases and vapor, are liberated from the sample when it was heated at high temperature, which determined by (ASTM E872-82, 1998). Finally, the percentage fixed carbon (PFC) was computed by subtracting the sum of the percentage of ash content, moisture content and volatile matter from 100. All the above methods detail described in Appendix A.

I. Determination of Calorific Value

The calorific value of samples was determined by using IKA C® 5000 Calorimeter System. First, prepare dried biomass and mixed carbonized sample powdered was determined by pelletizing 1g of samples and record the weight of prepared sample on screen. The decomposition vessel is fitted with a permanent ignition wire. Align the cotton thread with a pair of tweezers so that it is suspended into the crucible in order to initiate the combustion process, a cotton thread must be attached to the ignition wire. Then 1g pelletized prepared sample charge into crucible it must be well touched. This ensured that the burning thread ignites the sample during the ignition process. Close the decomposition vessel with additional amounts of distilled water then loaded on calorimetry finally the calorimeter would be ready to analysis.

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

3.2.3 Determination of Ash Composition

Determination of ash composition found in samples was done by using the colorimetric method (wet chemical analysis) in order to determine the amount of different oxides present such as SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO and sulfur. This method was selected because it can provide qualitative and quantitative data about oxides in the test sample.

Before the resolution of the above-mentioned major oxides, first, the samples prepared by measuring 0.3g of all samples ash was prepared separately at 950^0C in a muffle furnace for 1 hour and cooled in a desiccator. Then 7-8g of fusion mixture sodium hydroxide pellet and 0.3g of ash sample were weighed in a silver crucible and then melted in a muffle furnace at 650^0C for 20 minutes. After bathing the crucible by cooled distilled water, the melted solution was fused into prepared 100-125ml of boiled distilled water and dissolved in 250ml. 25ml of HCl was prepared and mixed with a dissolved solution. Then the crucibles were rinsed by 1:1 (HCl to water) for removing stick particles in the silver crucible. 1ml of nitric acid dissolved in solution, after very well mixing, it was boiled at 300^0C. Then the boiled solution was immersed in cool water, then put in the flask by added distilled water until prepared 250ml of solution for determined oxide analysis (SiO_3, CaO, MgO, Fe_2O_3 and Al_2O_3).

❖ Silicon oxide analysis

From above prepared solution, 50 ml solution was measured in to 250ml plastic cup.12 ml of concentrated HNO_3 was added and Cool the solution in cold water bath. after this,10ml of KF (150 g/l) was added to maximize the SiO_2 content and spatulas solid potassium chloride (KCl), was inserted until it can't well dissolved or gets saturated and the solution was filtered using filter paper and it put in to previous plastic beaker mix with 10 ml of potassium chloride with alcohol ($KCl+CH_3CH_2OH$) and 3 drops indicator of phenolphthalein were added to the solution Until pink color appear titrates by NaOH (0.15 g/l) then, hot pink water was added up to a 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. After all these experimental procedures were done, determine of $SiO_2$was obtained by eqn.3.1.

$$\%SiO_2 = (W_2 - W_1) - (W_3 - W_1) * 200 \text{…………}3.1$$

Where: W_1= weight of crucible
W_2 = weight of the ignited crucible
W_3 = weight of crucible with evaporation residue
200 = because the starting sample was 0.5g

❖ Iron oxide analysis

50 ml of solution was diluted with 50ml distilled water in a beaker. Mix 10 drops of Sulfosalicylic acid, ammonium hydroxide NH_3OH (1 gm/l) was added to the solution until look

like yellow color and dissolve hydrochloric acid (HCl) until pH value adjusted to 1.8- 2, then heated the solution up to 70^{0}C used by thermoset. Then, endpoint determination obtained was titrated by EDTA (0.015 mol/l) until colorless effect. Equation 3.2 formula which was used to determine

$$\%Fe_2O_3 = (0.7985)(F_{EDTA})(V_{EDTA}) \ldots\ldots\ldots\ldots 3.2$$

Where F_{EDTA} = the factor of EDTA and

V_{EDTA} = volume of EDTA used to endpoint

❖ Aluminum oxide analysis

After Fe_2O_3 was determined, add distilled water up to 200ml into colorless solution (left solution from Fe_2O_3). 15 ml mixture solution of acetic acid and sodium acetate (PH = 4.3) was added into a diluted solution then heated up to 90^{0}C. While stirring, 5-6 drops PAN indicator was added to the solution which was titrated by copper sulfate ($CuSO_4$, 0.015mol/l). Finally, endpoint determination was obtained changing the color from yellow into violet. Equation 3.3 formula which was used to determine

$$\%\,Al_2O_3 = (0.5098)(F_{EDTA})(V_{EDTA}) \ldots\ldots\ldots\ldots 3.3$$

❖ Calcium oxide analysis

25 ml of solution was pipetted into a beaker. 7 ml of KF (20 g/l) was added to the solution and wait for 5 minutes. The solution was diluted up to 200 ml. To mask the Fe_2O_3 and Al_2O_3, 5 ml of TEA (triethanolamine), add CMP indicator until changing color fluorescence and 20 ml of KOH 200g/l was added to the solution. Finally, the solution was changed into pink when it was titrated by EDTA. Equation 3.4 formula which was used to determine

$$\%CaO = 2.2432F_{EDTA}(V_{EDTA}) \ldots\ldots\ldots\ldots 3.4$$

❖ Magnesium oxide analysis

25 ml of solution was pipetted into a beaker and diluted with 200 ml of distilled water then, 2 ml of sodium tartrate, 5 ml of TEA, 25ml of ammonia hydroxide (pH adjusted to 10) and KB

indicator were added until the result color light pink. Then the solution was titrated by EDTA until changed into blue color.

$$\%MgO = (1.6128)(F_{EDTA})(V_{EDTA}) \ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

- **Determination of SO_3**

0.5gm of the sample was placed in a beaker. 25ml of distilled water & 13ml of concentration. HCl was added. Lumps were broken with the glass rod and heated to boiling. 100ml of boiled distilled water was also added. It was then filtered immediately with a medium filter paper and washed several times with hot water. The filtrate was then heated to boiling, while a glass rod & piece of filter paper was placed in it. 10ml of the $BaCl_2$ solution was added slowly and then removed from the hot plate & stirred well. 50 to 60ml of congo-red was also added and stirred well. After that, it was left for some minutes (20 to 25) for settlement. Clear upper layer showed that enough amount of congo-red was added; otherwise additional amount might have been needed. After the settlement, it was filtered through fine filter paper and the residue was washed with several times with hot water. The precipitate was first placed in a previously weighed crucible and then placed on a hot plate until the paper blackens. Finally, it was ignited in a muffle furnace controlled at 950±50 for an hour and then cooled in a desiccator & weighed.

$$\%\,SO_3 = \frac{(A-B)*0.343}{W} * 100 \ldots\ldots\ldots\ldots\ldots 3.6$$

Where: - A= weight of crucible and crucible

B = weight of empty crucible

W = weight of the sample 0.343 the factor between $BaSO_4$& SO_3

3.2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using a SDT Q600. To maintain pyrolysis (carbonization) conditions, the samples were analyzed by purging Nitrogen at a flow rate of 100 ml/min to remove all corrosive gases and avoid thermoxidative degradation. The pulverized samples weighed of chat stem and peanut shell were measured 41.2280mg and 46.7890mg respectively. The prepared samples loaded to platinum pans located in an autosampler tray and allowed to be heated from ambient temperature to 1200°C by setting the heating rate of 20˚C/min. Which was controlled from a remote desktop that was also used to record the weight of the sample as a function of increasing temperature, it was run using a software-controlled program.

3.2.5 Carbonization of a Peanut Shell and Chat Stem

The carbonization experiments were started from, first, the Peanut shell and Chat stem meshed with particle size 2-4mm and prepared the percentages of blending (mixed ratio) peanut shell to chat stem. The horizontal tubular stainless-steel reactor (carbonizer) equipped with a temperature controller and inert atmospheric nitrogen flow gas used to purge the oxygen from the reactor at 10°C/min of heating rate. The carbonization process was carried out by taking an initially 50g weighted sample of mixed ratio into the tubular furnace. The experiments were carried out three factors (temperature, residence time and mixed ratio) with three levels were controlled to see their effect on carbonization results. Temperature effect was maintained three levels at 350, 450 and 550°C according to the TGA with a corresponding time level for 60, 90 and 120 minute according to Xiwen (2016) and arranged mixed ratio level of 25, 50 and 75% for the mentioned temperatures, residence times and a mixed ratio under slow heating rate at 10°C/ min. After carbonization, the solid char was removed from inside reactor and determined the calorific value.

3.2.6 Design expert

Response surface methodology (RSM) is an empirical modeling approach for determining the relationship between various operation variables and response variables. It provides a sequential experimentation strategy for building and optimizing an empirical model. The objective is to optimize these variables taking into account the desired value of the response function.

The data were to be analyzed and processed with the use of Design-Expert 7.0.0 software. CCD experimental design with three numerical factors on three levels was used Temperature, residence time and the ratio of the sample raw materials was the main parameter for the carbonize process. As mentioned below on table 3.1, the experiment performed as a completely randomized design with three factors at three levels and one response. The response considers during optimization of the process is calorific value.

The design was applied to evaluate the effect of these three factors on calorific value and to optimized the parameters after studying the influence of dependent and independent variable on carbonized samples.

Table 3-1 Levels of independent variables based on Central Compost Design

Code symbol	Independent variable	Units	Minimum	Center point	Maximum
A	Temperature	^{O}C	350	450	550
B	Time	Min	60	90	120
C	Ratio	%	25	50	75

This design of the experiment helps us to differentiate the significance of the main and the interaction factors. CCD experimental design with three numerical factors on three levels was used and the experiments were carried out 20 runs, according to the number given by the statistical software. This design consisted of fourteen randomized runs with six replicates at the central point to minimize the error. Detail of the experimental runs with the set of input parameters that were conducted is given in below table 3.2.

Table 3-2 Three factors and levels face centered quadratic design with six centered point formulation

Run	Factors		
	Temperature (^{O}C)	Time (min)	Ratio (%)
1	350.00	60.00	25
2	550.00	60.00	25
3	350.00	120.00	25
4	550.00	120.00	25
5	350.00	60.00	75
6	550.00	60.00	75
7	350.00	120.00	75
8	550.00	120.00	75
9	350.00	90.00	50
10	550.00	90.00	50
11	450.00	60.00	50
12	450.00	120.00	50
13	450.00	90.00	25
14	450.00	90.00	75
15	450.00	90.00	50
16	450.00	90.00	50
17	450.00	90.00	50
18	450.00	90.00	50
19	450.00	90.00	50
20	450.00	90.00	50

3.2.7 Optimization

The optimization module in Design-Expert 7.0.0 searches for a combination of factor and levels that simultaneously satisfy the requirements placed on each of the responses and factors. To use optimization, first, it has to analyze each response to establish the appropriate model due to the engineering perspective and cost benefit.

3.2.8 Pelletization

After optimization, the optimum mixed carbonized sample was ground, sieved less than 120µm mesh size. The prepared pulverized samples were mixed with molasses of 10% and 20% for binding agent and well homogenized individually. Then 1 g of the measured mixture sample was put into the cylindrical shape of pellet diameter of less than 2 mm and with no more than 20 mm length using the press at 100 bar pelletizer according to (Pellet Fuels Institute Standard Specifications for Residential/Commercial Densified Fuel 2015). After compressed manually and waited for 15 min then the pelletized sample was taken out from the cylindrical shape holder and put in a vial. Then compare both the mixed carbonized pellets with coal by examine the bulk density and calorific value. Finally, the selected optimum mixed carbonized pellet sample prepared were further characterized to understand their physical and chemical characteristics.

3.2.9 Elemental Analysis

The determination of important chemical elements that make up biomass, namely carbon, hydrogen, oxygen, nitrogen, and sulfur was determined through ultimate analysis. These properties were determined in accordance with ASTM analytical methods using elemental analyzer (EA 1112 Flash CHNS/O- analyzer) in AACNS.

The optimum sample of 1.5 to 2.5 mg was weighed in a tin capsule and loaded in Device. The tin was then dropped into the high heat oxygen environment of the combustion tube. A carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900°C and an oven temperature of 75°C then created a dynamic exothermic reaction. The sample was first oxidized in a pure oxygen environment. Final products produced in the combustion zone included CO_2, H_2O and N_2 and S. Element such as halogens was removed by scrubbing reagents in the combustion zone. The resulting gases were then homogenized and controlled to exact conditions of pressure, temperature and volume. N_2, S_2, CO_2, and H_2O were moved by helium into the column, separated by a frontal chromatography and detected by a thermal conductivity detector. The whole procedure was controlled by a microprocessor taking into account data from analysis of blanks, internal and external standards. The sample was run in duplicate by taking six calibration points for every component and the average values were to be taken.

4 RESULTS AND DISCUSSION

4.1 Characterization of Raw Samples

Proximate Analysis

Parameters include moisture content, volatile matter, ash content fixed carbon and calorific value

Table 4-1 Proximate analysis of peanut shell and chat stem

Raw sample	Moisture content (%)	Volatile matter (%)	Ash content (%)	Fixed carbon	Calorific value (Cal/gm.)
Peanut shell	3.25 – 3.93	75.61 – 78.01	2.02 – 2.44	15.62–19.12	4691
Chat stem	2.68 – 3.01	77.24 – 80	1.48 – 1.56	15.43 – 18.6	4497

I. Moisture content

For the solid alternative fuel, the calorific value depends on the moisture content. As we have seen from the above table 4.1 shows, the moisture content of Peanut shell and chat stem were range from 3.25% to 3.93% and 2.68% to 3.01% respectively. The values found were very small which can be confirmed with the fact that high moisture content lowers the calorific value of biomass residue (Patel and Gami 2012). This results indicated that the moisture contained in both samples wouldn't hinder ignition and slow the rate of combustion to a large extent since there was no excessive moisture in the material.

II. Ash content

The amount of ash content is an important property since it influences the reactivity of the fuel and lowering the calorific value. According to (Schindler et al. 2012) the ash content of alternative fuels must be < 18%. From the above table, the ash content of Peanut shell and chat stem was found to be 2.02% to 2.44% and 1.48% to 1.56% respectively and both the result showed that a lower percentage. Insoluble compounds act as a heat sink in the same way as moisture, lowering combustion efficiency which favors in the formation of char (Demirbas

2010). Therefore, from this fact, we can say that the presence of soluble ionic compounds which have a catalytic effect on combustion of these raw materials is high.

III. Volatile matter

The other convenient parameter is a volatile matter which provides a rough indication of the reactivity or combustibility of the fuel. This property also helps in the estimation of the length of a flame. The result of the volatile content of Peanut shell and chat stem was found to be in table 4.1 75.61% to 78.01% and 77.24% to 80% respectively. According to the result, the chat stem content of volatile is higher than peanut shell and this is a result of lower lignin content but may burn with a smoky flame. This indicates that chat stem can easily ignite under low temperature and will have high flame length. According to Chiniyam (1998), if the alternative fuels have highly volatile matter the calorific value will be less due to their relatively low combustion temperatures hence peanut shell will have high calorific value rather than chat stem.

IV. Fixed carbon

Moreover, the fixed carbon content was obtained which gives a rough estimation of the heating value of a fuel and acts as the main source of heat capacity during burning. If the amount of moisture, volatile matter and ash content is high the fixed carbon content of a sample is small that conclude from the result obtained. From table 4.1 the fixed carbon content was determined to be 19.12% to 15.62% and 15.43 to 18.6% for peanut shell and chat stem respectively. According to the result, the fixed carbon content of peanut shell is higher than the chat stem. And it is expected that the calorific value of a peanut shell will be high. This means the fixed carbon content has a direct relationship with the calorific value.

V. Calorific value

The result of the calorific value shows in table 4.1 that peanut shell is 4691 Cal/g. The reason for the value of this much calorific value was due to its elemental composition and its fixed carbon. On the other hand, the calorific value of chat stem is 4497 Cal/g and this result was low when compared with that of the peanut shell. And this is the reason for the high volatile matter and low fixed carbon. These parameters were the main factor which affected the result to have low calorific value. Therefore, in order to enhance the gross heat of combustion, it is suggested to carbonize (Solomon 2016) by mixing the peanut shell and chat stem together. According to table 4.3, the calorific value of the mixed carbonized sample is 5068cal/g to 7757.11cal/g.

4.2 Ash Composition of Peanut shell and Chat stem

Clinker is constituent of oxides, obtained from lime stone and clay including CaO, SiO_2, Al_2O_3 and Fe_2O_3. Approximately 95 percent of clinker consists of these major oxides and the remainder consist called minor constituents. When coal is fired in cement kilns, the ash is incorporated into the clinker, therefore, it is important to adjust the composition of the raw material of lime stone and clay to the ashes (raw mix design) so that this inclusion does not change the quality of the final product (clinker). Ash has an important impact on the quality and the technical operation of pyro-processing for the use of fuel. It is carried along by combustion products, and since which is not combustible and eliminated on post firing.

The use of alternative materials in clinker recipe requires a cautious approach as any alteration in cement's chemistry even if when present in small amounts (< 1percent) will affect the quality of the end product or clinker and stability of production process (Mikul 2016). The composition and properties of the clinker, as well as the end product, must conform to technical specifications.

Weight concentrations of major oxide vary greatly between biomass species. Typically, herbaceous biomass has higher concentrations of silica and lower concentrations of calcium compared to woody biomass (Nyberg 2012). According to Kaddatz (2013), it was found that the use of these biofuels was beneficial to the process. The below table 4.2 result was obtained from the residue ash of peanut shell and chat stem by wet analysis. To resolution raw mix design which (limestone and clay) is feeding rate will depend on the oxide analysis result.

Table 4-2 Ash composition of Peanut shell and Chat stem

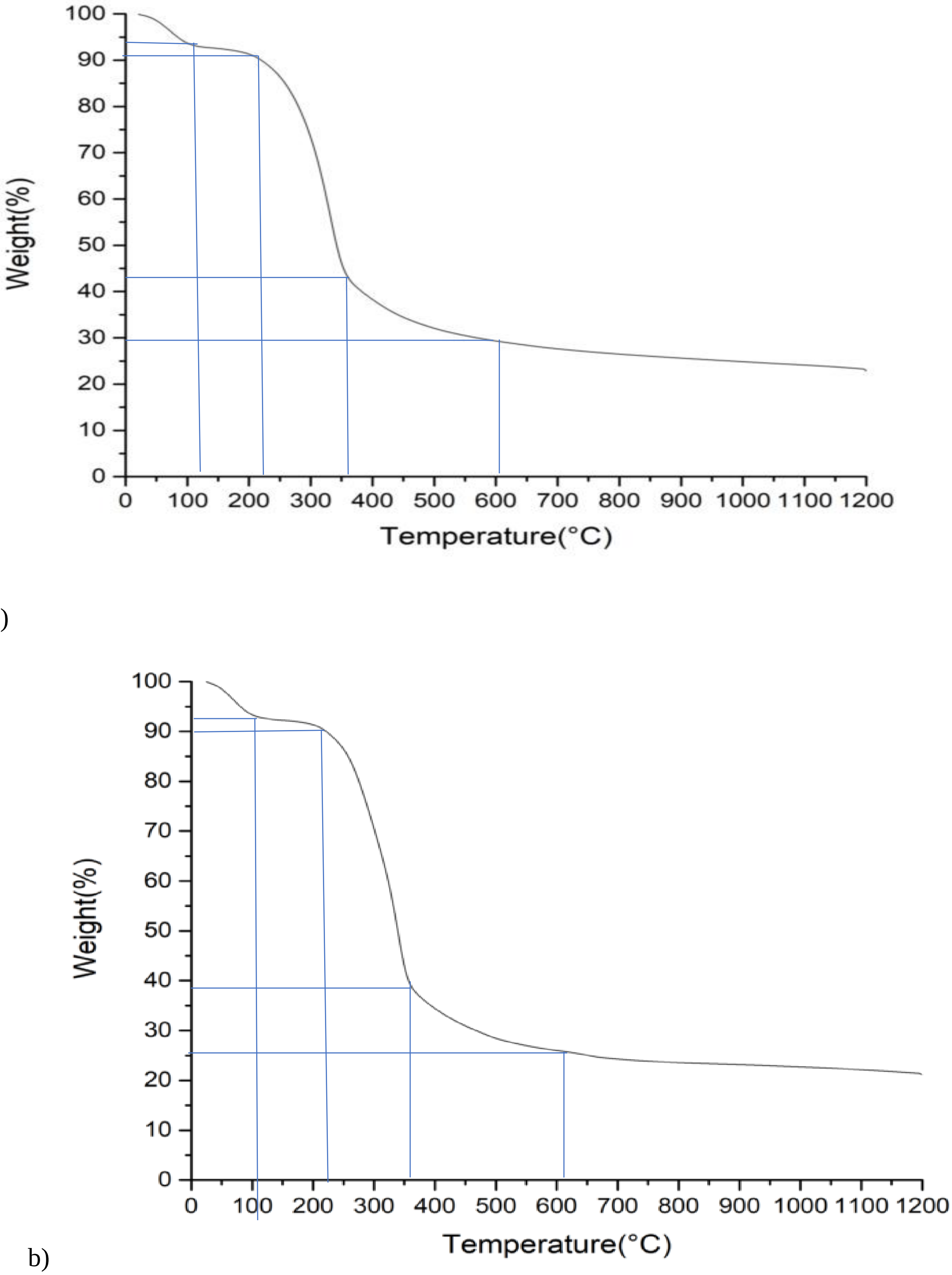
Raw samples	**%SiO_2**	**%Al_2O_3**	**%Fe_2O_3**	**%CaO**	**%MgO**	**%SO_3**
Peanut shell	23.74	10.22	5.82	15.78	11.55	0.16
Chat stem	6.78	1.03	0.6	57.78	14.38	0.23

As we can observe from the above results, the silica content of the peanut shell was found to be higher than that of the chat stem. Similarly, a research by (Rizvi et al. 2014) found a higher 35.26% silica content that was conducted by using x-ray fluorescence. And it was also described in the document that most biomasses like miscanthus husk, peanut shell and wood pine have significant silicon oxide content.

The calorific value of chat stem less when compare with peanut shell may be due to the content of calcium oxide, a non-combustible substance (Jittabut 2015). Therefore, in order to enhance the gross heat of combustion, it is suggested to utilize the chat stem by mixing it together with other properly selected biomass wastes.

4.3 Thermogravimetric Analysis Pyrolysis Characteristics

The thermogavimetric analysis in general means the measurement of the weight loss during the temperature of a sample is changed over time or heating process. At different heat rates, the mass loss characteristics showed a slight difference. At low heating rates, mass loss rate increased with the heating rate increases and the maximum mass loss rate occurred at a higher temperature. The residue mass of each species varied slightly with the heating rates. The weight loss occurred due to the removal of specific components of the sample such as water, carbonates, aluminates, silicates, oxides, organic carbon and other components under thermal degradation (Antero 2006).



a)

b)

Figure 4.1 Thermogavimetric curves of biomass pyrolysis: a) Peanut shell b) Chat stem

As observed from the TG curves in Figure 4.1 (a and b), the thermal decomposition of a peanut shell and chat stem are similar follows ramp mechanism. Both of similar curve of TG result was also obtained by (Solomon 2016) on Preparation of Prosopis juliflora Charcoal and the study of its use as energy mix in cement industries. The samples weight loss of both species is similar but varied slightly each other with the temperature rates. The first weight loss mainly occurs below120^{o}C. Further mass loss up to 230^{o}C was observed in second carbonization stage due to the removal of remaining moisture and volatile matter.

As we can see from figure 4.1, the third carbonization stage is located within 230 to 350^{o}C at which the maximum weight loss rate appears. High devolatilization of hemicellulose, cellulose, and lignin can be achieved in this temperature zone. As shown in fig the peanut shell was more than those of chat stem corresponding with more volatile in chat stem, as Table 4.1 showed. It was mainly due to higher hemicellulose in chat stem because hemicellulose pyrolyzed at around 210 to 320^{o}C (Meng et al. 2014). The temperature with the maximum mass loss rate of peanut shell was lower than that of chat stem. It might due to higher lignin content in a peanut shell. Furthermore, the largest weight loss of both samples takes place in third carbonization stage. Besides, with the temperature corresponding to the maximum decomposition rate shows a tendency to shift towards a higher temperature region, and this is in good agreement with respect to (Xiwen et al. 2016) who reported that a shift on the TG curves to higher temperature zones.

It is clearly observed during the pyrolysis of peanut shell the weighting loss was increased. When the temperature is higher than 350°C, it also can be found that the decomposition of the samples proceeds at a slow rate, which is associated with the pyrolysis of lignin at high temperatures. Both samples of a slow pyrolytic process of weight loss were almost similar after 600°C as observed on the TG curve.

As we can see from the Fig. 4.1, most of the volatile mass of the samples evolved before 350℃. Only about a quarter of the mass of the sample decomposed between 350 and 600°C, above 70% of them were lost before 600℃. It is therefore suggested that biochar production should be carried out at a temperature higher than 350°C but lower than 600°C for economical reason.

4.4 Experimental Design Results

4.4.1 Analysis of Variance

To improve the good calorific value of raw materials intended for suitable as an alternative energy source for cement production were studied determine the value of important parameters such as Temperature, Time and the Mixed ratio (peanut shell to chat stem). The response result of calorific value determine by three factors at three level is showed in table 4.3.

Table 4-3 Experimental design and response (calorific value)

Standard order	**Factor 1 A=Temperature ºC**	**Factor 2 B=Time min**	**Factor 3 C=Mixed ratio %**	**Response Calorific value Cal/g**
1	350	60	25	5068
2	550	60	25	7156.68
3	350	120	25	5558
4	550	120	25	7556.21
5	350	60	75	5162
6	550	60	75	7329
7	350	120	75	6205
8	550	120	75	7757.11
9	350	90	50	5495
10	550	90	50	7416.31
11	450	60	50	6346
12	450	120	50	7156.69
13	450	90	25	6347
14	450	90	75	7064
15	450	90	50	6914.4
16	450	90	50	6838
17	450	90	50	6704
18	450	90	50	6739
19	450	90	50	6812
20	450	90	50	7084

The resulting data, on table 4.3 were analyzed using design expert 7.0.0 software to determine the effect of variables on calorific value. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to minor factor, and the design summary for the experiment is shown in table 4.4

Table 4-4 Summary of the analysis of variance(ANOVA) result for the calorific value of charcoal

Response			**Calorie value**			
	ANOVA for Response Surface Quadratic Model					
	Analysis of variance table [Partial sum of squares]					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	**Remark**
Model	1.148E+007	9	1.275E+006	50.13	<0.0001	significant
A	9.462E+006	1	9.462E+006	371.95	< 0.0001	
B	1.006E+006	1	1.006E+006	39.53	< 0.0001	
C	3.353E+005	1	3.353E+005	13.18	0.0046	
AB	62191.59	1	62191.59	2.44	0.1490	
AC	16907.771	1	6907.77	0.66	0.4339	
BC	42279.41	1	42279.41	1.66	0.2264	
A^2	2.456E+005	1	2.456E+005	9.66	0.0111	
B^2	27.69	1	27.69	1.088E-003	0.9743	
C^2	6607.65	1	6607.65	0.26	0.6214	
Residual	2.544E+005	10	25439.35			
Lack of Fit	1.603E+005	5	32055.50	1.70	0.2866	not significant
Pure Error	94116.03	5	18823.21			
Cor Total	1.173E+007	19				

The statistical model was checked by F-tests, and the ANOVA for the response surface quadratic model is summarized in Table 4.4. The Model F-value of 50.13 implies the model is significant.

There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this model A, B, C, A^2 are significant model terms. Values of greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), the model reduction may improve your model. The "Lack of Fit F-value" of 1.70 implies the Lack of Fit is not significant relative to the pure error. There is a 28.66% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good. So we want the model to fit.

Table 4-5 Model adquasy signal for calorific value

Std. Dev.	159.50	R-Squared	0.9783
Mean	6635.42	Adj R-Squared	0.9588
C.V. %	2.40	Pred R-Squared	0.8468
PRESS	1.797E+006	Adeq Precision	26.121

The quality of the fitted polynomial model was expressed by the coefficient of determination R^2, which represents the proportion of variability in a set of data that is accounted for a statistical model. The correlation coefficient, the R-Squared value was important for validation of the model developed. For a good statistical model (Statistics et al. 1967). The R^2 values for Eqs. 4.1 is 0.9783. This indicates 97.83% of the total variation in the calorie value correlation between the experimental and predicted values. These high R^2 values indicate that the predicted responses were close to the experimental values and the models are suitable to correlate with the experimental data. Therefore, the R^2 shows good agreement between experimental data.

The other statistic model was “Adeq Precision‟. This is a kind of signal to noise ratio that measures the ratio of the range of variation in the predicted response to an estimate of the standard error of the predictions and is obtained by subtracting the minimum predicted value from the maximum predicted value and then dividing by the average standard deviation of a prediction. A value larger than 4 is required. From the ANOVA result ratio of 26.121 was obtained. So this model can be used to navigate the design space.

A high value designates that the variation that we are observing is large in relation to the underlying uncertainty of the fitted model. With respect to the following model adequacy signals, The "Pred R-Squared" of 0.8468 is in reasonable agreement with the "Adj R-Squared" of 0.9588. This indicated a good agreement between the observed and predicted value, if the "Pred R-Squared" was not as close to the "Adj R-Squared", it might have indicated us a large block effect or a possible problem with the data.

The percentage of coefficient of variance (CV%) is a measure of residual variation of the data relative to the size of the mean. Usually, the higher the value of CV, lower is the reliability of the experiment. The low value of 24% for the calorific value confirmed a good precision and reliability of this experiment.

Furthermore, The significance and adequacy of the models were justified through ANOVA. The mean squares were obtained by dividing the sum of the squares of each of the variable sources, the model and the error variance, by the respective degree of freedom.

The actual values of the independent factors and the response on 20 experimental points were used for prediction of model equations. Experimental data were fitted to higher degree polynomial equations. ANOVA analysis showed that experimental data are best fitted into a quadratic equation. ANOVA for a quadratic model was carried out to form its significance of variables toward response. The coefficient with one factor stands for the effect of the particular factor only, whereas the coefficients with two factors and also with second-order term correspond to the interaction between two factors and quadratic effect, respectively. The ANOVA was performed at 95% level of confidence for the designed experiments. The quadratic model for the carbonization process of a peanut shell and chat stem in terms of coded factors is represented as Eq. 4.1.

Final equation in terms of coded factors:

$$\begin{aligned} Calorie\ value &= +6810.95 + 972.73 * A + 317.13 * B + 183.12 * C \\ &\quad -88.17 * A * B - 45.97 * A * C + 72.70 * B * C \text{ ……………Equation 4.1} \\ &\quad -298.86 * A^2 3.17 * B^2 - 49.02 * C^2 \end{aligned}$$

A quadratic model equation in real terms for charcoal production is shown below:

$$
\begin{aligned}
\mathit{Calorie\ value} = & -6328.45852 + 40.18955 * A + 19.58474 * B + 1471.91391 * C \\
& -0.029390 * A * B - 1.83890 * A * C + 9.69300 * B * C \ldots\ldots\ldots \text{Equation 4.2} \\
& -0.029886 * A^2 - 3.52576E - 003 * B^2 - 784.29091 * C^2
\end{aligned}
$$

On the basis coefficient in the equation. 4.1 it was evident that calorific value increasing with temperature, time and ratio (peanut shell to chat stem). Temperature has a more profound effect on calorific value as expressed in equation 4.1. Temperature, time and ratio showed significant linear effects on calorific value, which clearly indicated by positive linear regression coefficient 972.73, 317.13 and 183.12 respectively. As shown in the final equation in term of a coded factor the response for calorific value by all three linear terms (A, B, C), quadratic term (A^2, B^2, C^2) and interaction quadratic term (AB, AC, BC). All coefficients of leaner term and interaction of BC term were positive and the response of calorific value was positively affected by this factor, but the coefficient of all quadratic term and interaction of AB and AC were negative, so the response of calorific value was negatively affected by this factor.

4.4.2 Model Diagnostics Plots

Model graphs and diagnostics plots are the experimental data analysis. The normal probability plots for the response are presented below the graph. The applied statistic and probability for engineering textbook by Montgomery and Runger experiment (2002) stated that good normal probability plot should show a linear straight line, as well stated that good residuals versus predicted response plot should be random scatter. An assessment on the normal probability plot for calorific value as shown in the figure revealed that the residues generally fall on a straight line concluding that the error is distributed normally which indicated that the normality assumption was valid for a response.

Graphical summaries for case statistics can be seen by selecting the Diagnostics button. Most of the plots display residuals, which show you how well the model satisfies the assumptions of the analysis of variance.

➢ Normal Probability

The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. Expect some scatter even with normal data. The normal probability plots for the response are presented below the graph. The applied statistic and probability for engineering textbook by Montgomery and Runger experiment (2002) stated that good normal probability plot should show a linear straight line.

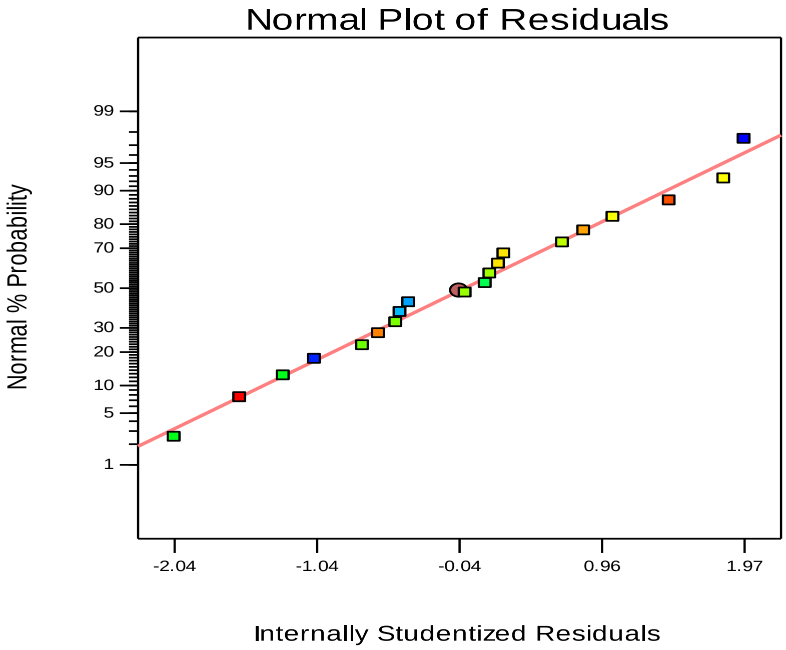


Figure 4-2 Normal plot of residual

➢ Residuals versus Predicted

This is a plot of the residuals versus the ascending predicted response values. It tests the assumption of constant variance. The plot should be a random scatter (constant range of residuals across the graph.) Expanding variance in this plot indicates the need for a transformation.

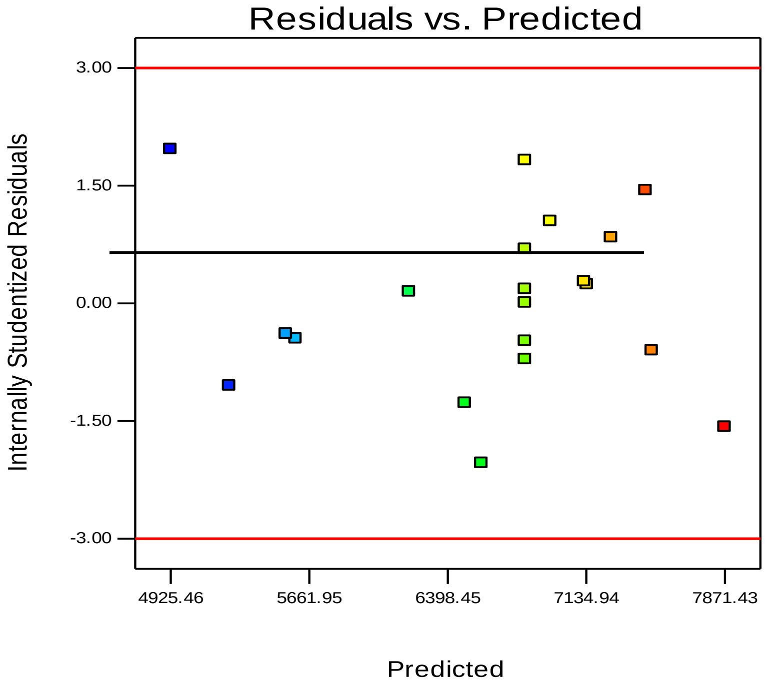


Figure 4.3 Studentized residuals versus predicted

- **Actual versus Predicted**

A graph of the actual response values versus the predicted response values. It helps you detect a value, or group of values, that are not easily predicted by the model.

The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4.4. The results in Figure 4.4 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the carbonized process variables to the calorific value.

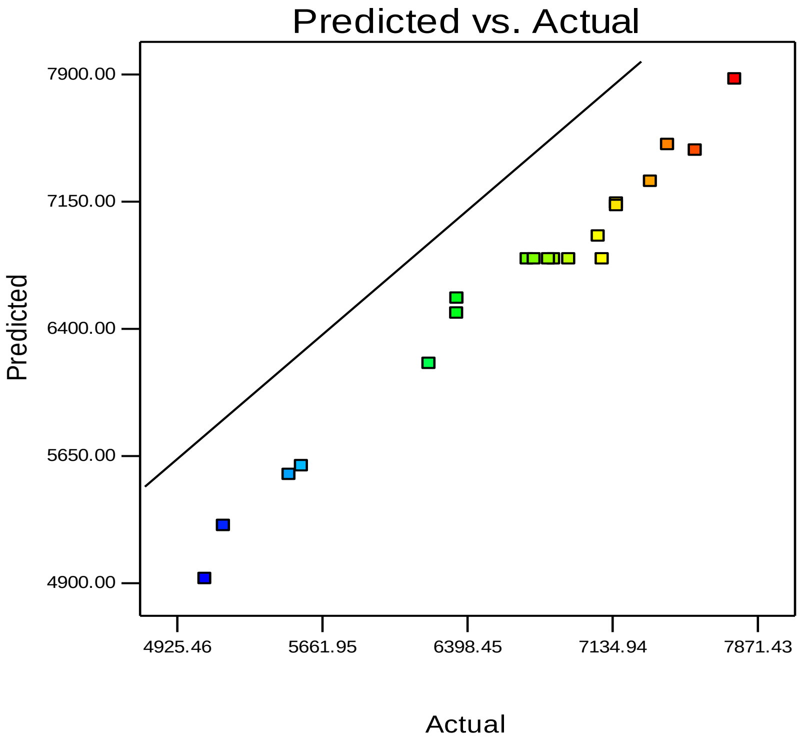


Figure 4.4 Predicted versus Actual

- **Residuals versus Factor**

This is a plot of the residuals versus any factor of your choosing. It checks whether the variance not accounted for by the model is different for different levels of a factor. If all is okay, the plot should exhibit a random scatter. The pronounced curvature may indicate a systematic contribution of the independent factor that is not accounted for by the model.

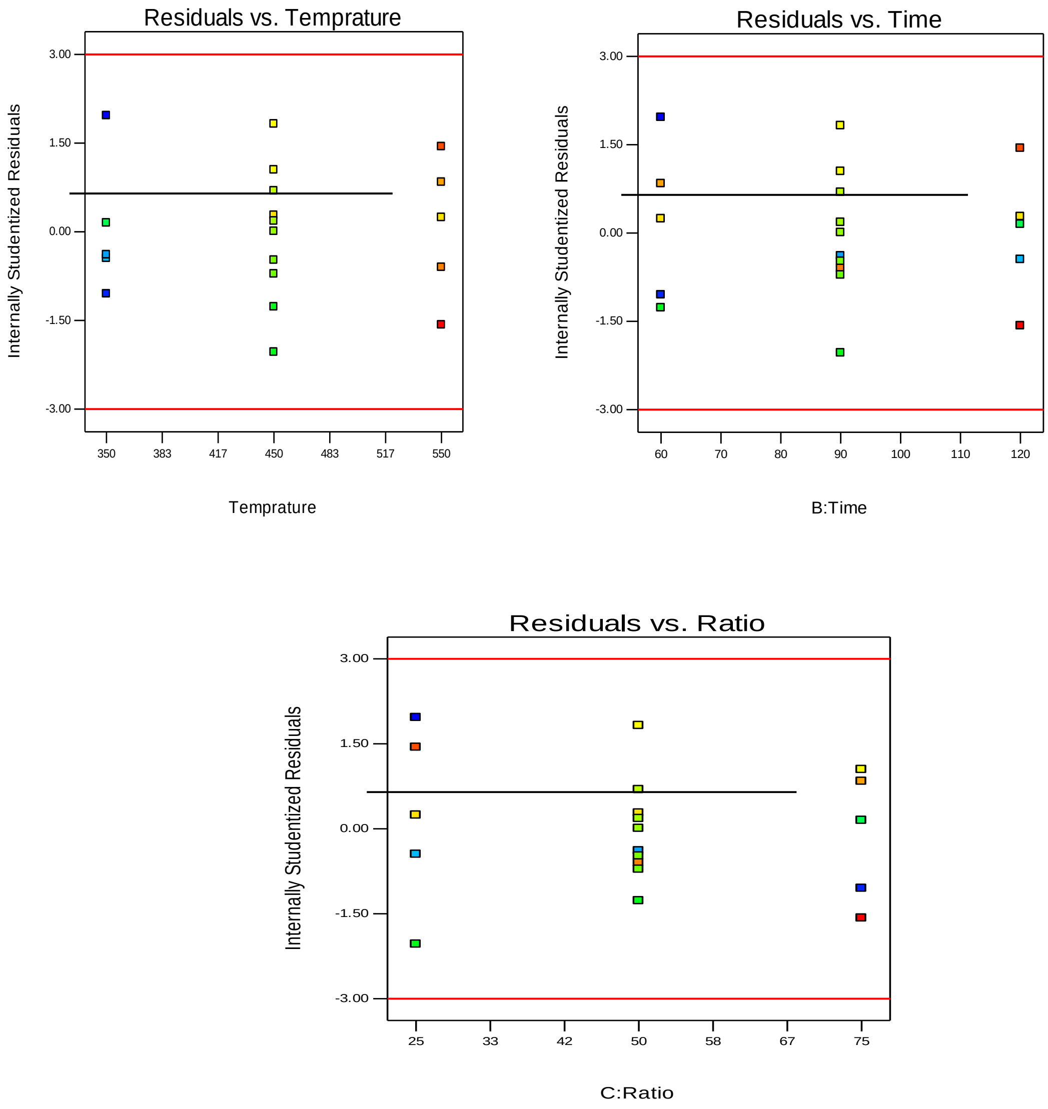


Figure 4.5 Residual versus factors

4.4.3 Effects of Process Variables

The effect of each independent variable on the response of calorific value was investigated by keeping other variables constant. Moreover, from the model equation, the coefficients of the independent variables show the effect of each independent variable and interaction on calorific value.

4.4.3.1 Effects of Individual Process Variables

- **Effect of temperature on calorific value**

The effect of temperature on calorific value was shown in the following figure 4.6. As we can observe from the figure, the temperature has a positive effect in calorific value. As we increased the temperature, the maximum of 550^{o}C a maximum calorific value of 7757.11 Cal/g was obtained and this implied that the amount of temperature plays a major role in the carbonation process. This attributed to the fact that as temperature increased it provided high energy due to complete burning of charcoal. The further increment of burning temperature would bring insignificant change in calorific value (Solomon 2016).

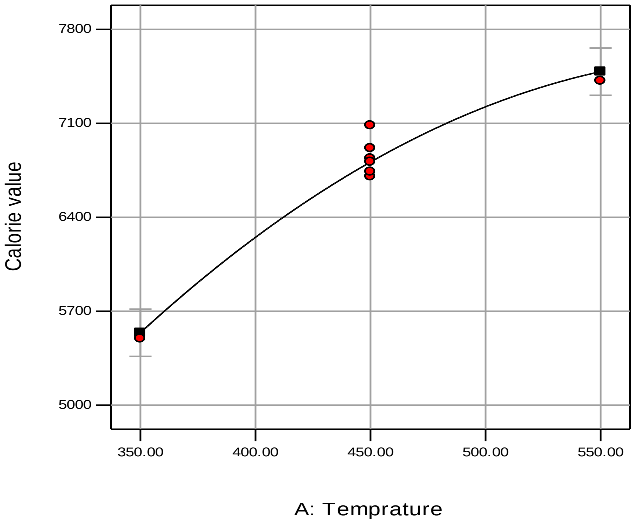


Figure 4.6 The effect of temperature on mixed charcoal calorific value

- **Effect of time on calorific value**

The Calorific value of mixed charcoal depends on the holding time. The calorific value of the sample was determined at a time interval of 60 to 120min with respect to different carbonization temperatures at 350, 450 and 550^{0}C. The maximum calorific value of mixed sample obtained was 7757.11 Cal/g at 550^{0}C and 120 minutes while the minimum calorific value was 5080 Cal/g at 350 ^{0}C and 60 minutes. The results revealed that the maximum calorific value of mixed charcoal was found at 120min. This attributed to the fact that as time increased it provided high energy due to complete burning of charcoal. As shown in figure 4.6 and 4.7 when increase rate of residence time minor effect on calorific value, compared to increasing temperature.

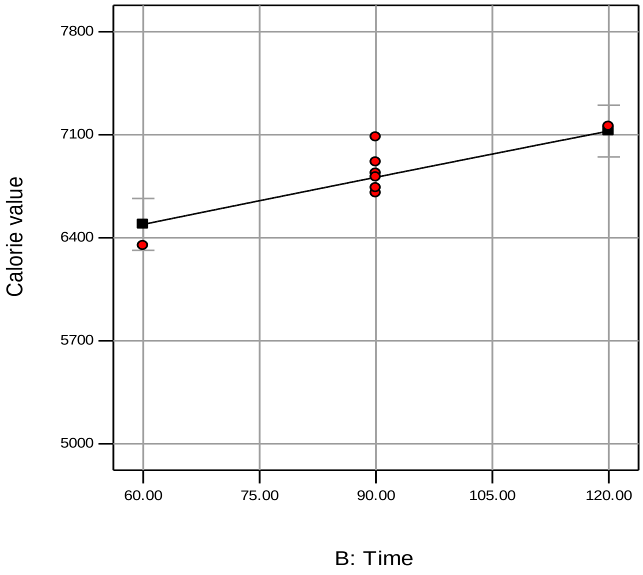


Figure 4.7 The effect of time on mixed charcoal calorific value

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

The effect of the percentage of the two materials on calorific value was shown in the following figure 4.8. As we can observe from the figure, the ratio has a positive effect on calorific value. As we increased the peanut shell percentage to the maximum of 75%, a maximum calorific value of 7757.11 Cal/g was obtained and this implied that peanut shell plays a major role in the blending process. Most of the calorific value came from the peanut shell and increasing to the maximum percentage bring a maximum energy content and this was due to the good characteristics of the peanut shell described in the above sections (proximate characteristics).

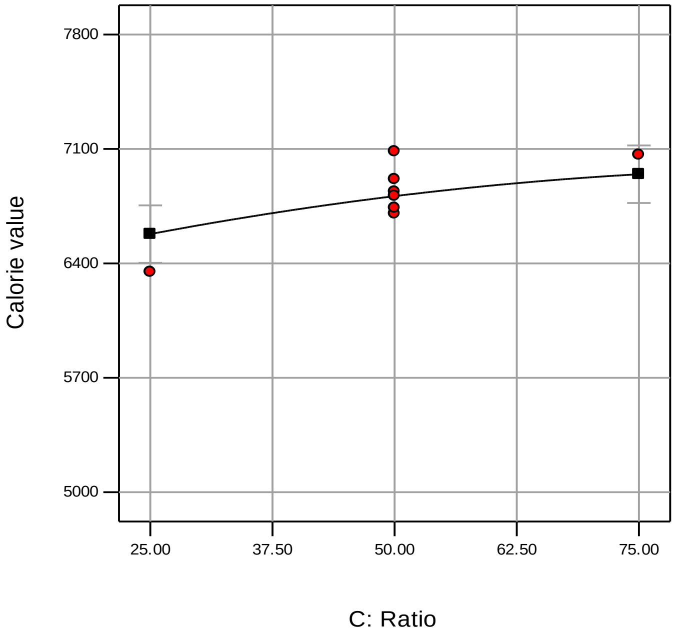


Figure 4.8 The effect of mixed ratio on calorific value

4.4.3.2 Effects of Interaction Variable

The relationship between the parameters was demonstrated clearly by plotting two independent variables with the calorific value on a three-dimensional contour map.

I. Interaction effect of temperature and time on calorific value

Figure 4.9 the response surfaces (a) and the contour plots (b) shows for calorific value variation as a function of temperature and time with the mixed ratio set at 50%. The calorific value gradually increased with temperature from 350 to 550^{o}C and time from 60 to 120min. Therefore, it can be observed that calorific value is favored with the increase in both temperature and time, in agreement with the results obtained in a previous work. Temperature and residence time on carbonizing has a strong influence on the calorific value of samples for instance when both factors increased the sample will increase the carbon content. As a result of calorific value, increase with higher temperature, to having a more notable impact than residence time in these experiments. But from the fig 4.9 shows that calorific value is more strongly affected by increasing temperature rather than residence time.

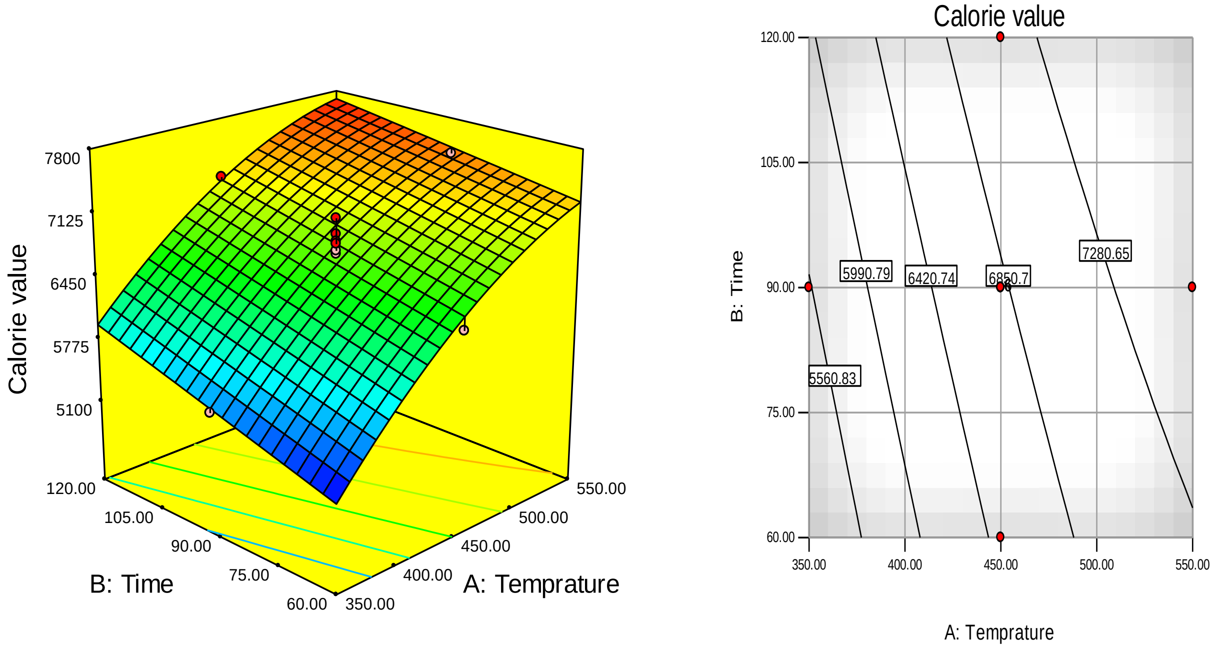


Figure 4.9 Interaction Effect of temperature and time: a) response surfaces and b) contour plots

II. Interaction Effect of Temperature and Mixed Ration on calorific value

Fig 4.10 presents the interaction between a temperature from 350 to 550^{o}C and mixed ratio from 25 to 75%with residence time set at 90minute respect to the response of calorific value. It is clear that high amount temperature and ratio favored high calorific value. The calorific value of peanut shell and chat stem decreased as the temperature and ratio reduced.

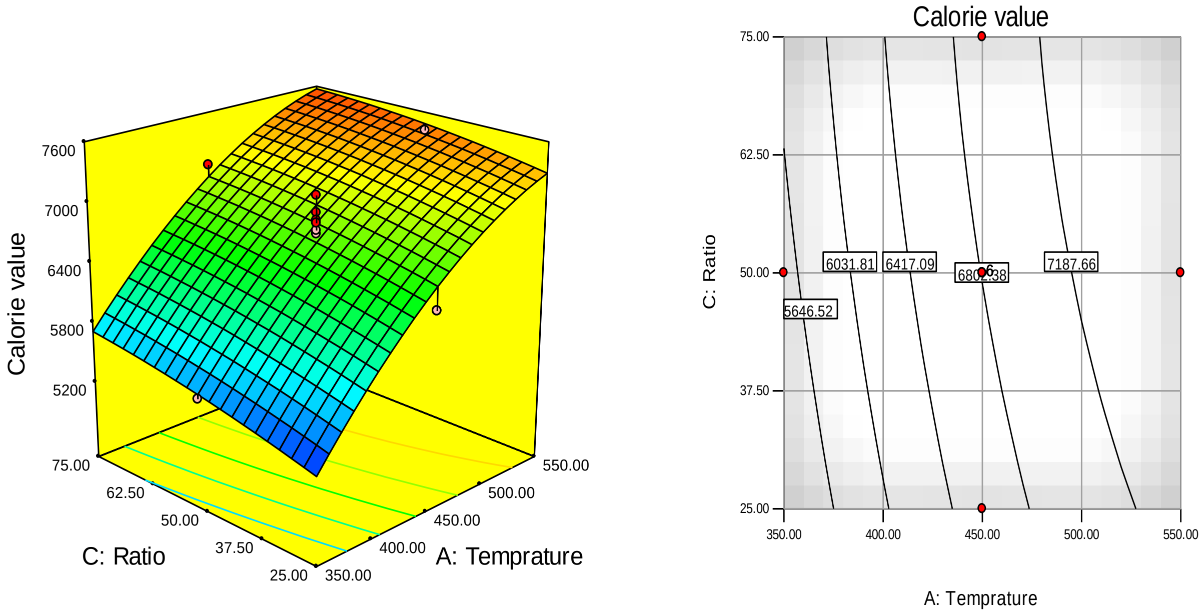


Figure 4.10 Interaction effect of temperature and mixed ratio: a) response surface and b) counterplot

III. Interaction Effect of Time and Ratio on calorific value

The regression equation for calorific value shows that charcoal production only depends significantly on the three individual dependent variables This indicates that the positive effect resulting from the interaction between residence time from 60 to 120 min and mixed ratio from 25 to 75% response on calorific value. Figure 4.11 shows the response surfaces (a) and the contour plots (b) for calorific value with the time and mixed ratio set at 450. In these plots, it can be observed that calorific value is preferred by a slight increase in the time and mixed ratio. But from the fig 4.11 shows that calorific value is more strongly affected by time rather than mixed ratio.

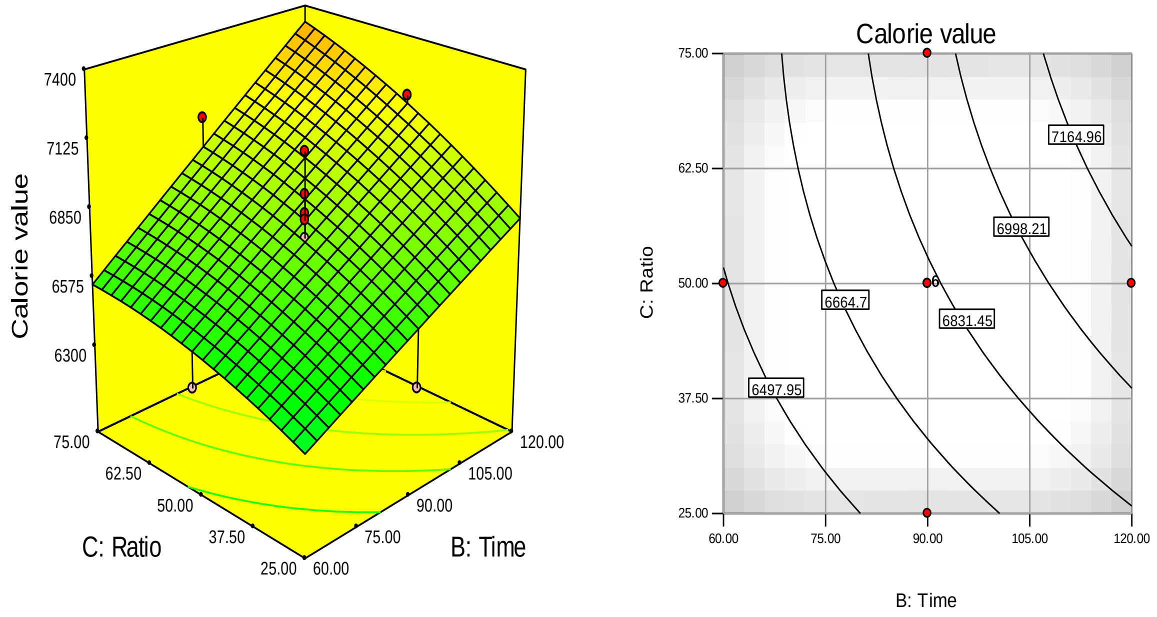


Figure 4.11 Interaction effect of time and mixed ratio: a) response surface and b) counterplot

4.4.4 Optimization of Operating Parameters

Optimized parameters were selected based on the highest desirability. Optimum condition selected was verified by CCD RSM. It was used to optimize the parameters where the targets were set at maximum values, while the values of the parameter were set in range and target under study.

The software searched for a combination of factors that simultaneously satisfied the requirements placed on the response and each of the factor. Table 4.6 shows the optimum working conditions ultimate goal, high and low limits of the response and factors, employed during the optimization analysis. The optimum conditions obtained were then evaluated by composite desirability, which has the value from 0 to 1, to determine the degree of satisfaction of the optimum conditions for the ultimate goal of response. In order to obtain the maximum calorific value. Carbonization at lower temperature produces a large quantity of char but good target at 450°C due to thermal breakdown of hemicellulose and cellulose (Oktaviani 2018). The optimum conditions of calorific value were achieved at targeted temperature, time and ranged mixed charcoal of 450°C, 60 min and 75%, respectively under cost estimation. To validate the optimum condition predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized carbonization process conditions and calorific value of 6552.6 with desirability value 0.82.was obtained.

Table 4-6 Model validation for calorific value

Response	**Model desirability**	**Temprature (°C)**	**Time (min)**	**Mixed ratio (%)**	**Predicted**	**Experimental**	**Error (%)**
Calorific value	0.82	450	60	75	6552.06	6580.47	0.43

Model desirability approaching unity and with low error value portrays the applicability of the model towards the responses. The result actual or experimental is closely related with the data of predicted obtained from optimization analysis using desirability function. From the table 4.6, the error was obtained 0.43%, relatively small because it is less than 0.5 for the predicted and the actual values indicating that the models are suitable and sufficient to predict the responses.
Therefore, this research shows that a mixture of a peanut shell and chat stem can definitely be replaced coal as an alternative energy source for cement production due to their calorific value at optimum carbonation condition.

4.4.5 Pelletization of Optimum Mixed Carbonized sample

For all types of binders, the density of pellet gradually increased with the increasing amount of the binders and increase in the applied pressure during the preparation of pelletizer also increased strength and density (J. Kamalabadi et al. 2013), This implies that bonding of adjacent particles of pellets increased with binder amount.

Densification of biomass charcoal was done using pelletizer. The bulk density of pellet with a constant compression pressure of 100bar the bulk density increased from 0.56 to 0.70 g/cm^3 with the ratio of molasses from 10 to 20%, respectively. The density increases with binder ratios agree with the finding of Sen (2016).

Table 4-7 Physical properties of optimum mixed carbonized, pellets sample and SA coal

Raw Sample	**Density (g/cm^3)**	**Calorific value (Cal/g)**
Optimum mixed Carbonized sample	–	6580.44
Mixed Carbonized pellet by 10% of molasses	0.56	6838.19
Mixed Carbonized pellet by 20% of molasses	0.76	7202.15
South African Coal	1.4-2.0	6467.26 - 6799.35

On another hand, the effect of the different amount of molasses as binders on the calorific value of the carbonized pellet sample is presented in table 4.7. The calorific value of optimum mixed carbonized sample without binder is 6580.44 Cal/g typically calorific values of mixed carbonized sample pellet by 10% and 20% of molasses were obtained 6838.19 and 7202.15cal/g respectively. As the data on the above table reveals, the calorific value of the pellet increases with the increasing percentage of molasses. Similar finding were reported in literature of “Influence of binders on physical properties of fuel briquettes produced from cassava rhizome waste” (Sen et al. 2016), cassava rhizome briquettes with a different percent of molasses.

These investigations have brought out that without binder and addition of binder (molasses) improved the physical properties of a mixed carbonized sample. One of the most important parameters that affect the quality of pellets are the operative variables of the pelletization process, which influence the physical and mechanical properties of the pellets produced and the characteristics of the material (Angela Garcia-Maraver1 & Manuel Carpio2) and as we can see from the table 4.7, the densities of mixed carbonized pellet samples with molasses in the range of 10 and 20% were less, when compare with South African coal. In pyro processing of clinker production, the fuel must be ground to suitable blowing with gas toward the flame-end of the rotary kiln therefor, the density of fuel is not important. However, the energy content of all samples on table 4.7 was comparable with coal, but due to cost-benefit the carbonized pellet sample by 10% of molasses is enough because the aim of the pellet is suitable for storage, handling and transporting. Finally, the optimized mixed carbonized pellet sample with 10% of molasses was prepared to further characterized to understand their physical and chemical characteristics.

4.4.6 Proximate Analysis

The proximate analysis gives moisture, ash and volatile matter on percentage weight basis. The differences among the result of South African coal, optimum mixed raw sample (75% peanut to 25% chat stem) and carbonized mixed sample values can be explained by the devolatilization during carbonization, which produces an increase in ashes content, fixed carbon and also decrease moisture content and volatile matter as shown in table.

Table 4-8 Proximate analysis of Uncarbonized mixed, mixed carbonized pellet sample and coal

Sample	**Moisture content**	**Ash content**	**Volatile matter**	**Fixed carbon**
Uncarbonized mixed	3.12	1.96	76.83	18.09
Mixed Carbonized pellet (10% molasses)	2.87	9.31	30.25	57.57
Coal (South Africa)	1.43	16.92	27.13	54.52

The moisture contents of the samples have the following effects. It absorbs a part of heat liberated in the combustion process. If the moisture content of the raw material is high, the result shows lower heating value and fuel efficiency. Further, most automation systems can not react to rapid variations in moisture content resulting in incomplete combustion which increases emissions. The moisture content of the uncarbonized mixed sample and carbonized pellet sample, are 3.12 and 2.87 respectively. From the result, we can determine due to carbonize the raw material decrees the content of water.

Volatile matter on heating of samples, volatile matter (flammable gas and smoke) is liberated. This burns as a visible flame on a supply of sufficient air, time, temperature and turbulence. If the volatile matter in the fuel is higher, then a large amount of secondary air with high pressure needs to be supplied at a strategic location for effective combustion. Complete combustion of volatile matter leads to dark smoke, heat loss, pollution hazard and soot deposition on boiler surfaces (Patel and Gami 2012). The uncarbonized mixed sample contains more volatile components and more reactive than carbonized pellet sample and coal. Due to the highly volatile matter, the combustion of biomass is rapid and tough to control.

Ash content is the incombustible solid mineral matter in the fuel. It mainly contains silica (SiO_2), Alumina (Al_2O_3), Iron oxides (FeO, Fe_2O_3), CaO and MgO etc. At higher temperature, the ash fuses/soften and forms clinker that entraps combustible matters and prevents proper air distribution. This lowers combustion efficiency but it is useful for clinker production because the silicon, aluminum and iron oxide need for raw mix design for full fill clay content.

4.4.7 Complete Oxide Analysis Result

Complete oxide analysis means the total content (chemistry) of the material out of 100%. The general sequence is LOI, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, K_2O, Na_2O, Cr_2O_3, Mn_2O_3, P_2O_5, Cl^-, F^-. The results of the major and minor oxide analysis of the mixed carbonized sample made from 75% peanut shell and 25% chat stem together with 10% molasses were shown below with the South African coal for comparative presentation.

Table 4-9 Oxide Analysis of a mixed carbonized sample, SA Coal and Clinker

Samples	**Oxides**										
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**MnO**	**P_2O_5**	**TiO_2**	**LOI**
Carbonized pellet sample	27.08	3.64	0.24	8.12	3.24	0.24	<0.01	<0.01	0.04	<0.01	87.4
SA Coal	47.28	24.49	4.22	15.3	1.34	0.14	0.62	0.01	1.5	0.04	79.9
Clinker	22.23	5.87	3.45	65.1	1.6	0.13	1.37	-	-	-	-

Portland cement clinker mainly consists of CaO, SiO_2, Al_2O_3 and Fe_2O_3; are accounting for more than 95%. The minor components in total less than 3% are MgO, TiO_2, $P_2O_5$and alkalis (Aldieb and Ibrahim 2010). The presence of these major oxides in the fuel ash has their own role in the clinker composition. Because, of cement fuel especially coals or lignite, produce significant quantities of ash to fulfill clay. Starting from silicon oxide, it was observed that the carbonized pellet sample result obtained was low when compared with that of the South African Coal result and this might be due to the percentage share of chat stem as shown in table 4.2 and the type of method used for the determination of the composition. The usual clinker composition of silicon oxide is in average 22.23% (Aldieb and Ibrahim 2010). Even though the silica content of the mixed carbonized sample was lower than coal, it can act as a significant supplementary material for the clinker.

With respect to the alumina content, the usual composition of aluminum oxide of clinker is 5.87% from the above results, we can observe the big difference in their content and these suggested that there is a deficiency of aluminosilicate minerals in the mixed sample when compared with that of the SA coal but according to (Aldieb and Ibrahim 2010) the smaller in the percentage was desirable because alumina is not essential to the final Portland cement product but, at temperatures above 1300^{o}Ca liquid phase containing alumina (Al_2O_3) and iron oxide

(Fe_2O_3) is formed and at this stage in the process, the liquid phase acts as a source of fluxes lowering the energy requirement thereby making the process economical.

The composition of iron oxide in the above table 4.9 showed a lower result when compared with coal. As we can understand from the mixed sample percentage, 75% of the mixture was peanut shell, therefore, the property of the other mixtures would not have a higher influence on the total. The usual composition limit of Portland clinker is 3.45%and this result was desirable. The main effect of clinker burning under reducing conditions is mainly due to the raw material component Fe_2O_3 (Fe(III)) being reduced to FeO (Fe(II)) or, in the case of strong reducing conditions, elemental Fe. Reduction of Fe(III) under reducing conditions takes place at temperatures above 1300°C. Fe(II) affects the clinker quality for the following reasons (Rooma and Boberg 2012) It catalyzes alite decomposition; the main strength giving component in cement and also less ferrite is formed. Instead, more aluminate is formed, which may lead to altered setting during the hydration of cement mortar. Therefore, the result of the ash mitigates the formation of all this problem.

As the above table 4.9 shows, the calcium oxide composition was found to be lower when compared with that of the South African coal. Similarly, a research by (Rizvi et al. 2014) found an approximate result of 9.92% CaO by the use of X-ray fluorescence analysis. Most of the biomass-derived fuels possess a little considerable calcium content (Rizvi et al. 2014). The composition of CaO of cement clinker is 63.76-70.14%. An increase in lime content beyond a certain value makes it difficult to combine with other compounds and free lime will exist in the clinker which causes unsoundness in cement (Odunayo et al. 2016). Therefore, the mixed carbonized sample ash will not supplement this mineral.

In addition to the main compounds mentioned above, there exist minor compounds, such as MgO, TiO_2, Mn_2O_3, K_2O and Na_2O. According to the above MgO result, the presence of magnesia compounds in the mixed carbonized sample was very low and a little bit higher than that of the SA Coal. Since the largest percentage was from peanut shell in the mixed carbonized sample, the ash mineralogical composition of the shell put a greater and significant influence in the mixed sample.

On the other hand, two of the minor compounds are of particular interest: K_2O and Na_2O, known as the alkalis (about 0.4-1.3% by weight of cement). The increase in the alkalis percentage has been observed to affect the setting time and the rate of the gain of strength of cement (Dr. Basil Salah, Concrete Technology). The usual clinker composition of K_2O and Na_2O is in the range of 1.37% and 0.13% respectively. And as we can see from the above result, the percentage of both K_2O and Na_2O was found to be under the specification limit and also lower than SA coal. Other minor compounds such as TiO_2, Mn_2O_3 and P_2O_5 represents are < 1%.

Loss on Ignition (L.O.I) is the loss of the cement sample weight when it exposed to the red temperature at 1000^oC. It shows the extent of carbonation and hydration of free lime and free magnesia due to the exposure of cement to the atmosphere. As it can be seen from the above table, the L.O.I of the carbonized pellet was found to be higher than coal and this suggested the prehydration and carbonation of the sample, which may be caused by the prolonged storage.

4.4.8 Elemental Analysis

Elemental analysis of fuel gives its chemical constituents such as carbon, Hydrogen, Oxygen, Nitrogen and Sulfur. Most chemical elements from the fuel ash are incorporated into the cement clinker. This analysis helps in estimating theoretical air required for complete combustion, fuel gas generated per kg of fuel fired, water vapor content in the flue gas, a sulfur content of flue gas and calorific value of fuel which depends upon carbon and hydrogen content of the fuel. However, volatile elements such as chlorine, sulfur will partly evaporate in the hotter regions of the kiln system. These volatile elements may condense from the gas phase again in the preheater, being captured in the bag filter, or being removed through a bypass or escape with the stack gases. In order to ensure the cement quality and process stability, it is, therefore, necessary to control and know the levels and composition of all chemical inputs via the fuel. The results of the elemental analysis of the uncarbonized mixed sample and carbonized pellet sample were shown in the following table compared with coal from literature. The samples were run in three duplicates. The result of the oxygen content of the sample was calculated by the difference of 100% and the sum of the C, H, N and S content.

Table 4-10 Elemental analysis of Uncarbonized mixed, mixed Carbonized pellet sample and coal

Element	**Uncarbonized mixed sample**	**Carbonized pellet sample**	**Coal** (Steyn and Minnitt 2010)
C (%)	42.7	70.86	70.8
H (%)	5.00	2.95	4.49
N(%)	-	-	1.61
S (%)	-	-	1.4
O (%)	50.76	26.19	23.1

As shown in the above table 4.9, the carbon contents and oxygen content of uncarbonized mixed sample were 42.7 % and 50.76% respectively, this result was found to be similar with (Xiwen et al. 2016), study on "Analytical pyrolysis of peanut shells". It indicates that the similarity result based on the sample dominated by peanut shell. The carbon and oxygen content of carbonized pellet sample was 70.86 % and 26.19% respectively. The increase in carbon content and decreasing oxygen content in carbonized sample indicated that the carbonization process has a high role of increasing the amount of carbon content due to the release of volatile-rich in hydrogen and oxygen, such as water, carbon mono oxide, and carbon dioxide. This result corroborates with the finding of (Ahmad et al. 2012) and (Amaya et al. 2015). The Oxygen content of uncarbonized mixed sample agrees with greater contents of moisture and hydrated minerals.

The main objective of carbonization process is to concentrate carbon and reduce the oxygen content and hence improve the energy performance of carbonized sample. It is known that approximately 90% of the oxygen present in the biomass is volatilized due to carbonization, while 60% of the carbon remains retained (Protásio et al. 2014). From an energy point of view, it is desirable to minimize the oxygen content and maximize the amount of carbon in the carbonized sample. The carbon source is the main chemical fuel element and is positively associated with a heating value. So, as we can see from the result, the amount of carbon is similar to the coal.

In contrast, the Nitrogen and Sulphur are significant in the formation of harmful emissions and have an effect on reactions forming ash. It is known that during the complete combustion of coal, these elements are converted into toxic oxides (NOx and SOx) and thus contribute to air pollution. The Sulphur and Nitrogen contents reported which are below 1% is a welcome development as there will be a minimal release of sulfur and nitrogen oxides into the atmosphere, thereby limiting the polluting effect of fuels (Jittabut 2015). The Sulfur contents of samples were negligibly low less than 0.1% (Ahmad et al. 2012), but the coal of sulfur content is higher, according to chinyam (1998) Since sulfur is introduced into the system through the fuel, the sulfur content of the fuel can become an important factor in kiln system operation. It is, however important to distinguish between the sulfur in the raw meal that enters the kiln system in the form of sulfates (such as calcium sulfates) and that which enters as sulfides. The latter can oxidize through an exothermic reaction at 400 to 600^{o}C in sections of the system (for example cyclones) where there is less calcium oxide available. Consequently, the SO_2 released is emitted and treated. On the other hand, the calcium sulfates present do not decompose until 900 to 1000^{o}C. This gives the oxides of sulfur an opportunity to react with the alkalis which have been volatilized and also with CaO that has already formed thereby increasing the chance of alkalis and sulfate being removed from the kiln system in the clinker. As already mentioned, if significant amounts of the low melting point mixtures of calcium and alkali sulfates form in and around the preheater sections can lead to blockages.

The Uncarbonized mixed sample and Carbonized mixed pellet sample have not nitrogen and Sulphur content, which is a typical characteristic of biomass (Kurchania 2012). Therefore, the result has shown that the use of biomass residues has the added benefit of reducing the cement's nitrogen oxide and sulfer oxides emissions.

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, carbonation of peanut shell and chat stem were analyzed and optimized by using the CCD RSM to substitute fuels as an alternative energy source for cement production. A design expert was used to optimize simplified solution mathematical model equations were building by using sets of experimental data and ANOVA. While this model was not able to calculate the chemical output, it was able to find the materials changed to carbonize caused by temperature, residence time and mixed ratio.

In this study a more effective to increase the carbon content and calorific value of raw material by using carbonization. The results of a carbonized mixed sample showed a better performance evaluation shows that the calorific value increases from 5068cal/g to 7757.11cal/g and direct relationship with temperature and time. The optimal condition of temperature, time and mixed ratio were at 450^{o}C, 60 min, and 75%, respectively. The calorific value of optimum carbonized samples predicted by design expert and actual result were closely related, 6552.6 and 6580.47cal/g respectively.

In terms of the change in feed material, the largest modification would be the mixed carbonized sample pellet with 10% of molasses. The calorific value of mixed carbonized pellet developed to 6838.19cal/g. This fuel was found to be the easiest to implement as the storage, handling and feed requirements are very similar to that for coal and would require minimal alterations.

The carbonized pellet sample was found to be the most suited fuel to use and have a positive impact on cement plant performance. Because the analyzed energy content was comparable with coal and the gaseous emissions seem not to be affected compared to coal. It has even been reported that the application of alternative fuels has led to decreased emissions so that it had a better emissions profile. Overall this study has successfully identified that this process could be used to model an alternative fuel without the need for expensive testing.

5.2 Recommendation

In this research the characteristic of mixed carbonized pellet sample was carried out to determine the proximate analysis values, calorific value and ultimate analysis were analyzed. It is a well-known fact that there are some levels of imperfections associated with physiochemical characteristics. So there is always the opportunity for improvement of characterization of alternative fuels. Further investigations are recommended to advance the performance of alternative fuels.

- According to the results of physiochemical characteristics almost all characteristics of mixed carbonized pellet related to commercial coal. However, the calorific value of pellet can replace totally for coal, but the ash chemistry or complete oxides of pellet result not satisfied, it needs further studies to improve ash chemistry of pellets for a complete substitute.
- Ethiopian cement industries must be adopted the alternative fuel biomasses to utilize and substitute the imported coal in order to minimize coal consumption and save foreign currency.
- The production of these alternative fuels must be established to increase a positive environmental impact on human industrial activities beyond, these fuels can also contribute greatly for safe environmentally sound disposal of residue and the mitigation of green gas house emission.
- Case studies in different industries must be done in order to conduct a detailed study on the technology of these alternative renewable fuels. In addition, a feasibility study of alternative fuels must be conducted in the future.

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APPENDICES

Appendix A: proximate Analysis Experimental method

Proximate analysis was as per ASTM procedure for the determination of the parameters ash content, moisture content, volatile matter and fixed carbon of peanut shell, chat stem, their mixed carbonized sample and pellet sample.

Moisture content

The moisture content was obtained by the oven drying method (ASTME871-82, 1998). The samples dried at 105 ± 5°C for 30 min in the oven, then cooled in desiccator at room temperature. Weighed and recorded the container weight, Wc. 1 g of samples placed in the container, weighed the samples and container to the nearest 0.01 g, and recorded as initial weight, Wi. Placed the sample and container in the oven at 105± 5°C then after16 h the samples were withdrawn from the oven, cooled in a desiccator and then weighed to the nearest 0.01g. The moisture content was found on a percentage basis using the following equation

$$\%\ Moisture\ content\ = \frac{(W_i - W_f)}{(W_i - W_c)} * 100$$

Where: -

- $W_c = $ Container weight, g
- $W_i = $ Initial weight, g
- $W_i = $ Final weight, g

Ash Content

The ash content was determined following (ASTM D1102-84, 2001). The prepared sample has been grounded to pass in 425μm sieve. The empty crucible was ignited and covered over a burner or in the muffle at 600°C.A sample weight of 2g was measured and placed in the cruciblethen dried on oven at 100 to 105°C with the crucible cover removed. After 1 h, replaced the cover on the crucible, cooled in a desiccator, and weighed to the nearest 0.1 mg. Recorded the weight (crucible plus sample minus weight of crucible) as the weight of the oven-dried sample. Placed the crucible and contents, with the cover removed, in the muffle furnace and ignite until all the carbon was eliminated. The sample was ashes at 580 to 600°C for 30 min in an atmospheric pressure air muffle furnace. Finally, the crucibles were carefully withdrawn and cooled in a desiccator. Then the samples were weighed again. The ash content was calculated on a percentage basis using the following equation.

$$\%\,Ash\ content\ = \frac{W_1}{W_2} * 100$$

Where: -

- W_1 = Weight of ash
- W_2 = Weight of oven dry sample

Volatile Content

The volatile matter was determined following (ASTM E872-82, 1998). Weighed the crucible and covered and recorded as crucible weight, Wc. 1 g of sample was measured into the crucible, cover, weighed the crucible, and sample to the nearest 0.01 g, and recorded as initial weight, Wi. placed the covered crucible with sample on platinum and insert directly into the furnace at a temperature of 950 ± 20°C. After 7 min heated removed the crucible from the furnace and, without disturbing the cover, then cooled in a desiccator. Then weighed the covered crucible with sample as soon as cold to the nearest 0.1 mg and recorded as final weight, W_f

$$\%\,volatile\ content\ = [\frac{W_i - W_f}{W_i - W_c}] * 100$$

Where: -

- W_i = Intial weight
- W_c = Crucible weight of
- W_f = Final weight

Fixed Carbon

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

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

Appendix B: Laboratory work photos

Peanut shell

Chat stem

Grinded Peanut shell and Chat stem

Centrifugal mill

Bomb calorimeter

5E Automatic proximate analyzer

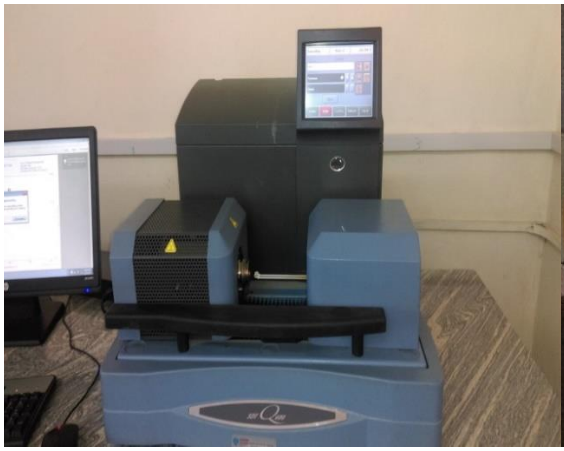
Muffle Furness

Preparation of solution for ash chemistry analysis

Titration using EDTA Solution

Determination of Silcon, Iron, Magnisium, Calcium and Almunium oxides

SDT Q600 Thermogravimetric analysis



Stainless steel tubular reactor (carbonizer)

Mixed carbonized samples

Carbonized pellet samples