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ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

CHARACTERIZATION AND PELLETIZATION OF SAWDUST MIXED WITH SEWAGE SLUDGE AS ALTERNATIVE FUEL FOR CLINKER PRODUCTION

By

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

Addis Ababa University, Ethiopia

June19/2017

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This is to certify that the thesis prepared by Bethlehem Mekasha, entitled: ***Characterization and Pelletization of Sawdust Mixed with Sewage Sludge as Alternative Fuel for Clinker Production*** and submitted in partial fulfillment of the requirements for the Degree of Masters of Science in Process Engineering complies with the requirement of the University and meets the accepted standards with respect to originality and quality.

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Declaration

I declare that this thesis entitled "***Characterization and Pelletization of Sawdust Mixed with Sewage Sludge as Alternative Fuel for Clinker Production"*** is my own original work done under the supervision of Prof.Dr.Ing. Belay Woldeyes at Addis Ababa Institute of Technology in School of Chemical and Bio engineering and I have not previously submitted it entirely or in part for obtaining any qualification at any other university.

Bethlehem Mekasha ……..

Acknowledgements

Above all, I would like to thank omnipotent God for giving me strength, patience, and wellness throughout the completion of this paperwork. Next, I would like to express my deepest and most gratitude to my advisor Prof.Dr.Ing. Belay Woldeyes for his valuable comment, magnificent assistance and guidance.

My special thanks go to Mr. Hintsasilasie Seifu for his technical laboratory assistance. Also Eng. Elias S., Eng. Bizunehe, and Mohammed for their laboratory assistance and nice cooperation in Mugher Cement Factory and am very thankful from the bottom of my heart to all staff members of Ethiopian Geological Survey especially Ms. Alemenesh.

Furthermore, I would like to convey my warm grateful thanks to my beloved families Mekasha W., Etetu B., and Amanuael M. for their unlimited love and cooperation in everything and also sisters and friends Elshaday H, Bruktawit S., Birhan G., Nigisti G., Dereje E. and Sewunet A. for their valuable suggestions and support in every step of the study. They made me realize that everything is possible with families who cares and supports about what you do.

Lastly, I would like to say thank you for Leather Industry Development Institute for their kind cooperation.

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Acronyms

ACC	Associated Cement Companies
BAT	Best Available Techniques
CDM	Clean Development Mechanism
DSC	Differential Scanning Calorimeter
DTA	Differential thermal analysis
ECD	Electro Chemical Detection
EERC	Energy & Environmental Research Center
FEV	Forced Expiratory volume
GHG	Greenhouse gas
GHO	Global Health Observatory
HxCDF	Hexa chloro- di-benzo-p- furan
HpCDF	Hepta chloro- di-benzo-p- furan
OCDD	Octa chloro-di-benzo-p-dioxin
PAH	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated biphenyls
PCDD/F	Polychlorinated dibenzo(p)dioxin and furan
PCDF	Penta chloro- di-benzo-p- furan
SRF	Solid recovered fuel
SRMs	Standard Reference Materials
TCDF	Tetra choro di-benzo-p-dioxin
TCPS	Thai Community Product Standard
TGA	Thermo gravimetric analysis
WBCSD	World Business Council for Sustainable Development
WHO	World Health Organization
U.S. EPA	United States Environment Protection Agency

Abstract

Interest in biomass as a renewable energy source in Ethiopia has increased recently in response to a need to reduce greenhouse gas (GHG) emissions and to attain a green economy on 2025. The main objective of this study was to co-pelletize sawdust mixed with sewage sludge as an alternative fuel for clinker production. All the necessary analysis that defines alternative fuels including complete oxide analysis were carried out following standard procedures for both the raw materials and the mixed pellet and the results were compared with hard coal. In addition, thermogravimetric analysis and heavy metal concentration of the mixed pellet were examined in order to investigate the combustion characteristics of the fuel and the presence of trace elements respectively. Effects of particle size and percentage ratio of the mixture were also analyzed in the range of 0.045-0.18mm and varying percentage ratio of 50 sawdust:50 sewage sludge(%), 60:40(%), 70:30(%), 80:20(%) and 90:10(%) respectively in order to examine the effects of these two parameters on the mixed pellet calorific value using design expert software. The results of the study showed that sawdust was a very attractive source of energy and was found to be a good material to enhance the property of the sewage sludge and to be utilized as alternative fuel. A medium grade fuel of calorific value 19.20MJ/kg was obtained at an average particle size of 0.125mm and sawdust to sludge percentage of 90% and 10% respectively.

1 INTRODUCTION

1.1 Background

The construction industry plays a significant role in socio-economic development. The industry is a distinct sector of the economy, which makes its direct contributions to economic growth. It provides the basis upon which other sectors can grow by constructing the physical facilities required for the production.

Cement as being one of the principal building and construction materials in the construction sector is an essential product, providing society with what it needs in terms of safe, comfortable housing and reliable modern infrastructure. It has played a key role as a construction material throughout the history of civilization. Cement is produced worldwide. According to the [Global Cement Directory 2016], there were 2273 active integrated cement plants around the world in 2015 with 3.75 Bnt/yr of capacity. In Ethiopia, the highest producers of cement, Messebo, and Derba Midroc have the capacity of producing 2.1 million and 2.3 million tonnes on a yearly basis, consuming 272,000 tons and 272 tons of coal respectively [Mahlet Mesfin., 2011]. Cement manufacturing is an energy and resource intensive process. It involves the heating, calcining and sintering of blended & ground raw materials, typically limestone and clay or shale and other materials to form clinker. Clinker is the main component of cement and is produced in the rotary kiln. The kiln is a huge furnace where the cement clinker is made. Clinker consists mainly of calcium-, silicium-, aluminum- and iron oxides.

The world has three major energy sources: fossil fuels, renewable and nuclear. Fossil fuels (such as coal, petroleum and natural gas) are fuels formed by natural processes such as anaerobic decomposition of buried dead organisms, containing energy originating in ancient photosynthesis. These conventional fossil fuels are known to provide the energy requirement of different chemical industries. Coal, for instance, is the predominant fossil fuel burned in most cement kilns. Fossil fuels are generally considered to be non-renewable resources because they take millions of years to form.

The finite nature of these global fossil fuels have high prices and most importantly, have a damaging effect on the environment especially in increasing concentration of greenhouse gases in the atmosphere, particularly carbon dioxide. Carbon dioxide levels strongly impact the characteristics of the biosphere and geochemistry because atmospheric carbon dioxide concentrations control the planet's average pH (acid–base concentrations) [David Archer et al., 2009]. The cement industry, due to the unique nature of the product it manufactures, emits approximately 5% of global, man-made CO_2 emissions which causes about 4% global warming [WBCSD, 2009]. These greenhouse gas emissions originate mainly from fossil fuel combustion at cement manufacturing operations. The remaining cement related emissions originate from the manufacturing process that converts limestone ($CaCO_3$) to calcium oxide (decomposition or calcination of limestone), the primary precursor to cement.

Alternative fuels refer to fuels that differ from today's standard. They include all fuels other than Gas, Heavy Oil, Coal, and Petcock. Alternative fuels used in cement industries can be solid or liquid, derived from municipal waste, industrial waste, or their mixtures [Mokrzycki E et al., 2003]. These fuels are required to have an appropriate chemical content depending on the type of components and their organic contents. Sawdust is one type of alternative fuel which can be used as a source of energy. It is a byproduct of cutting, grinding, drilling, sanding, or otherwise pulverizing wood or any other material with a saw or other tool; it is composed of fine particles of wood. On the other hand, Sewage sludge is also another alternative fuel substitute for energy production. It is a residual solid cake produced after treating the incoming sewerage of waste water treatment plant. The sawdust and sewage sludge combination for energy production can be utilized through a process such as sorting, drying, size reduction and pelletization (which are solid cylindrical compacted materials) and can be used as an excellent source of cheap energy and environmental friendly.

In general, the substitution of alternative renewable resources will have an attractive benefit. Ethiopian cement industries must develop to burn alternative fuels in their kilns in order to provide a viable and convenient end of life option for byproducts and wastes and also to achieve their main strategic plan of climate reliance green economy on 2025.

1.2 Statement of the problem

The world's inevitable depletion of fossil fuels; the demand of Ethiopian cement industries on imported fuels coupled with the volatile fossil fuel; the raising of fossil fuel prices and global warming caused by increased emissions of greenhouse gases compel the local industries to focus on energy production through the use of alternative carbon neutral renewable sources.

There are numbers of possible renewable resources exist to shift from conventional fossil fuel to alternative fuels such as biomass (saw dust) which is a residue generated in sawmills and sewage sludge for cement industries. Despite the possibilities, sawmill residues in remote areas of the cities have insignificant economic value. The off-cuts and slabs are used for firing the boilers, while saw dust is disposed of into the river or piled up in fields & allowed to rot for lack of alternative fuels. On the other hand accumulation of large volumes of dried sludge (cake) in kaliti and kotebe treatment compound has become common and the failure to properly manage and limitations of the existing means of disposing of sewage sludge keeps challenging Addis Ababa Water and Sewerage Authority.

Therefore, the above aforementioned critical limitations of conventional fossil fuels and the above-mentioned gaps to utilize wastes (byproducts) as an alternative fuel for cement industries highlight the need to propose this research.

1.3 Objectives

1.3.1 General Objective

To co-pelletize sawdust and sewage sludge as an alternative fuel (energy source) for clinker production.

1.3.2 Specific Objectives

The specific objectives of this research are;

- To determine the proximate, ultimate and ash chemical analysis of sawdust.
- To conduct elemental composition and mineral content analysis of sewage sludge.
- To develop mixed pellet and carry out physiochemical characterization.
- To examine the effect of particle size and ratio on pellet calorific value.

1.4 Significance of the research

This research provides a safe and sound solution for Ethiopian cement industries, the society and most importantly, to the environment. Co-processing byproducts and wastes as alternative fuels mitigate greenhouse gas emission with an optimized clinker production. It will also provide a sustainable energy security (maximization of the recovery of energy from waste) and hedges against volatile global energy market due to their unlimited resources availability. In addition, it facilitates the intimidating task of waste disposal in an environmentally sound manner, therefore, presents a win-win situation for our country which has a strategic plan of climate reliance green economy.

The financial and environmental benefits of fuel switching are attractive for most cement factories. Switching to alternative fuels has financial benefits arising from the reduced cost of fuels and the factories can also benefit from added revenue from the CDM, as biomass fuels can reduce CO_2 emissions from cement plants substantially. At the national level, there are benefits such as foreign exchange savings and job creation.

2 LITERATURE REVIEW

2.1 Review on Conventional Fossil Fuels

The literature review included in this chapter contains available information related to the use of alternative energy sources and conventional fossil fuels in clinker production (cement manufacturing). The most common conventional fuels used in the cement industry are coal, pet coke, heavy furnace oil and to a lesser amount natural gas. A few reports and studies related to combustion of fossil fuels especially coal were included in the following paragraphs to address the drawback and impact. In particular, studies related to the environmental, health and economic costs and benefits of the use of alternative sources were searched and analyzed. Moreover, the literature on combustion of alternative energy sources in cement kilns was reviewed. Many documents were retrieved (academic papers, institutional and reports, as well as case studies) in order to extract their main findings and only the latest literature was chosen from the retrieved documents and included. During this review, gaps also emerged and these gaps were discussed at the end of this section and explained what was missing from the overall literature retrieved.

The cement industry is responsible for approximately 5% of the global anthropogenic greenhouse gas emissions (Figure 2.1). It is important to note that extensive research has shown that the cement industry does not generate large amounts of other greenhouse gases compared to carbon dioxide and this carbon dioxide emissions results from two sources that are from the decomposition of calcium carbonate during clinker production and the combustion of fossil fuels. The emissions resulting from the conversion of limestone into CaO are fairly constant and equate to approximately 540 kg CO_2 per tonne of clinker produced [H M Jonkers & N N Carr., 2013]. Since multiple factors are involved (such as the thermal efficiency of the kilns), the CO_2 emissions resulting from the combustion of fossil fuels fluctuate. Studies have further shown that cement related greenhouse gas emissions emanate from fossil fuel combustion at cement manufacturing operations (about 40% of the industry's emissions), transport of raw materials (about 5%) and the combustion of fossil fuel required to produce electricity consumed by cement manufacturing operations (5%).

The remaining cement related emissions (about 50%) originate from the process that converts limestone to calcium oxide the primary precursor to cement [Hendricks et al., 2002]. Therefore unless something drastic and different is done to mitigate the emissions, the world's atmosphere will go on being destroyed by activities which lead to the production of greenhouse gases and the depletion of natural carbon sinks further intensifying the problem of climate change.

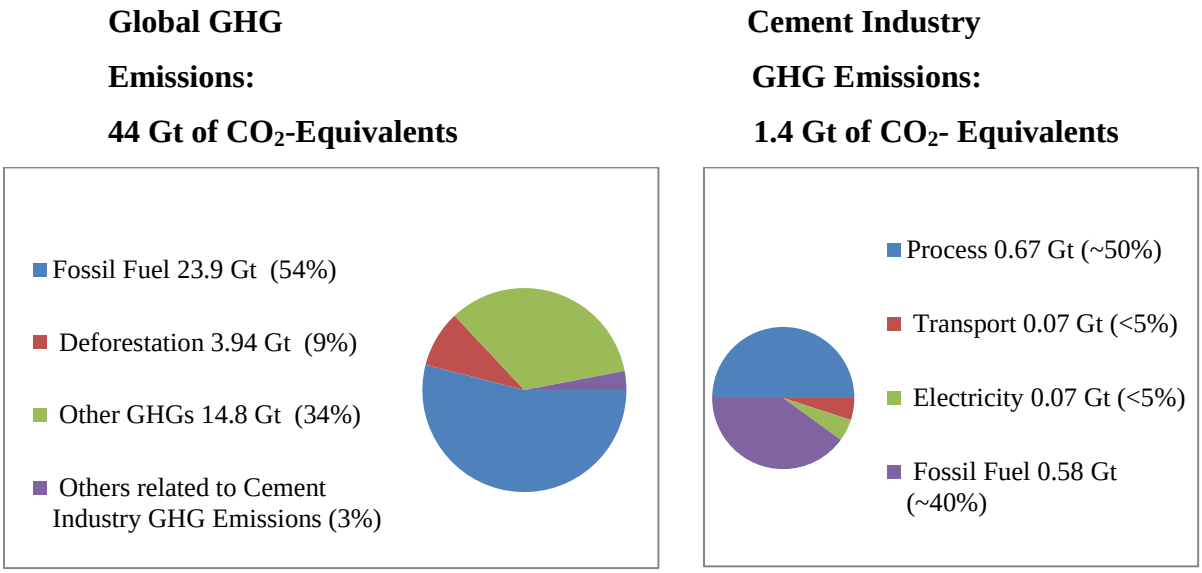

Figure 2.1 Greenhouse Gas Emissions from the Cement Industry for the year 2002 (WBCSD Report, 2002).

The [WBCSD, 2002] stated that approximately 40% of the GHG released during the cement manufacturing process are generated in the clinker formation process. However, the quantification of the CO_2 emissions from fossil fuel combustion is more difficult and inaccurate than that from the de carbonation process. In this case, the emissions from fossil fuel combustion are dependent on the types and quantities of the actual fuels burned, together with their interrelated carbon and heat factors (contents), as well as the kiln technology used for the burning process [Van Oss HG & Padovani AC., 2003]. The following table shows the different ranges of fuel derived CO_2 emissions per kg of clinker. Modern technologies based on the use of a dry rotary kiln with a preheater and pre-calciner have low emission ratios of approximately 0.31kg CO_2 per kg of clinker [Damtoft JS, et al., 2008][Szabo L, et al., 2003].

Table 2.1 CO_2 emissions per GJ of energy for fossil fuels (Pardo N. et al., 2011)

Fuel	Kt of CO_2/GJ
Petcock	97.5
coal	94.6
Fuel oil	77.4
Natural gas	56.1

On the contrary, the type of traditional fuel used also has a large impact on the CO_2 emissions because of the difference in their composition. As depicted in the above table, pet coke has one of the highest GHG emission ratios, releasing almost 98Kt of CO_2 per GJ of energy produced. Coal is also a high CO_2 emitter, as opposed to natural gas, which produces 56.1kt of CO_2 per GJ of energy and this is because it is composed chiefly of rings of six carbon atoms joined together in an extremely complex composition of layered arrangements that have in them, not only hydrogen but significant amounts of oxygen and nitrogen. The structure also includes varying amounts of sulfur and other environmental pollutants and these sulfur and nitrogen emissions of chemical oxides during coal burning can cause acid rain. Up to one tenth of the total mass of coal can be a material with no fuel value [NOOR-UL-AMIN & KHURSHID ALI, 2011].

A study by [Michael Ames et al., 2012] examined the patterns of dioxin emissions in a large set of stack tests at two Portland cement kilns in Portugal that use a variety of fossil fuels. A total of 152 stack tests provided data on PCDD/F congener concentrations during which the kilns combusted a variety mix of fossil fuels, various “special” supplemental fuels and refinery distillation ends, which are classified as hazardous wastes. The methodology for congener profile determination was well established. Overall PCDD/F congener concentration in units of picograms per normal cubic meter adjusted to 10% O_2 summary data for the stack gases at the two kilns are presented in (Table 2.2). It was described that the two similar Portland cement kilns operated by secil in Outao, Portugal have a nominal clinker production capacity of 2150 tons per day and a nominal clinker production capacity of 3500 tons per day. Both kilns use Greco type burners.

One substantial difference between the kilns is that following the preheater tower, one of the kiln uses a suspended pre-heater, while the other uses inline extra air calciner which obtains complete initial decarbonization than the kiln which uses a suspended preheater. Both kilns process the same aggregate feeds and use similar mixes of fuels. The primary fuel used to fire the kilns is petroleum coke, although occasionally coal has been used. The use of coal to fuel the kilns was found to generate significantly different emission profiles relative to the use of petroleum coke, but the addition of hazardous wastes as a supplement fuel did not significantly alter profiles.

In the result of the study, congener profiles were displayed for each secil kiln as distinguished by primary fuel (coke or coal), and by whether supplemental hazardous fuels were used in conjunction with the use of coke. As it was described in the result of the paper, there were substantial congener level variabilities within tests of the same kiln and the same fuel. This variability remained when the data were censored by eliminating tests with either low numbers of detected congeners or low total concentration. The profiles for the two secil kilns were found to be similar, with two PCDD/F congeners, namely 2,3,7,8-TCDF and OCDD almost always being measured at the highest concentrations. The overall profile shapes also generally match those based on data compiled by the U.S. EPA. Visually, the profiles for the two kilns appeared different with the suspended preheater kiln emissions having a more pronounced enrichment in 2,3,7,8-TCDF, while the other kiln emissions had a more even split between this congener and OCDD. Also, some of the fuel specific patterns in the profiles (notably the levels for 2,3,7,8-TCDF) appeared similar for the two kilns. However, statistically significant differences between profiles (as determined by the test) were found for some of kiln/fuel comparisons. None of the kiln to kiln profile comparisons (for a specific fuel) found significant differences (the greatest p value among the tests for the measured profiles being from identical true profiles was 0.044 for the intern kiln comparison of tests with coke plus hazardous waste fuel). Among the single kiln, fuel to fuel comparisons, the use of coal as a fuel produced significantly different profiles than when petroleum coke was used either with or without supplemental hazardous waste fuels. The overall finding that there were few statistically significant differences between profiles was perhaps attributable to the large variabilities in the profiles among otherwise similar tests as evidenced by the sizable standard deviations.

Table 2.2 Stack concentrations for the two Secil kilns (Michael Ames et al., 2012)

Congener	Kiln with a suspended preheater				Kiln which uses inline extra air			
	Mean	Std.dev	Max.	Det.%	Mean	Std.dev	Max.	Det.%
2,3,7,8-TCDD	0.7	1.1	6.5	28%	0.3	0.5	4.3	11%
1,2,3,7,8-PCDD	0.7	1.3	10.0	17%	0.2	0.3	1.5	10%
1,2,3,4,7,8-HxCDD	0.8	1.0	6.5	12%	0.3	0.2	1.0	9%
1,2,3,6,7,8-HxCDD	0.8	1.0	5.8	15%	0.3	0.2	1.3	9%
1,2,3,7,8,9-HxCDD	0.7	0.9	4.7	9%	0.3	0.2	1.0	8%
1,2,3,4,6,7,8-HpCDD	2.1	2.7	17.0	52%	1.3	2.2	18.0	46%
OCDD	5.3	6.6	41.0	62%	6.8	21.0	190.0	57%
2,3,7,8-TCDF	72.2	106.8	538.0	92%	11.4	43.8	371.0	84%
1,2,3,7,8-PCDF	7.4	12.4	71.0	58%	1.5	4.6	33.0	38%
2,3,4,7,8-PCDF	7.8	11.2	48.0	65%	1.7	6.9	62.0	34%
1,2,3,4,7,8-HxCDF	2.2	4.6	30.0	45%	0.6	1.0	7.2	25%
1,2,3,6,7,8-HxCDF	1.3	2.3	13.7	34%	0.4	0.7	4.2	17%
1,2,3,7,8,9-HxCDF	0.8	1.3	9.4	14%	0.3	0.2	1.2	11%
2,3,4,6,7,8-HxCDF	1.3	2.3	13.3	29%	0.4	0.8	5.0	18%
1,2,3,4,6,7,8-HpCDF	2.3	3.5	20.6	68%	0.9	1.0	4.2	66%
1,2,3,4,7,8,9-HpCDF	1.1	2.5	16.0	12%	0.5	0.7	5.5	17%
OCDF	3.3	5.1	34.0	37%	1.7	1.8	9.1	37%

A document by health care research collaborative [Erica Burt, MPH Peter Orris, MD, MPH Susan Buchanan, MD, MPH] has presented scientific evidence for the health effects from the use of coal for the generation of electricity and energy. Different recent research findings have been also summarized in the document. The document includes scientific evidence of health effects from the use of coal for energy generation. Its aim was to serve as a resource for those interested in the evidence from the health research literature addressing the health effects of the use of coal, focusing primarily on air emissions from coal combustion.

There was evidence of coal's impact on human health during every stage of its use for energy generation from mining to post combustion disposal. In particular, the combustion of coal has been well studied, with compelling evidence of widespread health effects on the population. It was described in the document that, in the vicinity of coal fired power plants; exposure to emissions depends on factors such as weather (temperature, precipitation, wind direction, and speed) and topographical features of the local area. Individual susceptibility to the health effects of coal emissions depends on age, underlying medical conditions, and use of medications.

According to the document, air pollution produced by coal combustion in power plants can affect the respiratory and cardiovascular systems as well as cause abnormal neurological development in children, poor growth of the fetus before birth, and can cause cancer. Moreover, coal combustion produces air borne pollutants of particulate matter, sulfur dioxide, oxides of nitrogen, carbon dioxide, mercury, arsenic, chromium, nickel, other heavy metals, acid gases (HCl, HF), hydrocarbons (PAHs) and varying levels of uranium and thorium in fly ash which in turn contributes to climate change and harm human health on a global scale. Specific pollutants from burning coal that cause a negative health effect on the respiratory system include PM, SO_2, and oxides of nitrogen such as NO_2. The mechanism of injury was also described in the document; it is to the airways and lungs via damage to cells caused by oxidizing molecules in pollutants. This leads to inflammation, cytotoxicity, and cell death. Populations that are especially vulnerable to health effects from air pollution include children, the elderly, pregnant women, and people with lung conditions like asthma and chronic obstructive pulmonary disease. Particulate matter generated from the combustion of coal is characterized by size small particles less than 2.5 micrometers ($PM_{2.5}$) and larger particles up to 10 micrometers (PM_{10}). $PM_{2.5}$ travels deeper into the airways than PM_{10}. A study of various power plant emissions in China found that of total particulate matter emitted, PM_{10} comprised 62-84% and $PM_{2.5}$ comprised 8-44 % [Yi H, Guo X, Hao J., et al., 2006]. In a report evaluating over 40 studies on the health effects of exposure to small particulate matter ($PM_{2.5}$), the U.S. EPA concluded that $PM_{2.5}$ likely causes respiratory symptoms, the development of asthma, and decrements in lung function in children [U.S. EPA, 2009]. Findings from the review concluded that a 10 $\mu g/m^3$ increase in $PM_{2.5}$ was associated with a 1% to 3.4% decrease in FEV1, a measure of lung function, in asthmatic children [U.S. EPA, 2009].

In addition to particulate matter, exposure of sulfur dioxide, oxides of nitrogen and cardiovascular effects were observed. It was also described that exposure to SO_2 emitted by coal burning power plants increases the severity and incidence of respiratory symptoms of those living nearby, particular children with asthma. There is a significant association between community level SO_2 concentration and hospitalizations for asthma and other respiratory conditions, and asthma emergency department visits particularly among children and adults over 65 [U.S. EPA, 2008]. A review of epidemiological studies in European cities, in Italy, Spain, France, and the Netherlands found that low concentrations of SO_2 (less than 10 ppb 24 hr. average) were associated with increased risk of death from heart and lung conditions [U.S. EPA, 2008]. Coal fired power plants also contribute to the global burden of cardiovascular disease primarily through the emission of particulate matter. Particles less than 2.5 microns in diameter ($PM_{2.5}$) have been causally linked to cardiovascular disease and death. The WHO estimates that worldwide, 5% of cardiopulmonary deaths are due to particulate matter pollution [WHO, GHO, 2013]. Long term exposure to $PM_{2.5}$ has been shown to accelerate the development of atherosclerosis and increase emergency department visits and hospital admissions for ischemic heart disease and congestive heart failure. The U.S.EPA reports that a majority of the studies it reviewed found a 0.5-2.4% increase in emergency department visits and hospital admissions for cardiovascular diseases per each 10 $\mu g/m^3$ increase in $PM_{2.5}$ concentrations [U.S. EPA, 2009].

2.2 Review on Alternative Fuels

The term alternative fuel refers to fuels that are different from today's standard. The term is dynamic, what are today's alternative fuels will become standard fuels in the future. They are known as non-conventional and advanced fuels. Alternative fuels are the solid, liquid, municipal or industrial wastes used in industrial and power plants as a substitute for conventional fuels. Alternative fuels have been in use for more than 10 years now and are gaining an increasing share of the global energy market [Eugeniusz Mokrzycki & Alicja Uliasz- Bochen czyk., 2003]. Alternative fuels used in the cement industry are usually classified according to the concentration criterion into gaseous (examples: landfill gas, pyrolysis gas), liquid (examples: pasty wastes, solvents, waste oils, greases) and solid (examples: animal powder, bark, paper, tyres, rubber wastes, plastics, fluff) [Jenkins BG and Mather SB, 1997: Pizant J and Gauthier JC, 1997]

According to the classification by Cembureau, alternative fuels are divided into the following five classes [Cembureau, 1999]:

- Class 1: gaseous alternative fuels (examples: refinery waste gas, landfill gas),
- Class 2: liquid alternative fuels (examples: low chlorine spent solvents, hydraulic oils),
- Class 3: pulverized, granulated or finely-crushed solid alternative fuels (examples: sawdust, dried sewage sludge, granulated plastic, animal flours, finely crushed tires),
- Class 4: coarse-crushed solid alternative fuels (examples: crushed tires, rubber/ plastic waste, wood waste, re agglomerated organic matter),
- Class 5: lump alternative fuels (examples: whole tires, plastic bales).

This section focuses on sewage sludge and wood related studies for energy production and a combination of different biomasses through a mechanism of briquette or pelleting.

The following research report was prepared by the EERC [Carolyn M. Nyberg, et al., 2012]. The purpose of this project was to help establish appropriate test methods for biomass characterization that are acceptable and reproducible and to promote their use among the industry. The specific objectives included a review of existing standard methods used for determining combustion characteristics for biomass fuel; characterization of common biomass materials, which included thermodynamic modeling to help predict slagging behavior; promotion of these biomass methods among industry through involvement in standards committees & evaluation of suitable biomass candidates for the development of SRMs. The project began with the collection and review of more than 50 analytical methods for biomass materials from various organizations. The methods included those used to determine parameters typically associated with fuel quality, such as proximate analysis (moisture, ash, volatile matter, and fixed carbon), ultimate analysis (carbon, hydrogen, nitrogen, sulfur, and oxygen), calorific value, halogens (bromine, chlorine, and fluorine), ash chemistry (major and minor elements), trace elements (arsenic, lead, mercury, etc.), ash fusibility, and bulk density. The final number of methods used in this project was narrowed down to 16. A total of ten different biomass samples were collected for the project. They included switch grass, corn stover, wheat straw, dried distillers grains, beet pulp, aspen, cottonwood, eucalyptus, loblolly pine, and waste wood.

The intent was to select candidates that are predominantly being used or have the potential to be used in the United States as feed stocks for energy production. Another factor that was considered when selecting these fuels was to choose materials that had varying chemical characteristics to better evaluate the test methods selected. The analytical results showed that the materials selected did indeed represent a wide range of chemical and physical characteristics. The ash and chlorine content varied greatly among the ten fuels analyzed. The alkali and alkaline earth metals (K, Na, Ca, Mg) were much higher in the herbaceous biomass materials than in the woody biomass. Many of the trace metals, including mercury, were very low in all of the materials, which make these materials an attractive energy source to help reduce overall emissions. They have a content of below detection limits for the wood fuels and were very low (≤0.0075 mg/kg) for the other biomass fuels. The woody biomass fuels have also very low sulfur and nitrogen contents and thus potential SO_2 and NO_x emissions (≤0.04 lb/MMBtu and ≤0.17 lb/MMBtu, respectively). They generally have low chlorine concentrations (<40 mg/kg), with the eucalyptus being the exception. The dried distiller's grains, switch grass, and wheat straw has the highest chlorine contents (>600 mg/kg). The corn stover and dried distillers grains fuels were predicted to cause little or no silicate based high-temperature fouling. The beet pulp, switch grass, eucalyptus, and waste wood pellet fuels may cause problematic silicate based fouling based on liquid concentration and viscosity predictions. The cottonwood and aspen were expected to pose no silicate based fouling because they lacked liquid silicate phases. In general, the woody biomass fuels were expected to present the lowest propensity for low-temperature fouling.

A paper by [E. Yilmaz M. Wzorek S. Akcay], conducted a research on the production and properties of alternative fuel pellets for using in thermal processes. The process of co-pelletization of sewage sludge and another biomass material such as animal and olive waste was presented in order to assess the influence of these wastes on physical parameters of pellets. The aim of the research was to identify the key factors affecting the sewage sludge and biomass pelletization processes conditions. The impact of raw material type, two different ratios of the materials, moisture content and particle size on the physical properties was investigated. The physical parameters of pellets, i.e.: drop strength, absorbability, and water resistance were determined.

Main energy parameters: low and high heat value, the content of ash and volatiles were presented. Due to the fact that all fuel components are characterized by high moisture content, a technology of their pelletization was selected and developed, which technology consists of initial mix of the components and then forming in a special devices. In order to identify the pellets, individual symbols were attributed to them: SOW (pellets which were based on the sewage sludge and olive waste), SAW (pellets obtained from the sewage sludge and animal waste). For comparison, pellets from sewage sludge alone were also made, which were marked with the SS symbol. In the study, only pellets with the sewage sludge content of 20% (SOW20, SAW20) and 30% (SOW30, SAW30) were covered. The energy properties of the pellets, i.e. high calorific value was conducted by using Oxygen Bomb Calorimeter KL-Mn (PN-EN 14918:2010), the ash content, the volatile matter content and moisture by differential thermal analyser Netzsch Jupiter STA 449 and the ultimate analysis of pellets were performed via Elemental Analyzer type Elementar Vario MACRO Cube in accordance with PN-EN 15104:2011 (C, H, N) and PN-EN 15289:2011 (S). Testing of physical properties such as drop strength (according to the PN-G-04651), water resistance (PN-G-04652) and absorbance (PN-G-04652). Results showed the range of energetic property analysis of pellets in comparison with hard coal is shown in the Table (2.3).

Table 2.3 Energy Properties of pellets (E. Yilmaz M. Wzorek S. Akcay.)

Parameter	Unit	SOW20	SOW30	SAW20	SAW30	SS	Hard coal
Water	%	5.89	6.22	6.05	5.18	5.09	5.0-10.0
Volatile matter	% d.m.	30.17	29.73	30.78	29.67	37.88	25.0-40.0
Ash	% d.m.	39.65	30.92	41.91	42.69	45.73	8.5-11.3
LHV	MJ/kg	12.41	14.52	10.78	8.58	10.08	23.7-28.3
HHV	MJ/kg	13.41	15.80	11.85	9.46	11.03	26.0-28.3
Elementary Composition							
Carbon		30.79	35.81	30.79	24.01	27.24	76.0-87.0
Hydrogen		4.49	5.16	4.211	3.47	3.77	3.5-5.0
Nitrogen	%d.m.	1.54	1.38	1.8	1.71	2.11	0.8-1.5
Sulfur		0.55	0.79	1.98	0.94	1.97	0.5-3.1

The SOW30 fuel was found out to be comparable with the RDF fuel, which is made from an inflammable fraction of municipal waste and according to [Genon et al., 2008], it may range from 13 to 18 MJ/kg. The addition in the form of olive waste positively influences the calorific value of pellets. It was stated that the fuels may be used in clinker baking as a substitute for hard coal and be put in a rotary furnace with transport and alternative fuel dosing systems already employed in cement plants. The result of physical properties of the small sized produced pellets also showed different characteristics. Pellets of the same type (but with different sewage sludge content) were characterized by similar drop strength, i.e. for the SOW fuel, it was from 80 to 90% while in the case of the SAW pellets from 75 to 80%. The highest index was obtained for pellets made of sewage sludge (95%). The obtained results showed that the pellets were characterized by high drop strength. The lowest absorbability was found in the SOW30 pellets. On the basis of the conducted research, an observation was made that water has a destructive effect on the strength of the fuel. It was found in the study that after the pellets absorb water its strength tends to drop dramatically.

A research by [N. Supatata, J. Buates, and P. Hariyanont., 2013] aimed to study the quality of the fuel briquettes made from sewage sludge mixed with water hyacinth and sewage sludge mixed with sedge for alternative energy production. Sewage sludge was mixed with water hyacinth and sedge at the ratios of 1:1, 1:2, 1:3, 2:1 and 3:1 then compressed with hydraulic pressure to obtain fuel briquettes and finalized them by analyzing fuel briquettes properties including moisture content, calorific value, and compressive strength. A homemade mold was designed and built to make fuel briquette, with the size of 5.5cm × 5.5cm × 5.5cm. Dried sewage sludge and water hyacinth samples with particle sizes between 74 and 300 μm were blended to produce homogenous mixes with the ratios of sewage sludge and water hyacinth or sedge; 1:1 (water hyacinth or sedge 50%), 1:2 (water hyacinth or sedge 66%), 1:3 (water hyacinth or sedge 75%), 2:1 (water hyacinth or sedge 33%), and 3:1 (water hyacinth or sedge 25%) by weight on a dry basis. Compacted samples were prepared by adding 15 % of starch and pressing by using hydraulic press machine to form the fuel briquette. Then the fuel briquettes were dried in the oven for 48 h at a temperature of 75℃.

The proximate analysis of the three materials result showed that the volatile matter and ash content of the sewage sludge sample were relatively high. In the result, it was found that all briquettes made from sewage sludge mixed with water hyacinth and sewage sludge mixed with sedge had fractures on the surface which will lead to decrease the quality of them. In the study, it was justified that the fractures on the surface were due to irregular size of particles. The result in the physical properties of fuel briquettes made from sewage sludge mixed with water hyacinth showed that the moisture content of the briquette made was between 4.78 % and 6.24 %. The calorific value of the briquette was between 2, 521. 8 cal/g and 2,785.9 cal/g, lower than TCPS standard. The ratio of sludge and water hyacinth at 1:3 provided the highest calorific value (2, 785. 9cal/g) and had a closer calorific value to the TCPS standard of wood charcoal briquettes. It also showed the highest compressive strength value (4,545 N). The result from the physical properties of fuel briquettes made from sewage sludge mixed with sedge showed that the moisture content of the briquette made from sewage sludge mixed with sedge was between 6.04 % and 7.86 % higher than the briquette made from sewage sludge mixed with water hyacinth. The calorific value of this mixture was between 2,774.5 cal/g and 3, 362.1 cal/g and the ratio of sewage sludge and sedge at 1:3 gave the highest calorific value. Even though its calorific value was higher than briquette made from sewage sludge mixed with water hyacinth (2,521.8cal/g-2,785.9cal/g), it was still lower than TCPS standard. The ratio of sewage sludge and sedge at 1:3 showed the highest compressive strength value (1,068 N) but lower than the briquette made from sewage sludge and water hyacinth at the ratio of 1:3.

The combustion process of two kinds of biomass and sewage sludge was studied by [Aneta Magdziarz and Małgorzata Wilk., 2013]. The biomass fuels were wood biomass (pellets) and agriculture biomass (oat). The sewage sludge came from the waste water treatment plant. The sample of studied coal was from a Polish coal mine. The biomass and sludge percentage in blends with coal were 10 %. Before thermogravimetric analysis, the fuels were analyzed to determine the main properties affecting thermal conversion. The properties include volatile matter, ash, moisture content, heating value and also chemical composition were tested in accordance with standards (Polish standards: PN-EN 15403, PN-EN 15400, PN-EN 14774, PN-EN 14775). Metal analysis of the fuels was conducted by inductivity coupled plasma spectrometry and spectrophotometry.

The behavior of studied fuels was investigated by thermogravimetric analysis (TG, DTG, and DTA) using a Mettler Toledo TG/SDTA 851 apparatus. The samples were heated from an ambient temperature up to 1,000 ℃ at a constant three rates: 10, 40 and 100℃ min^{-1} in 40 mL min^{-1} air flow. TG, DTG and DTA analysis showed differences between coal, biomass fuels, and sewage sludge. Evolved gaseous products from the decomposition of the studied samples were identified, using a ThermoStar GSD300T Balzers quadruple mass spectrometer (QMS). In the result, the carbonaceous materials found to have very different properties, a moisture content of 2.9% wood biomass, 7.1% Oat, 5.3% Sewage sludge and 7.8% coal were obtained. A result of 0.3%, 1.5%, 38% and 4.9% ash content was obtained for wood biomass, Oat, Sewage sludge and Coal respectively. This was about thirty times higher for sewage sludge than for oat or wood biomass. When it comes to calorific values, the energy content was widely higher for biomass (17.59 MJ kg^{-1}) than for sewage sludge. The HHV~12 MJ kg^{-1} for sewage sludge was two times lower as compared to coal (the coal used in the study has an HHV around 25 MJ kg^{-1}). The result of the ultimate analysis was shown in (Fig 2.2), the C and H contents of these two kinds of biomass were found to be comparable, as well as their calorific value. The 30 % carbon content of sewage sludge was two times lower than for coal, and the sulfur content was also lower as compared to coal. The nitrogen content of sewage sludge was the highest among the investigated fuels (4.3%).

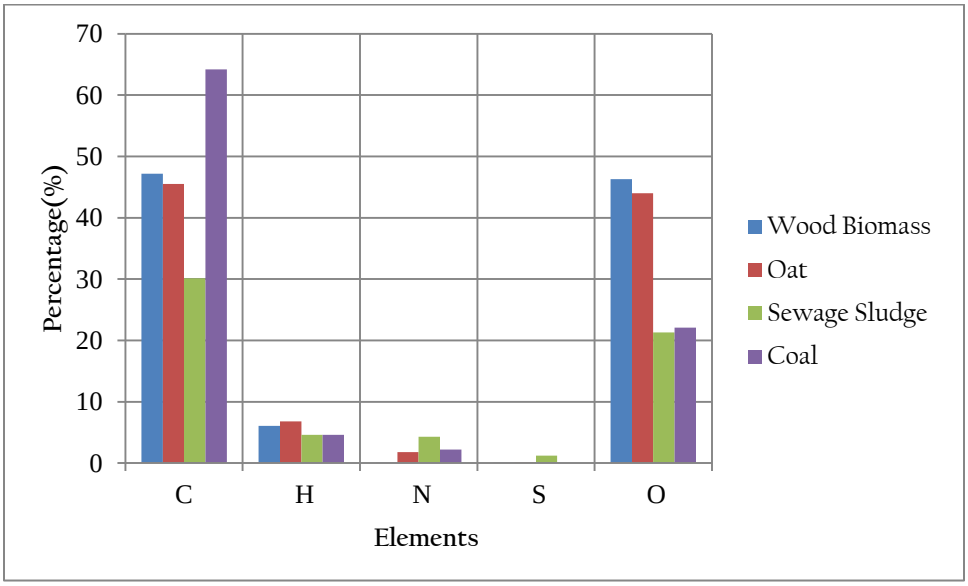

Figure 2.2 Ultimate Analysis of studied fuels **(**Aneta Magdziarz & Małgorzata Wilk., 2013)

It was also observed in the result of the ash composition that the oat and sewage sludge have significantly higher silica content (21.13 and 25.10% respectively) compared to the wood biomass (12.08%). On the other hand, the content of P_2O_5 was found to be very high for wood and oat biomasses (16.49% & 18.02% respectively).The oat ash includes a very high content of K_2O (16.21%), but the lowest content of Na_2O (0.22%). The higher concentration of Fe_2O_3 (13.81%) in sewage sludge was obtained and the result of the study was shown in (Fig 2.3). It was also noted in the investigated sludge amount of harmful heavy metals was low. It contains the following trace elements: chromium (0.083 %), copper (0.112 %), lead (0.010 %), mercury (0.002 %) and nickel (0.056 %).

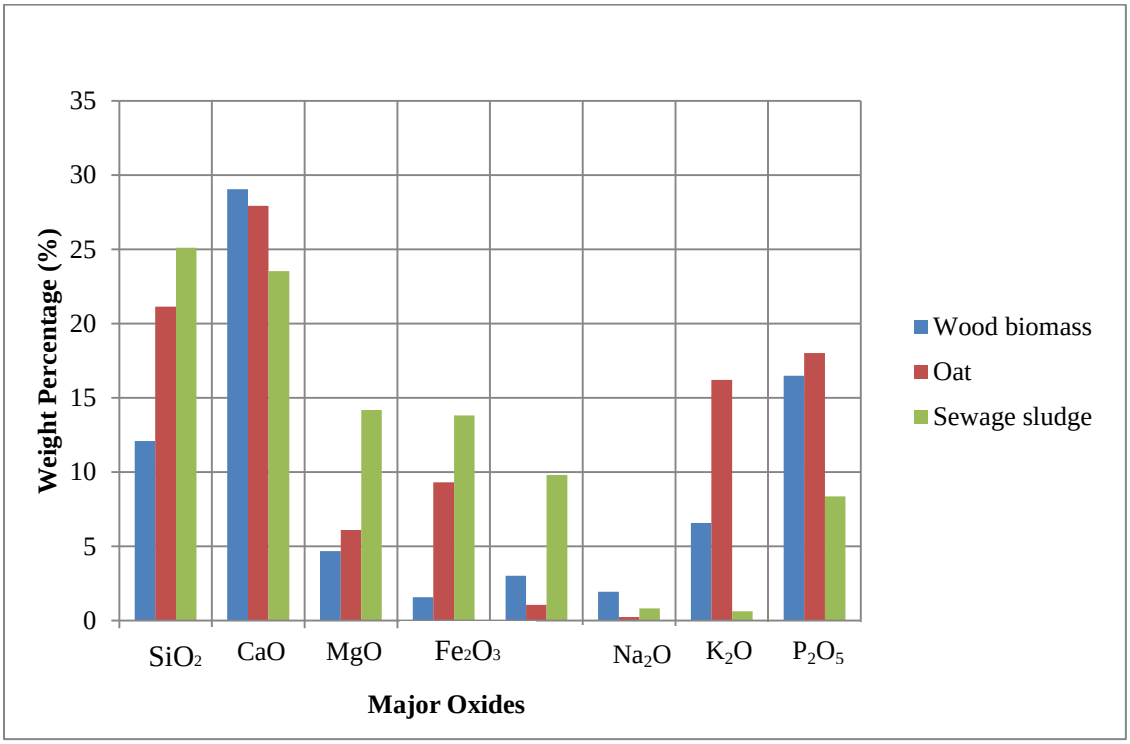

Figure 2.3 Ash compositions of the studied fuels **(**Aneta Magdziarz & Małgorzata Wilk., 2013)

According to co-combustion results of coal and the studied fuels, the coal shows typical combustion profiles, with the main peak ranging between 300 and 700 ℃ with a maximum mass loss rate at 519℃, the result of thermal decomposition and loss of volatiles, as well as char gasification. The 10 wt% addition of renewable fuel to coal behaves similarly to coal, although some differences were noted. For the wood biomass and coal mixture, additional peaks were observed at 342 and 476℃.

The maximum mass loss rate for all mixtures was 513 ℃ , which was higher than for pure coal. Mass spectrometry analysis result showed that two species are identified with m/z value: ethane C_2H_6 and nitrogen monoxide. In the discussion of the study, it had passed that m/z = 30 correspond to NO. Nitrogen oxide was released during the second stage of combustion of the fuels (200-600℃). The highest NO concentration was observed during sewage sludge combustion as a consequence of the higher nitrogen content in the material. The NO emission for sewage sludge shows a close relationship with the combustion process; at c.a. 480 ℃ the highest lost mass took place, which corresponds to NO emission. SO_2 is associated with m/z = 64. The SO_2 emission was much lower than the CO_2 emission during combustion.

Table 2.4 Characteristic parameters obtained from DTG and DTA profiles of studied fuels

Sample	Heating rate /℃ min^{-1}	T_m/℃	DTG_{max} /mgs^{-1}	Solid residue char + ash (%)	DTA_{max}/ ℃	Main region/℃	Mass loss /%
Wood biomass	10	324	0.030	1.46	455	180-632	98
	40	340	0.067	4.61	493	180-608	94
	100	345	0.215	2.10	480	180-758	97
Oat	10	295	0.036	2.75	351,482	160-688	90
	40	308	0.172	3.08	385,522	193-729	88
	100	313	0.246	4.35	533	240-695	96
Sewage sludge	10	483	0.014	34.92	486	161-726	58
	40	287	0.026	35.41	537	168-779	56
	100	293	0.062	37.23	549	168-828	55
90% C-10% WB	40	513	0.031	7.26	534	185-875	84
90% C-10% WB	40	520	0.027	8.69	567	218-830	92
90% C-10% WB	40	513	0.028	11.86	545	292-808	88

On the other hand, SO_2 peaks occur at lower temperatures than CO_2 peaks for all the fuels. The highest emission of this compound was noted for coal combustion, a result of the elementary composition of the fuel. Only one SO_2 peak was observed at about 432℃. The SO_2 emission for sewage sludge was about eight times lower, but emission of gaseous particle monitored occurred at lower temperatures for sludge than for coal. There were two SO_2 peaks, the first at 298℃ and the second at 461℃. The case of sewage sludge the emission of methane is the highest and takes place at around 490℃. A relatively large amount of H_2O (m/z = 18) was formed for oat sample. The H_2O evaluation profile was similar for wood and oat biomasses. For sewage sludge, the H_2O profile exhibits two visible maxima at around 300 and 474 ℃ . The experimental results showed that kinetic parameters are in good agreement, and used calculated model can better understand the combustion process. The value of Ea calculated by Kissinger–Akahira–Sunose method was also shown in (Table 2.5). The activation energies for coal were in the range of 21,1145.7 kJ mol^{-1}, for wood biomass 81.1-223.1 kJ mol^{-1} and for oat 11.9-282.5 kJ mol^{-1}. From all studied fuels, the coal had lower activation energy than biomasses or sewage sludge.

Table 2.5 Values of activation energy obtained by KAS method for coal, WB, Oat and SS

α	Coal (E_a/ kJ mol^{-1})	Wood biomass (E_a/ kJ mol^{-1})	Oat (E_a/ kJ mol^{-1})	Sewage sludge (E_a/ kJ mol^{-1})
0.1	119.91	143.99	117.68	29.64
0.2	145.69	177.65	184.50	109.16
0.3	110.19	195.06	189.66	136.43
0.4	76.85	191.94	178.60	150.45
0.5	53.32	188.27	199.64	146.80
0.6	37.67	223.07	253.49	161.03
0.7	28.26	208.41	282.52	122.00
0.8	23.36	129.61	164.75	87.32

According to another study by [Małgorzata Wzorek, 2012] showed that the fuels manufactured with the use of waste materials offered the energy values which were satisfactory for the cement industry as specified for alternative fuels in that branch. The tests for physical properties also revealed that such fuels may be subjected to mechanical handling operations in the transport and storage processes. The main objective of the paper was to study the characteristics of the properties (including physical properties, combustion properties and other additional properties) of alternative fuels containing sewage sludge and to provide a suggested route for the use of the sewage sludge in combination with other selected wastes, i.e. with coal slurry, with the meat and bone meal and with wastes from the wood industry. In order to identify the produced fuels, individual symbols were attributed to them: PBS fuel which was based on the sewage sludge and coal slurry, PBM fuel obtained from the sewage sludge and meat and bone meal, PBT fuel which was produced with the use of sawdust.

Physical and chemical properties of those fuels [Małgorzata Wzorek, 2012] were investigated, with special attention paid to their calorific values and physical properties. Those compositions could then be converted into granulated fuels with the performance properties as required by the cement industry. The fuel production method comprised two steps: pre-mixing the sludge with other waste materials at pre-defined ratios, granulation, and drying. The composition of the fuel were as follows PBS (60 wt.% of sewage sludge, 34 wt.% of coal slurry, and 6 wt.% of burnt lime); PBM (75 wt.% of sewage sludge, 24 wt.% of meat-and-bone meal, 1 wt.% of burnt lime); PBT(80 wt.% of sewage sludge, 19 wt.% of sawdust, 1 wt.% of burnt lime). Then the fuels obtained were subjected to numerous tests and investigations. The energy properties, the i.e. calorific value was conducted by using Oxygen Bomb Calorimeter KL-Mn, in accordance with PN-ISO 1928:2002, the ash content in accordance with PN-ISO-562:2002, and the volatile matter content in accordance with PN-ISO-562:2000. The ultimate analyses of the samples were performed via Elementary Analyser Vario Macro EL. The flash point values for the fuels were found by the Marcusson method, up to the standard PN-82/C-04008, and characteristic temperatures for ash fusibility according to PN-82/-04535:1982. The thermal and thermogravimetric analyses involved the differential thermal analyzer NETZSCH, type STA 4009EP, within 0÷1400℃ and under the oxygen atmosphere. The chemical composition of ashes was analyzed by using the ICP method, and the remaining component levels using the

PANalitical XRF method. The mass spectrometer ICP MS Perkin Elmer, 'Elan' 6100, was used to learn the heavy metal contents, while PCBs were determined as the total of congeners: PCB 28, PCB 52, PCB 101, PCB 138 and PCB 180, with the use of the Agilent 6890N gas chromatograph which was equipped with the ECD detector. The total PAHs were analyzed with the use of the liquid chromatography assembly: HPLC 1200 Series. The analysis yielded (PAHs). Within the physical properties of the fuels, the following parameters were also studied: bulk density (according to PN-ISO 567), strength by dropping, water resistance, water absorbability, and frost resistance. In the result, the heating potential of the sludge derived fuels was shown and compared with the properties of hard coal and with the requirements as set by the cement industry for the alternative fuels (Table 2.6).

Table 2.6 Energy Properties of sludge-derived fuels, coal, and requirements of the cement industry (Małgorzata Wzorek,2012, B. Mokrzycki, et al., 2003)

Parameter	Unit	PBS fuel	PBM fuel	PBT fuel	Hard coal	Requirements of cement industry
Proximate analysis						
LHV	MJ/kg	19.30	14.59	13.23	20.5-31.9	≥13
HHV	MJ/kg	21.71	15.97	15.54	-	-
Moisture	%	8.58	8..67	10.37	5.5-10.00	<30
Volatiles[a]	%	34.44	56.84	66.74	2.40-5.90	-
Ash[a]	%	27.86	33.72	20.36	3.10-24.00	<40
Ultimate analysis wt.% of dry matter						
Carbon	%	50.28	36.64	31.42	64.1-72.5	-
Hydrogen	%	3.91	4.12	4.43	4.00-5.60	-
Nitrogen	%	1.72	6.87	2.61	2.60-12.80	-
Sulfur	%	1.16	0.68	0.65	0.60-1.4	<2.50
Oxygen	%	15.01	17.95[b]	40.50[b]	No data	-
Chlorine	%	0.06	0.02	0.03	<0.10	<0.30

[a] In dry matter.

[b] Calculated from the balance (difference).

Within the alternative fuels prepared in this study, the highest heating value was offered by PBS fuel. The chemical compositions: for the ash from the studied fuels and for the coal slurry, were arranged for comparative presentation in the (Table 2.7). The ash materials from sewage sludge, meat and bone meal and sawdust fuels were found to have different properties as compared to the coal slurry ash. The former result show much higher contents of Calcium oxide and lower contents of acidic components (Silicon oxide and Aluminum oxide), which is specific for biomass derived fuels [A. Demirbas., 2004], but they contained the similar oxides composition as the raw materials which were used for the production of clinker.

Table 2.7 Chemical analysis of ashes of different biomass and coal slurry

Parameter wt.%	Sewage sludge	Coal slurry	Meat and bone meal	Sawdust
SiO_2	24.26	47.36	13.61	16.34
Al_2O_3	6.18	28.83	1.55	3.16
Fe_2O_3	12.88	9.57	0.72	1.43
CaO	31.62	4.23	42.79	38.89
MgO	1.33	2.26	3.09	7.44
P_2O_5	13.00	0.78	33.79	2.06
SO_3	5.49	3.55	0.64	2.62
Mn_3O_4	0.29	0.10	0.02	2.02
TiO_2	0.54	1.21	0.06	0.20
SrO	0.15	0.09	0.04	0.08
Na_2O	0.41	1.02	1.92	0.60
K_2O	1.16	2.89	0.86	11.06

Besides the regular mineral components, the ash from PBS, PBM and PBT fuels contains also heavy metals. The heavy metal contents for sludge based fuels were also included in the result (Table 2.8). The results demonstrated that the levels of heavy metals contained in the studied fuels comply with the limits for hard coal. The highest concentrations were noted for manganese (PBM and PBT fuels), zinc (PBT fuel) and chromium (PBS fuel). The content of volatile heavy metals (mercury, cadmium, and thallium) was lowest in PBM fuel where it amounts to 0.9% of the acceptable limit. That level for PBS fuel was 2.28%, while for PBT fuel it was 2.69% of the

allowable value. Table 2.9 shows the contents of PCBs and PAHs in the produced alternative fuels. As regards the PCBs level, the limit value of 50 ppm was defined by Lafarge Cement. The PCBs contents were determined in the tested fuels and they were found to be very low, close to the determination limits in practice.

Table 2.8 Heavy metal contents in sludge derived fuels & in hard coal

Heavy metal ppm	PBS fuel	PBM fuel	PBT fuel	Hard coal	Requirements of cement industry
Mn	165	350.9	319.3	4-1990	Total content
Cr	<181	22.08	93.68	0-60	<2500
Zn	250	446.1	881.2	2-3560	-
Pb	63.20	19.43	24.93	2-370	-
Co	14.12	3.89	6.27	0-140	-
Ni	<25	4.92	15.92	0-130	-
V	1.14	2.53	3.10	2-100	-
Cu	58.88	43.84	71.77	0.5-50	-
As	1.53	0.997	2.254	0-170	Cd+TI+Hg
Sn	0.478	0.030	0.028	0.02-1	<100
TI	0.048	0.051	0.089	-	-
Cd	1.25	0.434	1.690	0.1-3.0	-
Hg	0.987	0.421	0.859	1-10	Hg<10

The result of the finding on poly chlorobenzene and PAHs contents are as follows. The requirement was defined by Lafarge cement.

Table 2.9 PCBs and PAHs contents in sludge derived fuels

Parameter ppm	PBS fuel	PBM fuel	PBT fuel	Requirements of cement industry
PCBs	<0.05	<0.05	0.11	<50
PAHs	9.1	2.9	9.3	-

The flash point and the ash fusibility were also studied for the complete specification of a fuel. The flash point values, as measured by the Marcusson method, were also presented in the result (Fig. 2.4). The lowest flash point (~315℃) was offered by PBT fuel. The flash point for PBM fuel equals to ~345℃, while it was ~415℃ for PBS.

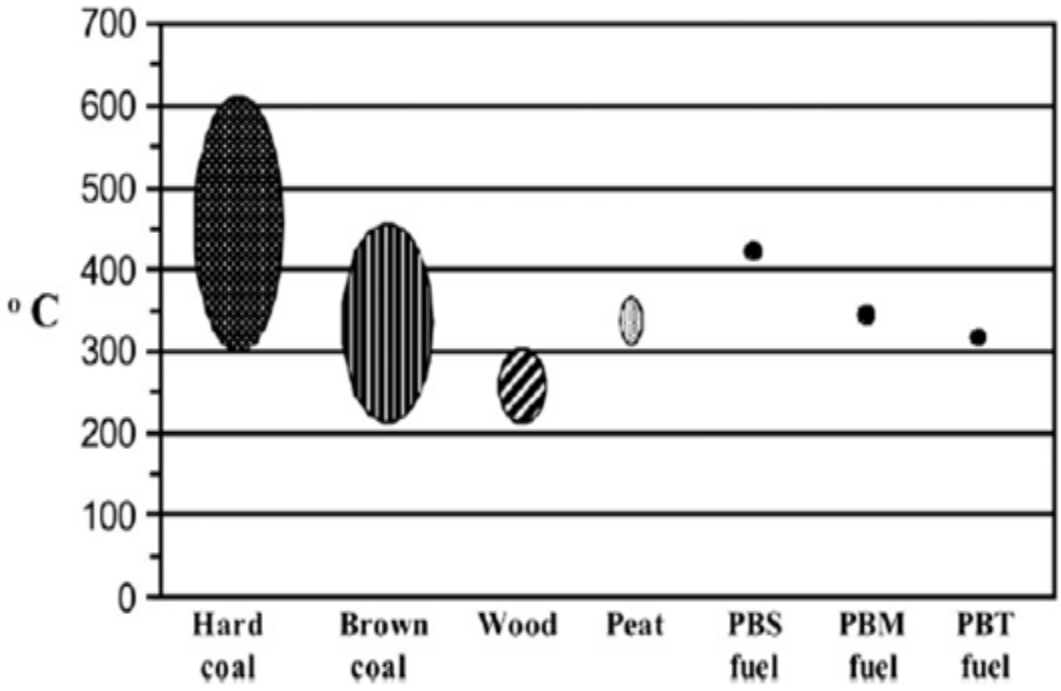

Figure 2.4 Flash Point values for selected fuels

The results of DTA and TG, of tested fuels, demonstrated similar behaviors for those fuels. Two peaks were observed, however, for PBS fuel: at 320 and at 360℃. It was also observed in the result that the combustion process takes place up to the temperature of 800℃. The loss in weight for PBS fuel was no longer observed at 1200℃ and it amounted to 77%. The same for PBM fuel takes place at 920 ℃ (loss in weight of 55%), and for PBT fuel at 820 ℃ (loss in weight of 69.7%). In the result of physical properties of sludge derived fuels, the PBM fuel and PBT fuel were characterized by similar and very high values of the strength by dropping factor: it was 97% for PBM fuel and it reached as high as 100% for PBT fuel. The factor for the PBS fuel, however, was much lower. The strength properties of the fuels were not impaired by a month long storage, and they even improved slightly for PBM. The water resistance tests showed that water was destructive for the strength by dropping that value decreased for all the tested fuels.

PBM fuel was found to be least water resistant, and its strength by dropping was reduced dramatically after absorption of water. That parameter declined by 30% for PBM fuel and by 10% for PBS fuel. With regard to frost resistance, the impact of varying temperatures (and in particular of negative temperatures) was not as extensive on the structure of fuels as it was observed for water. After the frost resistance test, the strength by dropping of PBS fell down by 30%. The PBM and PBT fuels, on the other hand, were more resistant to that type of impacts as their strength was reduced on average by 10% only. The highest water absorbability potential was noted for PBT fuel (120%). The lowest imbibition level was measured for PBM fuel (70%). Therefore the result showed that the fuels which were produced with the use of the sludge could be employed in the clinker burning process instead of hard coal.

In the study by [Hui Li, Long-Bo Jiang et al., 2015], the pelletization of biomass materials mixed with sewage sludge (SS) was investigated. The effects of process parameters on energy consumption and pellet properties especially physical properties were mainly studied. Three types of raw materials (Chinese fir, camphor sawdust, and rice straw) were prepared for the experiment. Sludge and single biomass sample were weighed and mixed manually with a constant ratio of 50 wt. % and pelletized with a laboratory presser. A single factor variable method was applied to investigate the variables of pressure, temperature, and water content which were conducted at 90℃ with 15% water content, 55 MPa with 15% water content, and 55 MPa with 90℃, respectively. The moisture uptake of pellets was measured in a humidity chamber (GT-TH-S-150Z, China), which was set at 30℃ and 90% relative humidity. Ultimate analyses were obtained by CHNOS Elemental Analyzer Vario EL III. Proximate analysis was carried out according to the Chinese Standard Practice for the Proximate Analysis of solid biofuels (GB/T28731-2012). The amounts of cellulose, hemicellulose, and lignin were obtained by automated fiber extraction analyzer (Gerhardt fibre therm FT12, Germany). Protein was also calculated by using [Shao et al., 2013]. The higher heating value (HHV) was determined using an oxygen bomb calorimeter (SUNDY SDACM5000, China). The results of properties of sewage sludge and biomass sample were shown in the following (Table 2.10).

Table 2.10 Properties of raw sewage sludge

Parameter	Sludge	Chinese fir	Camphor	Rice straw
Proximate analysis (wt. %)				
Moisture	5.42	7.63	6.67	6.56
Volatile	57.22	74.49	79.02	64.59
Fixed carbon	6.09	16.68	12.53	13.51
Ash	31.27	1.20	1.78	15.34
Ultimate Analysis (wt. %)				
Carbon	36.11	49.08	48.18	45.04
Hydrogen	5.25	5.96	6.09	5.05
Nitrogen	6.50	0.63	0.70	1.06
Sulphur	1.03	0.00	0.00	0.00
Chemical analysis (wt. %)				
Protein	35.5	-[a]	-[a]	-[a]
Hemicellulose	-[a]	12.05	20.82	24.60
Cellulose	-[a]	36.22	38.87	41.33
Lignin	-[a]	27.61	24.40	9.22
HHV (MJ/kg)	15.59	18.38	18.40	14.64

-[a] Not measured

With respect to compression energy consumption, it was described in the result that the compression energy consumption was affected by applied pressure, die temperature and water content. The compression energy consumptions for Chinese fir-SS pellet (CFSP), camphor-SS pellet (CSP) and rice straw-SS pellet (RSSP) increased with the increase of pressure at the die temperature of 90℃. For comparison, the compression energy consumptions for sludge biomass pellets of different sludge ratio produced at 55 MPa, 90℃ and 15% water content were also included. It was found in the result that, the compression energy consumption of biomass decreased distinctly after mixing with sludge. Furthermore, the lower the compression energy consumption was the higher the sludge ratio.

The energy consumptions of pellets with 50% sludge ratio were much lower than those of the pure biomass pellets. Therefore, the sludge ratio was controlled at 50% in the study according to a comprehensive consideration of the energy consumption and pellet properties described in a previous paper [L.B. Jiang et al., 2014]. With respect to Pellet density and volume expansion, it was found that higher density of pellet could be obtained above 55 MPa and 70℃. It was speculated that the natural binding components such as starch, protein, lignin, and water soluble carbohydrate in the SS and biomass materials could be squeezed out of the particles under the pressure of >55 MPa. However, the pellet density increased slightly with incremental pressure and temperature (above 55MPa and 70℃). The optimum water content for co-pelletization in the study was 10–15%. Comparing the results, it was found that the pellet density was independent of the pressure above 55MPa and temperature above 70℃, but was highly affected by the water content increases in the range of 5–25%. It was described that the volume expansion was related to pellet density. Furthermore, the lower of volume expansion was obtained when the pellet density was higher. In the result of maximum braking force, it was found that the maximum breaking force was independent of the pressure of >41 MPa, but was highly influenced by the temperature and water content. In addition, the moisture uptake ability was also found to be independent of applied pressure. The pellet made at 30℃ exhibited a higher absorption rate (0.01201 min^{-1}) when compared with pellets produced at 150℃ with the absorption rate of 0.00779 min^{-1}. And it was justified in the study that it was mainly ascribed to the weak bond within particles and the corresponding voids and gaps structure.

2.3 Current Status of Alternative Fuels in Cement Industries

Burning biomass and waste residue like sewage sludge in cement kilns is occurring in different cement industries of the world due to volatile energy price and environmental benefits. Cement kilns are well suited for waste combustion because of their high process temperature. Several years of experience with the use of waste as alternative fuels by different cement industries in the world have shown that their application is justified both from an economic and an ecological point of view [Junior LM., 2003].

Some cement factories in Belgium, France, Germany, the Netherlands, and Switzerland have reached substitution rates ranging from 35% to more than 70% of the total energy used [Taylor et al, 2006]. The following are a few examples of current status and real life application of alternative fuels in cement kilns included in [Yisehak Seboka et al., 2009] which were reported in various publications.

- **Austria:** Austria's cement factories were amongst the earliest to start burning tires since the 1980s, and have been burning solid waste such as plastics, paper, sewage sludge, 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].
- **Germany:** Heidelberg Cement claims to have increased the use of alternative fuels up to 78 percent in one of its plants and 66 percent in another. It uses tires, plastics, paper residues, animal meal, grease and sewage sludge to replace fossil fuels. It states that the company had to invest EURO 8 million in one plant and another EURO 4 million on storage equipment, homogenization and dosing installations for flexible use of alternative fuels [Hridelberg Cement, 2009a].
- **India:** Cement companies in India are using non fossil fuels including agricultural wastes, sewage, domestic refuse and used tires, as well as a wide range of waste solvents and other organic liquids [Bernstein and Roy, 2007]. The Indian Cement firm ACC is using cow dung, old shampoo, soap, plant sludge and municipal waste as alternatives to fossil fuels [Cement World, 2008].
- **Netherland:** Since March 2000, the ENCI cement plant located in Maastricht (Netherlands) has been working together with the Limburg Purification Board, receiving pre treated sewage sludge from their sewage water treatment plants (following further treatment in the Board's own thermal sludge dryers). 80,000 tonnes of dried sewage sludge is co processed annually in a kiln with a capacity of 865.000 tonnes of clinker per year. [CEMBUREAU, 2009].

- **Spain:** In 2005, the cement sector in Catalonia (Spain) reached an agreement with the Catalan administration, trade unions, and the local councils, to launch a trial to monitor the environmental behavior of thermally dried sewage sludge from the Barcelona area as an alternative fuel in cement plants. The aim is to use more than 60,000 tonnes of dried sewage sludge every year as a petcock substitute, providing a solution for the high amount of sewage sludge which cannot be used in agriculture. [CEMBUREAU, 2009].
- **USA:** In the United States, approximately 5 percent of the fuel used in the cement industry comes from renewable and non-renewable waste fuels such as wood, tires and other non-hazardous 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 [Mackes and Lightburn, 2003].
- **Costa Rica:** An example of an international experience, CEMEX in Costa Rica has successfully implemented a United Nations Certified CDM project that substitutes conventional fossil fuels such as petroleum coke, fuel oil, and natural gas with more environmentally friendly local biomass products such as rice husks and wood chips. CEMEX‘s Costa Rican operations currently have a 20% alternative fuels substitution rate and CEMEX claims that this project alone helps them to avoid 21,000 metric tons of CO_2 from being emitted annually.
- **Kenya**: 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].

2.4 Gaps in the Literature Retrieval

Academic papers covering the social impact of the use of alternative energy sources in cement manufacturing were not identified. In addition, none of the institutional documents that were retrieved analyzed the social impact of using alternative fuels, which indicates that a thorough knowledge of the topic is missing.

Researchers findings of the calorific value and other chemical properties related to the use of different alternative fuels are available but a gap on feeding position of these alternative fuels in cement kilns was 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 reliability of findings and to give a knowledge and evidence for process engineers all over the world.

More details about the costs related to the use of alternative fuels in cement kilns are required in order to see the economic benefits of different alternative fuels in detail; in fact, few findings of this topic emerged from the institutional journals and this highlights another gap in the literature. In addition reports or studies on life cycle assessment of alternative fuels in cement, industries are not identified clearly which implies that more studies on life cycle assessment of alternative fuels have to be researched in different countries of the world which use more alternative fuels in their kilns.

Another gap which was noticed during literature retrieval was a detailed study of the different bio masses found in Ethiopia for use in thermal processes. One document which dealt in detail with a lot of biomass resources and their residues for use in Ethiopian cement industries was found and reviewed thoroughly, but this was deemed insufficient for a comprehensive knowledge of the different properties of biomasses which can be used or utilized in cement industries.

2.5 Process Technology of Pellet Fuel Production

The combustion of biomass for process heat or electricity production can be conducted indirectly via the combustion of pre-processed biomass products such as compressed or torrefied wood pellets, mixed biomass pellets, pyrolysis char and etc. The biomasses may also be blended with coal in a process called co-firing. The residues from this combustion are essentially ash, which can be part of a specific product or which can be process wastes. This direct or indirect combustion is a commercially proven and established large scale technology which is suitable for heat production in cement kilns. It is currently the highest volume bio energy market worldwide. The process flow diagram of pellet fuel production is shown in the following figure.

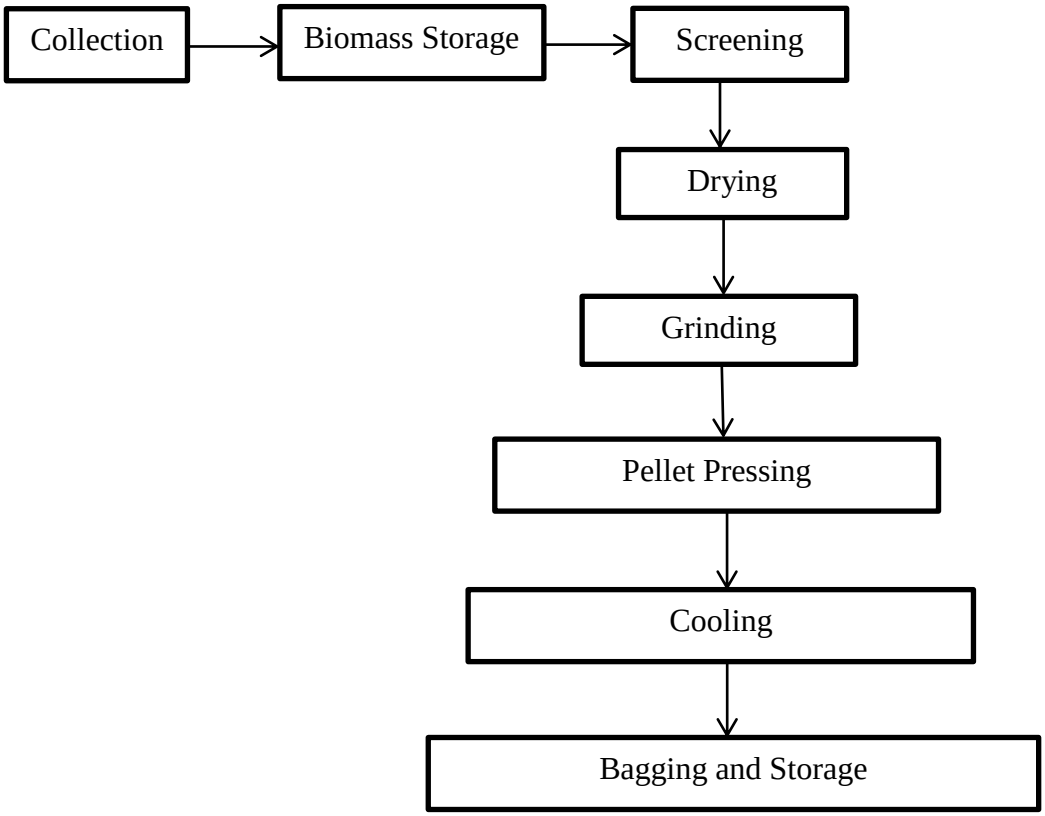

Figure 2.5 Schematic Process flow diagram of pellet production

The process description of the above schematic flow diagram is described as follows. Prior to densification or pelletization, biomass residues have to undergo a number of stages including collection, storage, cleaning, drying, and size reduction. Depending on the residue, each of the above stages will require a certain expenditure of equipment, materials, and labor.

2.5.1 Collection

Depending on the biomass residue, collection or reception of the raw material can be a major component of the densification process. Materials such as sawdust, cotton stalks tend to be widely dispersed in the fields and must be collected and transported to a location where it will be further processed for pelletization.

2.5.2 Storage

The collected raw materials should then be stored in a good place for processing. The type of storage required will depend on the residue and the environmental conditions it is subjected to. Usually, the residue will be stored in an open-air heap, a shed, a bin or within retaining walls or fences. If the collected residue is dry and open-air storage would result in the accumulation of moisture and dust hazards (in the case of sawdust), then closed or sheltered storage is necessary to prevent the material from getting wet. Conversely, the wet residue can be reduced in moisture content through carefully managed open storage.

2.5.3 Cleaning/screening

Cleaning is the same as screening for foreign materials such as stones and metal. The raw materials (sawdust or sewage sludge) has to be screened for stones and pieces of metals that could damage the processing and densifying equipment before they can be passed to the hammer mill for homogenizing. Foreign particles in the raw materials are likely to damage the press or could conceivably cause sparks in the hammer mill which might lead to a dust explosion. Screening can usually be achieved with pneumatic, mechanical and/or magnetic screens.

2.5.4 Drying

To ensure a good quality pellet, the raw material should be dried until it reaches a residual moisture content of approximately 10% prior to densification. In general, most extrusion-type densification equipment requires that the feedstock is in the range of 10-20% moisture content on a wet basis. If the moisture content of the feedstock is too high (above 20%) the excess water becomes a superheated liquid because of the high pressure required for densification and the resultant frictional heat build-up. The water will flash to steam as it exits the densifier and the pressure is lowered, usually exploding the briquette or pellet [Yisehak Seboka et al., 2009]. 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, the type of densifying equipment, etc. There is different dryer equipment such as rotary/drum dryers, pipe dryers.

2.5.5 Size reduction/Fine Grinding

Most densification equipment requires that the maximum particle size of the incoming feedstock be no more than 25% of the diameter of the resulting briquette or pellet [Yisehak Seboka et al., 2009]. Feedstock size reduction or fine grinding is usually achieved with a hammer mill. It is considered the most suitable and it is always recommended to use this hammer mill in order to achieve homogeneous pellets. The mixing of the material is also completed here. The large surface and open fibers of ground products facilitate steam absorption in the cascade mixer. Steam and high temperature in the cascade mixer soften the lignin in the wood, after which pelleting can take place without the addition of binders.

2.5.6 Pellet Pressing

After pre-processing, they are finally subjected to densification in order to make a good quality fuel. Many presses need the materials to be warmed up to 120-130°C using dry steam. The heat makes the lignin in the wood biomass, become more plastic which helps to stick the particles together. The material is extruded through a matrix and the pellets are cut off on the outside of the matrix. The matrix can either be standing, with the pressure rollers moving on its inside, or can be

lying down with the rollers moving over the matrix in a revolving fashion. The wood and biomasses are pressed through the matrix under very high pressure [Pieter D. Kofman, 2007].

2.5.7 Cooling

Pellets, as they leave the machine, are quite hot (~150°C) and fairly soft. Therefore, they must be cooled and dried before they are ready for use. This is usually achieved by blowing air through the pellets as they sit in a metal bin. During this process, the pellets become rigid and lose moisture, so that the final moisture content after the cooler can be as low as 6%. They will take up moisture from the surrounding air and stabilize at a content of between 8 and 10% [Pieter D. Kofman, 2007]

2.5.8 Packaging and Delivery

The produced pellets are then checked or screened before packaging. After packaging, pellets delivered in bulk can be transported by truck, tipped off at the receiving end, or be transported by a vacuum vehicle that sucks up the pellets in the factory. These trucks are also equipped with weigh cells so that they can measure the exact amount that is delivered.

3 MATERIALS AND METHODS

3.1 Characterization of sawdust, sewage sludge and mixed pellet (proximate, ultimate and ash chemistry analysis)

3.1.1. Materials and Reagents

The equipment used during characterization of sawdust and sewage sludge were jaw crusher, grinder, sieves, Erlemayer flask, volumetric flask, funnel, porcelain dish, pipette, burette, beakers, hot plate or Bunsen burner, electronic balance, ceramic and metallic crucibles, drying oven, muffle furnace (0-1200℃), desiccators, elemental analyzer (EA 1112 Flash CHNS/O- analyzer) and oxygen bomb calorimeter.

The instrument used during pellet formation and characterization were jaw crusher, centrifuge mill, sieves, Erlemayer flask, volumetric flask, funnel, spatula, pipette, burette, beakers, hot plate or Bunsen burner, electronic balance, cleanol, platinum and metallic crucibles, drying oven, muffle furnace (0-1200℃), desiccators, bomb calorimeter, 25 ml polyethene jerrican, plastic dispenser with 3 ml fitted pipette, magnetic stirrer, thermogravimetric analyzer, single tablet presser, rack, hollow cathode lamps and atomic absorption 10/20 (Spectra AA) Varian.

Chemicals and reagents used during series of experiments for sawdust and sewage sludge were ammonium chloride, ammonium hydroxide, ammonium acetate, acetic acid, nitric acid, copper sulfate, ethylene di amine tetra acetic acid (EDTA), flouroxone, hydrochloric acid, sulfuric acid, sulpho-salicillic acid, PAN indicator (0.1% in ethanol), PAR Indicator (0.1% in water), potassium chloride, potassium hydroxide, sodium potassium carbonate, tri ethanol amine (TEA), thymol-phthalein, filter paper and distilled water.

The chemicals and reagents used for mixed pellet were nitric acid, hydrochloric acid, sulfuric acid, potassium chloride, sodium chloride, calcium carbonate, magnesium ribbon, La_2O_3, spex product, lithium meta borate (anhydrous), lithium tetra borate, hydrofluoric acid, saturated boric acid solution, 1000 ppm $Fe(NO_3)_3.9H_2O$ Spectro sol, 1000 ppm manganous nitrate, Spectro sol and distilled water. All chemicals were analytical reagent grades and obtained from Mugher Cement Factory and Ethiopian Geological Survey.

3.1.2. Methods

The sawdust and sewage sludge collected from shiromeda industrial zone and kaliti treatment compound were first cleaned from other very coarse contaminants. Prior to grinding, the samples were first dried and then reduced its size using both jaw crusher and centrifugal mill for sewage sludge. The samples were then allowed to pass through in the range of 0.5 mm to 1 mm mesh and prepared for characterization. The proximate and ultimate analysis of both samples was carried out in AAiT, school of chemical and bioengineering and AAU, faculty of science respectively. Proximate analysis was as per ASTM procedure for the determination of the parameters ash content, moisture content, volatile matter and fixed carbon. 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). The determination of major oxides found in both samples was done using colorimetric method (wet chemical analysis) in Mugher Cement Factory. All the determination was based on a dry basis.

After characterizing the sawdust and sewage sludge samples, a laboratory tablet presser (single pellet presser) which has been widely applied in the experimental study was used to produce the mixed pellets with a very small size. Dried samples of sewage sludge and sawdust with different particle sizes were weighed and homogenized manually to produce homogeneous mixes with a different blending ratio of the two samples. Approximately 1 g of the mixed materials were filled in the hole of a tablet presser cylinder to make a single pellet of 1mm in diameter. After keeping the manual set pressure for 60 seconds, the sample was taken out of the presser and put in vials. The samples calorific value was first determined in order to choose the best calorific value result. Then the pellet sample with a good calorific value was then subjected to characterization and analysis. Pellet physiochemical analysis was determined following ASTM procedures to determine their moisture, ash, volatile content and fixed carbon. Determination of complete oxides such as LOI, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, K_2O, Na_2O, MnO, TiO_2, P_2O_5 and trace elements of the mixed sample were determined by using the Lithium Metaborate + Lithium Tetraborate fusion method followed by atomic absorption in Ethiopian Geological Survey.

Thermo gravimetric analysis of the mixed sample was determined using TGAnalyzer in Leather Industry Development Institute.

I. Moisture Content

The sawdust, sewage sludge, and mixed pellet moisture content were obtained gravimetrically by the oven drying method (ASTM D 3173, 2002). 10g to 60g of the sawdust and sewage sludge samples were first weighed and then dried at 105±5℃ for 24hours. A total of 3 g pellets, 1g each for the mixed pellet were also weighed and dried at 105±5℃ for 24hours. After 24 hours, the samples were withdrawn, cooled in a desiccator and then weighed to the nearest 0.001g. The moisture content was found on a percentage basis using the following equation.

$$\%\ \mathrm{M.C} = \frac{w_1 - w_2}{w_1} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

Where w_1= weight of sample before drying

w_2= weight of sample after drying

II. Ash Content

The ash content was determined following (ASTM E830, 2008). First, a porcelain crucible was weighed and oven dried until its weight was constant. A sample weight of 2g was then measured and placed in the crucible. The Crucible and content were then weighed to the nearest 0.001g. The sawdust and sewage sludge sample was ashed at 550℃ & 600±10℃ for 4 hours & 6 hours respectively in an atmospheric pressure air muffle furnace. The mixed pellet was also ashed at the same temperature and time with the sewage sludge. 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.

$$\%\ \mathrm{A.C} = \frac{w_3 - w_1}{w_2 - w_1} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Where w_1= weight of crucible

w_2= weight of crucible + weight of sample before drying

w_3= weight of crucible + ash

III. Volatile Content

A weight of 2g of sawdust and sewage sludge sample was measured into the crucible and oven dried at 105℃ for 1 hour. The oven dried sample was then cooled in a desiccator and reweighed. The cooled and dried sawdust and sewage sludge sample were then heated at a temperature range of 550℃ for 10 minutes & 950℃ for 7 minutes (ASTM D2974, 2002) respectively. Dried mixed pellets of the weight of 1g sample were also measured into the crucible. The sample was then heated at a temperature range of 950℃ for 7 minutes. After heating the samples, the crucibles were withdrawn and cooled. Then, the crucibles were weighed again. This parameter was then calculated on a percent basis (ASTM D3174, 2002).

$$\% \text{ VM} = \frac{\text{A}-\text{B}}{\text{A}} * 100 \quad \text{....3.3}$$

Where A = the weight of the OD sample at 105℃ (g)

B = the weight of the sample after 10 min in the furnace at 550 ℃ (g)

IV. 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.

$$\% \text{ FC} = 100 - (\%\text{AC} + \%\text{VM} + \%\text{MC}) \quad \text{.....3.4}$$

V. Elemental Analysis

Sawdust and sewage sludge sample of 1.5 to 2.5 mg was weighed in a tin capsule and loaded in the instrument. The tin was then dropped into the high heat oxygen environment of the combustion tube (heated at 925℃); it then created a vigorous exothermic reaction. The sample temperature could reach 1700℃, which aids in the combustion process. 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 analysis was finished in approximately 6 min.

VI. Calorific Value Determination

The calorific value of sawdust was determined using oxygen bomb calorimeter via the equivalent methods of (ASTM D 5468, 1999). First 1g sawdust sample was prepared and then the oxygen bomb was charged. A distilled water of 2000 gram was filled in the calorimeter bucket and the bucket was set in the calorimeter. The calorimeter was left to run for five minutes while the controller brings the jacket temperature up to equilibrium with the bucket. Then the bomb was fired and the bucket temperature was raised within 20 seconds after firing. Temperature reading was started at about 6 minutes after firing. Within one minute interval, the thermometer was read until the temperature reached a stable maximum and remained constant for at least two minutes. Then the final temperature was recorded. After recording, the thermometer was raised and the bomb was removed from the bucket. The interior surfaces of the bomb were washed with distilled water and collected in a beaker. All unburned pieces of fuse wire from the bomb electrode was removed, straightened and measured their combined length in cm in order to know the net amount of wire burned. Finally, the bomb washings were titrated with a standard sodium carbonate solution using methyl orange. Then the sawdust gross heat of combustion was computed by using the following equation

$$H_g = \frac{tW - e_1 - e_2 - e_3}{m} \quad \text{.....3.5}$$

Where t = temperature rise

W = energy equivalent of calorimeter in cal/℃

e_1 = correction in calories for heat of formation of nitric acid

= c_1(ml of standard alkali solution used in acid titration) if 0.0709N alkali was used for the acid titration

e_2 = correction in calories for heat of formation of sulfuric acid

= 13.7*m*c_2 (c_2 = percentage of sulfur in sample)

e_3 = correction in calories for heat of combustion of fuse wire

m = mass of the sample

VII. Ash Chemistry Analysis of Sawdust and Sewage Sludge

Cement raw materials composed mainly of CaO, SiO_2, Al_2O_3, Fe_2O_3 with little MgO. Therefore the sample mineral composition was done using colorimetric methods. Before determination of the above mentioned major oxides, the sample was first prepared following the procedures.

- 1g of both the samples was taken and ashed in a muffle furnace at 1000℃ for 1 hour and cooled in a desiccator.
- 2.5g fusion mixture ($NaKCO_3$) and 0.5g samples were weighed in a platinum crucible and covered with 0.5g $NaKCO_3$ again on the surface of the mix. The crucible was then covered with a lid and placed in a muffle furnace at 1000℃ for 20 minutes.
- The samples were removed from the furnace & gently swirled in order to spread the melt on the sides of the crucible.
- Afterward, the samples were placed on porcelain basin and held in about 50ml cold distilled water of the basin. The crucible and the lid were then removed from the basin & placed in a dry porcelain dish. The fuse was then loosed with about 20ml of Conc. HCl.
- The crucible and the lid were rinsed with distilled water.
- The contents of the dish were then evaporated on the sand bath to dryness. Washed with another 20ml Con. HCl while it was dried.
- It was removed from the sand bath and baked for an hour in a drying oven at 105℃. Then taken out from the oven, cooled and 20ml of 1+1 HCl was added and digested for 10minuets.
- The contents were filtered in the 500ml volumetric flask while hot with coarse filter paper.
- Washed repeatedly with hot water, cooled and filled up to the mark.
- The precipitate was used for SiO_2 analysis, while the filtrate was used for CaO, MgO, Fe_2O_3 & Al_2O_3.

Then a determination of the major oxides was followed by using the above-prepared filtrates and different laboratory reagents.

A. Determination of pure SiO_2

The precipitate obtained above was dried and charred in previously dried and weighed porcelain crucible (W_1). Then it was ignited in a muffle furnace at 975±25℃ for 1 hour and cooled in a desiccator and checked for constant mass. After that 0.5-1ml of distilled water and 0.5-1ml of 1+1 H_2SO_4 was added and the content was evaporated at low heat to dryness, and then continued in an electric furnace 1175±25℃ for 20 minutes. Then left to cool in a desiccator and weighed. Finally, the silica was calculated in percent as;

$$\%SiO_2 = (W_2 - W_1) - (W_3 - W_1) * 200 \quad \text{.....3.6}$$

Where W_1= weight of crucible

W_2 = weight of the ignited crucible

W_3 = weight of crucible with evaporation residue

200 = because starting sample was 0.5g

B. Determination of CaO

25 ml of the filtrate was pipetted out in 300 ml flask from the previously obtained filtrate and diluted to about 100 ml with distilled water. 13 ml of 30% tri-ethanol amine and 50mg of the mixed flourexone indicator was also added and the PH was adjusted between 12 & 13 with 10% KOH. Finally, the solution changed from light green to pink with titration of 0.01M EDTA.

$$\%CaO = 2.2432F_{EDTA}(V_{EDTA}) \quad \text{.....3.7}$$

Where F_{EDTA}= the factor of EDTA and

V_{EDTA}= volume of EDTA used to endpoint

C. Determination of MgO

25 ml of the filtrate was pipetted out and diluted to about 100 ml with distilled water. In this determination, the volume of EDTA consumed for CaO was taken and 10ml of 30% T.E.A was added. The PH was adjusted between 10 & 11 with PH = 10 buffer.

Finally, 5 drops of par & 5 drops of copper complex mate were added and titrated with 0.01M EDTA from red to orange yellow.

$$\%MgO = (1.6128)(F_{EDTA})(V_{EDTA}) \quad \text{.....3.8}$$

D. Determination of Fe_2O_3

100 ml of the filtrate was pipetted out and about 50mg of sulpho-salicilic indicator was added. The 1+4 NH_4OH solution was added drop wisely until the yellow color was observed which was initially colorless then to violet and finally to yellow. 1+4 HCl solution was added to return back the color to violet. After that, the PH of the solution was checked to be between 1 & 2 and was heated not exceeding 50℃. Finally, it was titrated with 0.01M EDTA from violet to colorless.

$$\%Fe_2O_3 = (0.7985)(F_{EDTA})(V_{EDTA}) \quad \text{.....3.9}$$

E. Determination of Al_2O_3

100 ml of the filtrate was pipetted out and the volume of EDTA consumed for Fe_2O_3 was taken. 30-35ml of PH = 3 buffer was added and heated just to boiling. Exactly 3 drops of copper complex mate and 10 drops of PAN indicator were added. It was then boiled and titrated while hot from red-violet to yellow. Boiling and titrating was repeated until yellow color was stable.

$$\%\, Al_2O_3 = (0.5098)(F_{EDTA})(V_{EDTA}) \quad \text{.....3.10}$$

F. Determination of SO_3

0.5gm of the sample was placed in a beaker. 25ml of distilled water & 13ml of conc. 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. 50-60ml of congo-red was also added and stirred well.

After that, it was left for some minutes (20-25) 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.

$$\% SO_3 = \frac{(A-B)*0.343}{W} * 100 \quad \text{.....3.11}$$

Where A = weight of crucible & the precipitate

B = weight of empty crucible

W = weight of the sample

0.343 the factor between $BaSO_4$ & SO_3

VIII. Complete Oxide Analysis of Mixed Pellet

The determination of major and minor oxide of the mixed sample was carried out using $LiBO_2$ Fusion, HFattack, gravimetric, colorimetric and AAS. Before determination of oxides, the sample was decomposed first by weighing 1.25g of the mixed flux (1g $LiBO_2$ + 0.25g $Li_2B_4O_7$) into a crucible and then mixed with the prepared blended fuel sample. The sample was then fused in a muffle furnace for 45 min. at 1000℃. After taking out the crucible, the crucible and the contents were put in 400 ml beaker containing 100 ml of HNO_3. The contents were heated and the crucible was tilted to help digestion, and then kept overnight. The crucible was then stirred until there was a complete dissolution. When the crucible became clear, it was taken out from the solution and then the samples were checked. Finally, the solution was transferred into a 500 ml volumetric flask. Then Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, K_2O, Na_2O, MnO, TiO_2, and P_2O_5 were analytically determined from this solution and by following the procedures of AAS according to the instrumental parameters. SiO_2 was determined using HFattack. In here 0.1g of the well mixed and homogenized sample was first weighed into a 125 ml polyethylene bottle. Then with the help of a plastic dispenser, 3ml of 48% HF was added. After the bottle was shaken, it was allowed to stand overnight. 50 ml of the saturated boric acid solution was added in the morning and shaken vigorously and left to stand for about 60min. then 47 ml of water was added and shaken well.

Finally using the instrumental parameters SiO_2 was read. The alkali index and base to acid ratio of the mixed fuel were then calculated to describe the overall influence of catalytically active species within the ash using the following equation [Sebasteian W., 2013]. In addition, trace elements such as Cu, Zn, Pb, Co, and Ni were determined using mixed acid attack first and then finished using AAS.

$$AI = ash\% * \frac{CaO+MgO+K_2O+Na_2O+Fe_2O_3}{SiO_2+Al_2O_3} \quad \text{.....3.12}$$

$$R_{b/a} = \frac{\%(CaO+MgO+K_2O+Na_2O+Fe_2O_3)}{\%(SiO_2+TiO_2+Al_2O_3)} \quad \text{.....3.13}$$

IX. Thermo gravimetric Analysis

A mixed and homogenized sample of 20 mg was first measured and put into a small platinum pan placed in an auto sample tray which was controlled from a remote desktop. The sample was combusted with the help of nitrogen. The TA universal analysis program was then run by setting the heating rate at 20℃/min which was heated from 25℃-1200℃.

X. Pellet Physical Property Analysis

Within the physical properties of the selected pellet, the following parameters were studied: strength by dropping, water absorption and water resistance of a fuel. In the strength by dropping test, as per (PN-G-04651), the sample was dropped down twice from 1.5m against a concrete surface. The strength by dropping factor is calculated from the formula

$$W_{ZR} = \frac{N_1}{N} * 100 \quad \text{.....3.14}$$

Where N-number of samples which were subjected to testing

N_1-number of samples which survived with no damage

The water absorbability test was based on finding the amount of water, which had been absorbed by the pellets under conditions as defined by the standard (PN-G- 04652).

The pressed small pellets were left to stand in water over 24 hours, and the difference between the sample weights after and before water absorption made the measure of this parameter.

3.2 Experimental Design

3.2.1. Materials

The materials which were used for preparing different particle sizes of the samples were centrifuged mill, mortar and pestle, sieve analysis, mass balance, oven and laboratory tablet pellet presser and design expert 6.0.8 software.

3.4.2. Methods

Samples of sewage sludge and sawdust were first meshed with particle size range of (45-63μm), (63-80μm), (80-100μm), (100-150μm) and (150-180μm) for 8 min. until enough amounts was achieved for making different pellets. The prepared different sizes were then stored with polyethylene plastic bags. A total of 25 experiments were done with the help of design expert 6.0.8 software in order to investigate the effect of these two factors (particle size and ratio) with five levels on pellet calorific value. This design of experiment was also helped us to differentiate the significance of the main and the interaction factors. The percentages of blending of the samples were 50%, 60%, 70%, 80% and 90% of sawdust with the remaining percentage for sewage sludge. First a mixture of 50% sawdust and 50% sewage sludge with average particle size of 54 μm was prepared and homogenized well physically. Then 1 g of the measured mixture sample was put into the cylindrical shape of pellet presser. After it was compressed manually and waited for 1 min. The pellet was token out from the cylindrical shape holder and put in vial. A similar procedure was followed by changing the particle sizes and percentages of the samples.

4 RESULT AND DISCUSSION

4.1 Characterization of sawdust, sewage sludge and mixed pellet (proximate, ultimate and ash chemistry analysis)

All proximate sample analysis was performed in triplicate forms. The results of the following table were discussed in detail as follows.

Table 4.1 Proximate analysis of the samples

Sawdust					
Parameters	Run 1	Run 2	Run 3	Average	Coal [Akinyeye et al., 2016]
Moisture content (%)	7.2	7.6	6.8	7.2	0.78
Ash content (%)	2.25	2.75	1.27	2.09	9.44
Volatile matter (%)	73.62	70.94	73.53	72.69	5.58
Fixed carbon (%)	16.93	18.71	18.02	17.88	84.2
Sewage Sludge					
Moisture content (%)	10.15	10.33	9.86	10.11	0.78
Ash content (%)	45.02	47.07	44.81	45.63	9.44
Volatile matter (%)	54.43	47.14	52.47	51.34	5.58
Fixed carbon (%)	9.6	4.54	7.14	7.09	84.2
Mixed pellet					[Małgorzata W, 2012]
Moisture content (%)	6.5	7.0	7.0	6.8	10.37
Ash content (%)	4.77	4.01	5.02	4.6	20.36
Volatile matter (%)	63.52	64.12	64.9	64.18	66.74
Fixed carbon (%)	24.68	22.88	22.6	23.38	2.53

I. Moisture Content

As the above table shows, the moisture content of sawdust sample was greater when compared with the hard coal. And this was due to the fact that wood biomasses store moisture in spaces within the dead cells and within the cell walls [Demirbas, A. 2004]. According to [Bolesław Karwat et al., 2014], the preferred value of moisture content of alternative fuels must be <20% and requirements of cement industry are <30 [B. Mokrzycki, A. Uliasz-Bocheńczyk, 2003]. This result thus indicated that the moisture contained in the sawdust 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, on the other hand, is an important property since it influences the reactivity of the fuel and lowering the calorific value. According to [Sarna *et al*., 2003; SPC, 2008: Trezza, Scian, 2005], the ash content of alternative fuels must be <15% and requirements of cement industry are <40 [B. Mokrzycki, A. Uliasz-Bocheńczyk, 2003].

As it can be seen from the above table, the ash content of sawdust was lower than coal and this implied that the presence of inorganic compounds in sawdust was very low and this was because insoluble compounds act as a heat sink in the same way as moisture, lowering combustion efficiency which favors in the formation of char [Demirbas, A. 1998]. Therefore from this fact, we can say that the presence of soluble ionic compounds which have a catalytic effect on combustion of the sawdust was high and the presence of inorganic compounds in coal was high.

III. Volatile Matter

The other useful parameter is a volatile matter which provides a rough indication of the reactivity or combustibility of the fuel. This property also helps us in the estimation of the length of a flame. According to the result specified in the table, the sawdust content of volatiles was very higher than that of the coal and this is a result of lower lignin content [BISYPLAN., 2012**]**. This indicates that sawdust can easily ignite under low temperature. This high volatiles give a faster combustion rate while devolatilizing during pyrolysis. And this will make sawdust attractive for the combustion process [Xing Yang et al., 2017].

Therefore it can offer an important advantage as a combustion feedstock due to the high volatility property and the high reactivity of both the fuel and the resulting char.

IV. Fixed Carbon

This fixed carbon is the mass remaining after the releases of volatiles, excluding the ash and moisture contents. This fuel property represents the amount of carbon available for char combustion during pyrolysis [Mohan et al. 2006]. The fixed carbon in a material gives a rough estimate of heating value. The heat content is related to the oxidation state of the natural fuels in which carbon atoms generally dominate and overshadow small variations of hydrogen content. With respect to the result of fixed carbon, sawdust was found to have a lower fixed carbon than that of the coal and the result implied that sawdust carbon found in the residue was not as high as that of the coal and that is also why coal has high heating value.

V. Elemental Analysis of Sawdust and Sewage sludge

Most chemical elements from the fuel ash are incorporated into the cement clinker. 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 e.g. 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 sawdust and sewage sludge composition were shown in the following table. The samples were run in duplicate. 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. Likewise, the elemental compositions of coal were included in order to compare the results.

Table 4.2 Ultimate analysis of the samples

Sawdust				
Elements	Run 1	Run 2	Average	Coal [Akinyeye R.O et al., 2016]
Carbon (%)	42.818	43.233	43.025	45.8
Hydrogen (%)	5.716	5.454	5.585	3.50
Nitrogen (%)	0.662	0.837	0.7495	1.16
Sulphur (%)	0	0	0	0.68
Oxygen (%)	50.804	50.476	50.64	48.86
Sewage sludge				
Carbon (%)	24.967	25.193	25.08	45.8
Hydrogen (%)	3.714	4.753	4.2335	3.50
Nitrogen (%)	2.381	2.410	2.3955	1.16
Sulphur (%)	-	-	-	0.68
Oxygen (%)	68.938	67.644	68.291	48.86

As it can be seen from the table, the carbon content of sawdust determined by the elemental analyzer was found to be high but lower than coal. It is generally known that wood biomass comprises organic substances composed mostly of carbon, hydrogen, and oxygen. These are the main elements that comprise woody biomasses. While secondary elements like nitrogen, sulfur, chlorine and such are all grouped together in "other" since they typically amount to much less than the three major elements [BISYPLAN., 2012]. This much percentage of carbon in sawdust comes from the atmospheric CO_2 which became part of the plant matter during photosynthesis. During combustion, it is mainly transformed back into CO_2, which is again released to the atmosphere and taken out of the atmosphere by the species during the growth phase [Intergovernmental Panel on Climate Change, 2006]. Therefore, the growth of woody biomass and its usage as fuel occurs on a very short time scale, the entire cycle is said to have zero net impact on atmospheric carbon emissions.

On the other hand, hydrogen is another major constituent of biomass, as can be expected from the chemical structure of the carbohydrate and phenolic polymers. During combustion, hydrogen is converted to H_2O, significantly contributing to the overall heating value.

The result showed that the weight content of hydrogen was higher in the case of sawdust and this result was relatively comparable with the elemental analyses of sawdust fuel samples found in the literature [Demirbas, 2004] which contains 5.2%. With respect to nitrogen, it was observed that the percentage was lower than coal. This composition in the sawdust mostly comes from their high growth rate and the application of fertilizers. During combustion, this nitrogen does not oxidize in any significant quantities and released in the gas phase as N_2 therefore; its contribution to the overall heating value is zero. According to [Kliopova at al. 2010], sawdust fuel is characterized by a significantly lower N and S content compared to peat fuel and compost. Therefore, adding sawdust into the compost or other biomass would reduce the content of Cl, N and S in SRF. The other element sulfur shows that there was no concentration at all and this implies that there will not be a probability of formation and emission of sulfur related gases like SO_2 at all. When we come to the oxygen result, it was observed that the content was high. This amount resulted from the nature of the photosynthetic process and the chemical composition of the wood. This fuel oxygen reduces the amount of air needed for combustion and is found in the combustion products chemically bound in the molecules of CO_2 and H_2O. The above-described property and result signified that sawdust is a very attractive source of energy in combustion facilities.

According to the above table, the carbon content of sewage sludge determined by the elemental analyzer was found to be lower than both the sawdust result and coal. The results of hydrogen and nitrogen were also lower and higher respectively than the sawdust but it was found to be relatively comparable with the coal. The sulfur result indicated that it was below the detection limit of laboratory devices. In general, the sewage sludge ultimate and proximate results showed similarity with the Ph.D. project conducted by [Anders Rooma et al., 2012]. Therefore, it was observed from these analyses that sewage sludge fuels didn't have a very attractive property when compared with that of the sawdust.

VI. Calorific Value

The other most important key parameter which defines the quality of alternative fuel is the calorific value and is one of the most widely employed parameters used in classification schemes. It makes the principal parameter which is decisive for the share of the conventional fuel which may be substituted in the clinker manufacturing process. A good quality clinker can be produced only when adequate thermal conditions are maintained in individual sections of the kiln; and that is affected by the calorific value of the fuel employed and by the way of its combustion [Małgorzata Wzorek, 2012]. The minimum calorific value of alternative fuels has been established as ≥13.0 MJ/kg (3104.9 cal/g) [Małgorzata Wzorek, 2012] which can assure both proper kiln operation and satisfactory quality of the clinker product.

The result of the calorific value (heat of combustion) of sawdust was found to be 4578.28 cal/g. The reason for the value of this much calorific value was due to its elemental composition and its low moisture content. On the other hand, the calorific value of sewage sludge which was determined using bomb calorimeter was found to be 2752.94 cal/g and this result was very low when compared with that of sawdust. And this was a consequence of the high moisture and ash content present in the fuel. These parameters were the main one which affected the result to have a low calorific value. Therefore, in order to enhance the gross heat of combustion, it is suggested to utilize the sewage sludge by mixing it together with other properly selected wastes, i.e. with under-grade sized coal, with waste from animal waste utilization plants, and with wood waste [Wrozek, 2012].

The calorific value of mixed pellet which was prepared with particle size of 0.125mm and a weight percentage of 90% sawdust and 10% sewage sludge was found to be (4587.31 cal/gm) which passes the low calorific value established for alternative fuels (≥ 3105 cal/g) and this result implied that it can be used in the clinker sintering zone and also can assure both proper kiln operation and satisfactory quality of the clinker product [J. Duda., 2004]. In addition, The Italian standard establishes the quality parameters for energy pellets from biomass which includes untreated wood from wood yielding industry; untreated wood and wood without bark after being used; a mixture of these materials and they recommended the heating value to be >4039 kcal/kg [CTI-R04/5, 2004].

Different results of calorific value had been found from different kinds of literature. For instance according to [E. Yilmaz M. et al.,(n.d)], different calorific values of 3202.92 cal/g and 3773.76 cals/g was found from a 20% sewage sludge and 80% olive waste pellet and also from 30% sewage sludge and 70% olive waste pellet respectively.

VII. Ash Chemistry Analysis of Sawdust and Sewage Sludge

Determination of the ash chemical composition of alternative fuels is really helpful in clinker production. Selected waste and by-products containing useful minerals such as calcium, silica, alumina, and iron can be used as raw materials in the kiln, replacing raw materials such as clay, shale, and limestone.

Some materials have both useful mineral content and recoverable calorific value, the distinction between alternative fuels and raw materials is not always clear. For example, sewage sludge has a low but significant calorific value and burns to give ash containing minerals useful in the clinker matrix [WBCSD, 2005]. The following table shows the results of the ash mineral composition of sawdust, sewage sludge, and the results were discussed by comparing with the South African coal.

Table 4.3 Ash major oxide analysis

Sawdust		**Sewage Sludge**	**Hard Coal [Akinyeye R.O et al., 2016]**
Minerals	Percentage wt.%	Percentage wt.%	Percentage wt.%
SiO_2	18.68	34.66	16.9
CaO	51.53	9.20	0.18
MgO	5.79	9.76	0.12
Fe_2O_3	5.73	6.14	0.37
Al_2O_3	6.54	10.72	11.4
SO_3	0.31	0.92	2.8

A. SiO_2 content

The most component of cement are oxides of calcium, silica, aluminum, and iron. Approximately 95 percent of clinker consists of oxides of CaO, SiO_2, Al_2O_3, and Fe_2O_3 and the remainder consist of the so called minor constituents [Mohamed A. Aldieb & Hesham G. Ibrahim, 2010]. These oxides are used to calculate the theoretical cementitious compounds and they are formed by the transformation of raw materials and minerals in the kiln. The raw materials for cement yield the oxide required for clinker in the appropriate proportions. In recent years, about 3-4% of raw materials used in the production of clinker in Europe consisted of alternative raw materials and ashes from fuel totaling about 14.5 million tonnes per year [CEMBUREAU., 2013]. The silica content of Portland cement clinker is 19.71-24.25% [EIPPCB, 2010 and CEMBUREAU 1999] and as it can be seen in the table the sawdust weight percentage was relatively higher when compared with that of the hard coal.

Fuel ash with high content silica can provide a very satisfactory means of increasing the silica modulus of the clinker, thus making it possible to reduce the amount of ground sand incorporated into the feedstock [Hewlett, 2004]. The silica content of sewage sludge was found to be higher than sawdust result and lower than South African coal. But even this presence implied that the ash can also contribute in reducing the need of raw material, making the cement production more economic. When the organic component of the sludge undergoes combustion, the inorganic fraction will remain as ashes and be incorporated into the cement clinker. It was also seen in other researchers that the silica compositions in sewage sludge vary, for instance, according to [Aneta Magdziarz & Małgorzata Wilk., 2013] the silica composition of sewage sludge was found to be 25.10. And these are due to the fact that sewage sludge composition varies from country to country and also it depends on the equipment (methods) used in the analysis.

B. CaO content

Portland cement clinker is composed of mainly CaO which constitutes about 63.76-70.14% [EIPPCB, 2010 and CEMBUREAU 1999] that come from the main raw material, limestone. From the table, the calcium oxide in the sawdust ash was very high when compared with that of the hard coal.

Approximately, similar result (50.64%) was obtained from sawdust ash by [Egbe Ngu Ntui Ogork & Solomon Ayuba., 2014] and this implied that it has high self-cementing properties and the presence of this much composition will help in reducing the main raw material (limestone) amount which needs to be quarried. But this much presence itself will not be significantly helpful without a proper amount of feed rate of the fuel in the kiln and this is because the increase in lime content beyond the certain value makes it difficult to combine with other compounds and at last free lime will exist in the clinker which causes unsoundness in cement. Therefore, with a careful design of the fuels and the raw materials, a good quality clinker can be produced without having any slight difference in the clinker composition and cement.

According to the result in the above table, the percentage of calcium oxide present in the ash was lower than sawdust but it was found to be higher than coal. As it was already described in the above discussion, the majority of cement clinker is composed of CaO and this is mainly derived from the raw material limestone which is first mined. And this small presence in the sewage sludge ash can help in a significant change incorporation into the clinker and can help in reduction of the exploitation of natural resources. A small percent decrease in extraction, processing, and transportation of the traditional raw materials can bring a lot of reduction in cost and environmental footprints of such activities in cement industry.

C. Determination of MgO

The magnesium content of Portland cement clinker is 0.00-4.51%. The sources for these oxides are magnesia compounds which are limestone, clay, sand, iron ore and bauxite having a composition of 0.2-6%, 0.3-5%, 0.3-0.5%, ≤1.5% and 0.04% respectively [EIPPCB, 2010 and CEMBUREAU 1999]. The result of the sawdust in the above table showed that sawdust could also be a better source of magnesium oxide when compared with that of the coal. As it was already described in the above discussion, the raw mix composition must also be adjusted accordingly to stick to the given chemical set points.

An excessive amount of magnesia (usually considered to be over 5 percent of the clinker as a whole), can crystallize out from the flux as a periclase: the presence of which has been associated with long term unsoundness and causes delayed expansion [Boynton, 1980; Hewlett, 2004].

From the above result, we can understand and conclude that sewage sludge could also be a better source of manganese when even compared with that of coal and the magnesia compounds. But the feed rate of these fuels with the raw mix design must be well understood in order not to influence the final clinker composition.

D. Determination of Fe_2O_3

Alumina and iron oxide are not that much essential to the constitution of the final Portland cement product but at a stage of temperatures above 1,300℃, a liquid phase containing alumina (Al_2O_3) and iron oxide (Fe_2O_3) is formed and these liquid phase acts as a source of fluxes lowering the energy requirement thereby making the process economical [Hewlett, 1998]. which facilitates the formation of calcium silicates at a lower temperature than required. While burning of raw meal in kiln iron ore melts itself and liquidize the material to easily pass from kiln, avoid coating in the kiln and it supports the perfect formation of clinker. Clinker composition of ferrite contains in the range of Iron composition of 1.29-4.64%, Lime marl, clay and sand which contain a composition of 0.2-5.9%, 4.0-15%, and 0.0-4% respectively are a good source of iron oxide [EIPPCB, 2010 and CEMBUREAU 1999].

The main function of iron oxide in the cement is as a fluxing agent. With respect to the result, sawdust seemed to have a relatively comparable composition with that of lime marl or chalk and it was found to be higher than the coal. Therefore, in order to produce the clinker with a desired composition, this sawdust can be fed into the kiln with an optimized substitution rate that will not affect the clinker composition. The weight percentage composition of ferrite in the above result was found to be a little bit higher than sawdust and coal.

E. Al_2O_3 content

Oxides of alumina composition in clinker are in the range of 3.76%-6.78% [EIPPCB, 2010 and CEMBUREAU 1999]. The result indicated that the alumina content of sawdust was found to be lower than that of coal. This alumina is very helpful for quick setting and is mainly responsible for the production of heat during hydration of cement.

This alumina and the above described three major oxides in the right proportions make the cement clinker: CaO-65%, SiO_2-20%, Al_2O_3-10%, Fe_2O_3-5%. These elements combine when heated by the flame at a temperature close to 1450℃ and form new compounds namely ferrites, silicates, and aluminates of calcium [Cement Bureau, 2014].

According to the result above, the alumina content of the sludge was found to be higher than sawdust. But when compared with coal it appeared to be lower and this much weight percentage by itself in the sludge indicated that it could act as a material constituent.

F. SO_3 content of sawdust

The alkali metals Na_2O and K_2O have a very strong affinity for SO_3 and where there is sufficient sulfate present in the clinker, the alkalis are normally present as compounds of sulfates such as K_2SO_4, Na_2SO_4, aphthitalite $Na_2SO_4{\cdot}K_2SO_4$ and langbeinite $2CaSO_4{\cdot}K_2SO_4$ [Hewlett, 2004; Newman, et al., 2003]. Higher levels of alkali sulfates in cement affect the reactivity of the cement, thus leading to possible setting problems [Hewlett, 2004]. From kiln operational point of view, it is desirable that as much as possible the alkalis (and sulfates) get discharged from the system with the clinker. If this does not take place, the presence of these alkalis (and sulfates) can have an extremely disruptive effect upon production especially in kiln systems with highly efficiency heat exchangers such as the cyclones. Therefore, the above result of sawdust indicated that the presence of sulfate in sawdust was very lower compared with that of the coal and this implied that the probability of formation of compounds of sulfate is low.

The sewage sludge sulfate percentage was found to be lower when compared with the result of coal. Normally sulfate concentration in the fuel comes from the impurities associated with the type of material. SO_3 form low percentage of cement weight. SO_3 also appear in cement analysis which comes from adding gypsum (4-6 % by weight) during clinker grinding. The Iraqi and British specification for normal high rapid Portland cement pointed that SO_3 content must be between (2-3.5) % according to the type of cement and C_3A content.

VIII. Complete Oxide Analysis of Mixed pellet

By complete analysis mean 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, TiO_2, Cr_2O_3, Mn_2O_3, P_2O_5, Cl^-, F^-. The following table shows the result of the major and minor oxide analysis of mixed sample made from 10% sewage sludge and 90% sawdust with a particle size of 0.125mm. The results of the studied fuels and the coal are arranged in the following table for comparative presentation.

Table 4.4 Major and minor oxide Analysis of mixed sample (Akinyeye Richard et al., 2016)

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2
Mixed sample	3.76	0.72	0.26	2.68	0.58	0.16	0.14	0.02	0.65	0.01
Coal	16.9	11.4	0.37	0.18	0.12	0.14	0.62	0.01	1.5	0.44

As it was already described in detail in the above discussions, the presences of the above oxides have their own role in the clinker composition. With respect to the above table, the result of contents of the mixed sample was totally different from the individual raw material composition; the former individual properties showed much higher contents of major oxides and this result showed comparatively result with coal except in silica and alumina content. This result might be a consequence of the different equipment applied in here. The result implied that the ash of the mixed sample wouldn't provide a very significant importance and wouldn't act as a supplemental fuel to the clinker when compared with the coal but the small percentages of minor oxides such as K_2O, Na_2O were found to be desirable. Two of these minor oxides referred to as alkalis in cement are of particular interest and expressed in terms of Na_2O. These alkalis basically react with active silica in aggregate and produce what is called alkali-silica gel of unlimited swelling type under favorable conditions of moisture and temperature in voids and cracks and further, it causes disruption and pattern cracking and due to these problems and difficulties in regulating set times of cement. ASTM has an optional limit in total alkalies of 0.60%. Other minor compounds such as TiO_2, Mn_2O_3, and P_2O_5 represent <1% and they have little importance.

In relation to the above oxides, the results of calculation of the alkali index and the base to acid ratio of the mixed fuel was found to be (5.7 and 0.8) relatively higher than that of the coal which in turn means the slagging tendency and fouling tendency of the mixed fuel was higher than the coal and these result might come from greater ash contents of mixed pellet. Even though greater amounts of bottom ash is produced, the ash themselves can be a good source of energy and would not pose a significant problem in the kiln which operates in 1450 ℃.

The result of heavy metals found in the mixed sample was also presented in the following table. The samples were duplicated and the averages were taken in order to ensure the reliability of the result. The contents of these heavy metals in hard coal and mixed pellets of sewage sludge, sawdust and burnt lime (PBT fuel) were also included from literature for comparative presentation.

Table 4.5 Heavy metal contents in mixed pellet Coal: Akinyeye Richard Oduna et al., 2016)

Heavy metals ppm	Run 1	Run 2	Average	[Małgorzata W, 2012]	Coal (mg/kg)
Cu	16.00	13.00	14.5	71.77	32.8
Zn	67.00	69.00	68	881.2	38.6
Pb	30.00	30.00	30	24.93	7.02
Co	19.00	21.00	20	6.27	2.22
Ni	29.00	29.00	29	15.92	20.6

According to the above table, the results demonstrated that the levels of heavy metals contained in the mixed fuel comply with the limits for hard coal and it was found out to be lower from both the hard coal in all heavy metal content listed above and the pellet from [Małgorzata Wzorek., 2012] in copper and zinc content. The heavy metals found in the fuel came predominantly from the sewage sludge and their amounts in a fuel are contingent upon their contents in the sludge which was taken for the production. The other low volatility trace elements, i.e. Cr, Co, Cu, Zn, Sb, Mo, Ni, and V become completely embedded in the clinker structure. The American research revealed that those elements could be fixed in various clinker phases up to 99.9% [Małgorzata Wzorek., 2012].

IX. Thermo gravimetric Analysis

The result of the DSC-TGA analysis is showed in the following graph and a detailed discussion of the result follows.

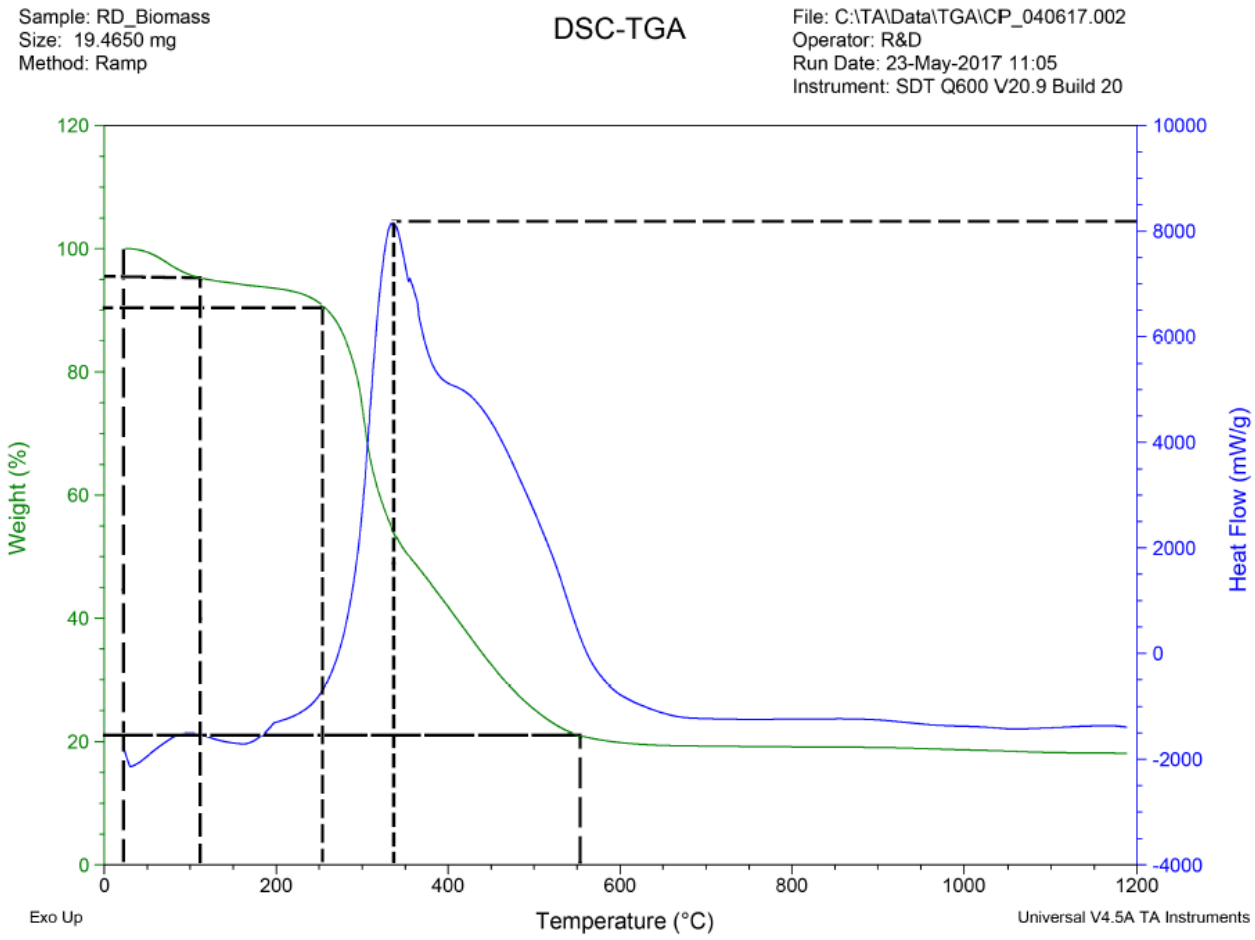

Figure 4.1 Thermo gravimetric analysis of the mixed sample

From the above figure, we can see that the temperature at which the maximum mass loss rate occurs at a lower temperature of about 24.1126℃. It was also true to say about temperatures that the maximum mass loss rate increased with the increased heat flow. A similar curve of TG result was also obtained by [Aneta Magdziarz & Małgorzata Wilk., 2013] on combustion characteristics of wood and oat biomasses. These kinds of characteristics might result from the large percentage share of sawdust.

As we can observe in the above figure, the combustion process can be divided into three stages. The first stage corresponded to a loss of moisture and very light volatile compounds. The temperature range of the first stage was from ambient temperature to about 108℃. In the second stage (108–255℃) a further drop in mass was observed, caused by the removal of remaining carbons and moistures within the fuel. A significant mass change on the fuel was noticed at a temperature range of (255-552℃) caused by other thermal decomposition of hemicellulose, cellulose, and lignin due to the high percentage of sawdust present in the mixed sample. Once the temperature was higher than 552℃ mass losses was brought to an end by thermal decomposition.

With respect to the DSC plot, the highest peak of DSC signal was achieved at a temperature of about 340℃ which was due to the carbon content of the mixed sample. An increase in temperature beyond that, brought the curve down which was caused by degradation of the mixed sample organic content.

X. Pellet Physical Property Test

The results of the physical tests which include strength by dropping and water absorbability were discussed here. The strength by dropping was found to be 50%. From the two samples subjected to this test, one of the fuel samples was suffered a lot from cracking. This showed that there will be a half probability of disintegration of the fuel during transportation. This result was accounted by the efficiency of the presser.

With respect to the water absorbability, the highest potential of absorbability was noted (139%). That can be accounted for by its high content of sawdust which absorbs water quickly. Similar results were also observed by [Małgorzata Wzorek., 2012] from a mixed pellet of 80 wt.% sewage sludge, 19 wt.% sawdust and 1 wt.% of burnt lime.

4.2 Experimental Design Results

4.2.1 Analysis of Variance

The experimental results of the influence of two factors which were particle size and the ratio of the response variable pellet calorific value were designed using the general factorial of ANOVA and the results of the analysis of variance are presented in the following table and discussed.

Table 4.6 Analysis of variance table [Partial sum of squares]

Source	Sum of squares	DF	Mean square	F value	Prob>F
Model	3.753E+006	5	7.506E+005	27.82	<0.0001
A	7.104E+005	1	7.104E+005	26.33	<0.0001
B	2.484E+006	1	2.484E+006	92.09	<0.0001
A^2	3.642E+005	1	3.642E+005	13.50	0.0016
B^2	17860.21	1	17860.21	0.66	0.4259
AB	18857.33	1	18857.33	0.70	0.4135
Residual	5.126E+005	19	26977.87		
Cor Total	4.266E+006	24			

According to the table, the Model F-value of 27.82 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 case, A, B, A^2 (particle size and percentage) are significant model terms. Values 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 the model.

Another useful statistic here was the one labeled ‘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 high value indicates 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 0.7905 was in reasonable agreement with the "Adj R-Squared" of 0.8482. A ratio greater than 4 is desirable. The ratio of 18.994 indicates an adequate signal. This model can be used to navigate the design space. 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 model and/or data.

Table 4.7 Model adequacy measures

Std. Dev.	164.25	R-Squared	0.8798
Mean	3955.54	Adj R-Squared	0.8482
C.V.	4.15	Pred R-Squared	0.7905
Press	8.938E+005	Adeq Precision	18.994

The following table shows the numerical coefficient estimates for all the single sources and interaction sources listed in the ANOVA table.

Table 4.8 Coefficients of fitted model

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	4181.78	1	67.58	4040.33	4323.22	
A-Particle Size	236.48	1	46.08	140.03	332.94	1.00
B-Sawdust Percentage	455.49	1	47.47	356.14	554.84	1.04
A^2	-298.96	1	81.37	-469.26	-128.66	1.00
B^2	-63.89	1	78.53	-228.25	100.46	1.00
AB	-54.43	1	65.10	-190.69	81.83	1.04

Final Equation in Terms of Coded Factors:

$$C.V = 4181.78 + 236.48 * A + 455.49 * B - 298.96 * A^2 - 63.89 * B^2 - 54.43 * A * B$$

The above mathematical equation was developed for the response variable (calorific value) as a function of Particle size (A) and sawdust percentage (B) and calculated as the sum of a constant, first order effects, second order effect, and interaction effects.

Final Equation in Terms of Actual Factors:

$$C.V = -201.29949 + 28948.88330 * \text{Particle Size} + 50.50650 * \text{Sawdust Percentage} + 4.9 - 97057.11540 * \text{Particle Size}^2 - 0.15973 * \text{Sawdust Percentage}^2 - 49.03482 * \text{Particle Size} * \text{Sawdust Percentage}$$

4.2.2 Effect of Experimental Variables on Pellet Calorific Value

A. Effect of Particle Size on Pellet calorific value

Particle size was one of the factors that affect the calorific value of most pellets. The effect of different particle sizes over the range of 0.054-0.165mm with a constant percentage of materials (70% sawdust and 30% sewage sludge) was shown in the following figure in order to know the influence of this single factor. As it can be observed from the figure, the pellet calorific value increased as the particle size of the samples increased up to 0.12mm. Approximate values of calorific value was obtained on particle sizes of 0.054 and 0.072 mm and further increase in calorific value was seen up to that point (particle size of 0.12mm) but an increase beyond this particle size brought no significant improvement in the response variable, it eventually became smaller than the value obtained on particle size of 0.112 mm. Therefore this implied that the finesse of the material for pellet preparation must be small enough in order to get a good calorific value. The result also proved that particle size of a material was one of the main parameters that defines the pellet quality in terms of energy property.

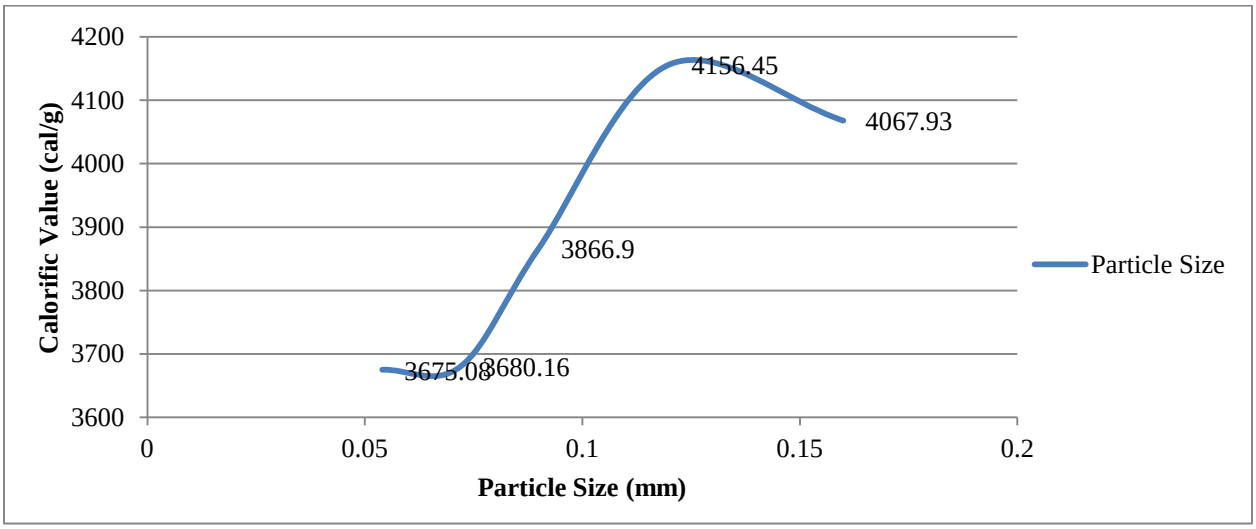

Figure 4.2 The effect of particle size on pellet calorific value

B. Effect of Percentage on Pellet Calorific value

The effect of percentage of the two materials on the pellet calorific value was shown in the following figure. As we can observe from the figure, the ratio has a positive effect in the pellet calorific value. As we increased the sawdust percentage to the maximum of 90%, a maximum calorific value of 4573.38 cal/g was obtained and this implied that sawdust plays a major role in the blending process. Most of the calorific value came from the sawdust and increasing to the maximum percentage bring a maximum energy content and this was due to the good characteristics of the sawdust described in the above sections.

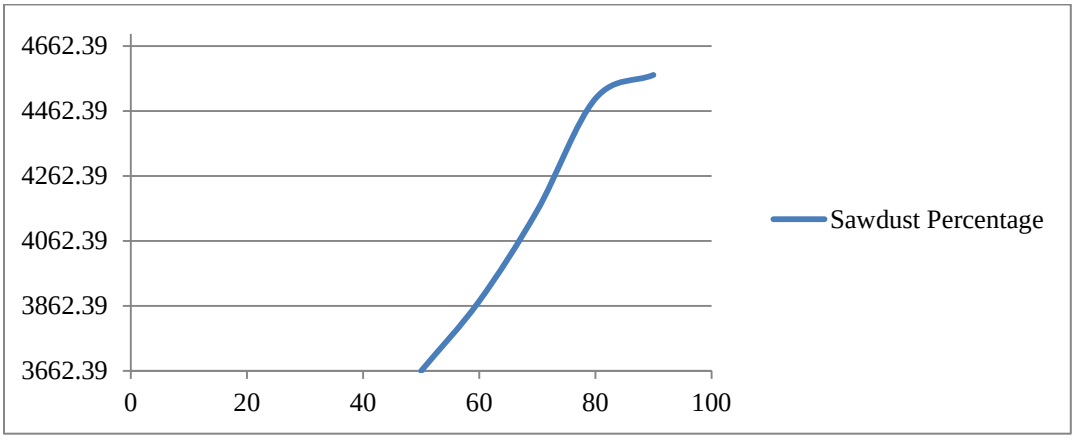

Figure 4.3 Effect of Sawdust Percentage on Calorific Value

C. Interaction Effect of the factors

According to the design of expert output, the interaction of sawdust percentage and ratio was observed in the following figure. Design points were included in the plot. And these points are points on the graph which helps to develop a mathematical model of the predicted response based on these points. This interaction plot was to show how the effect of changing one control varies with changes in a second control and as it can be observed in the figure, the lines of the two factors seemed to be parallel with a huge gap between them and this indicates that the effect of changing sawdust percentage or particle size didn't have a significant variation in the other parameter. This was also described in the ANOVA table that the interaction effect of the two parameters (experimental variables) was insignificant with a Prob>F value of 0.4135.

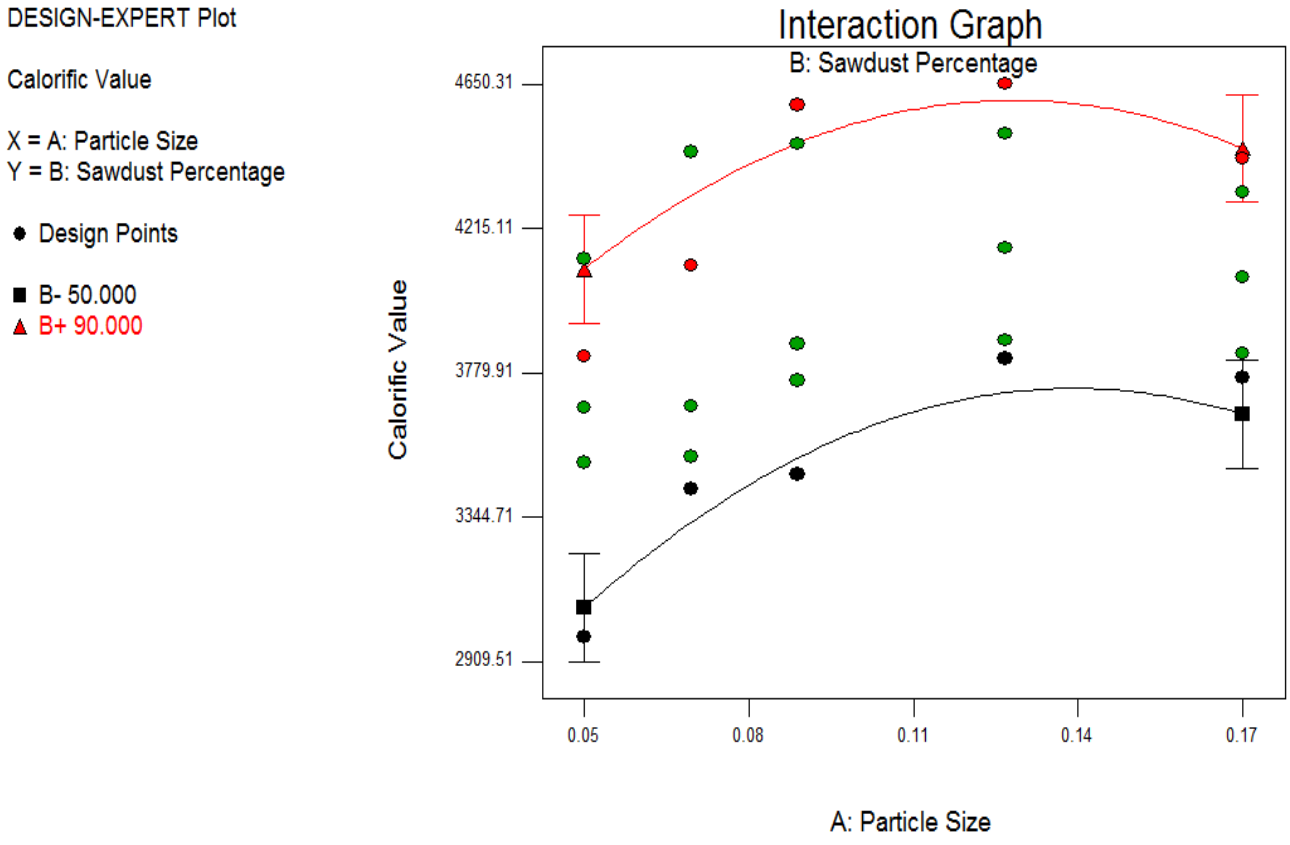

Figure 4.4 Interaction effect of sawdust percentage and particle size

4.2.3 Diagnostics and Contour plots

Under this tab residual plots, Box-Cox plot for power transformations and Plots of leverage and influence statistics were available. The residual plots are the main notes that offers the usual range of residual plots for checking assumptions such as Normality and constant variance, the Box-Cox plot for power transformations help us to decide whether we could improve the fit of the model by measuring the response on a different scale e.g. by using the log of the response values. And Plots of leverage and influence statistics show the influence of individual data points on the fitted model. So for standard designs such as Factorials, these statistics will not usually be needed. Only the residual plots were included in here.

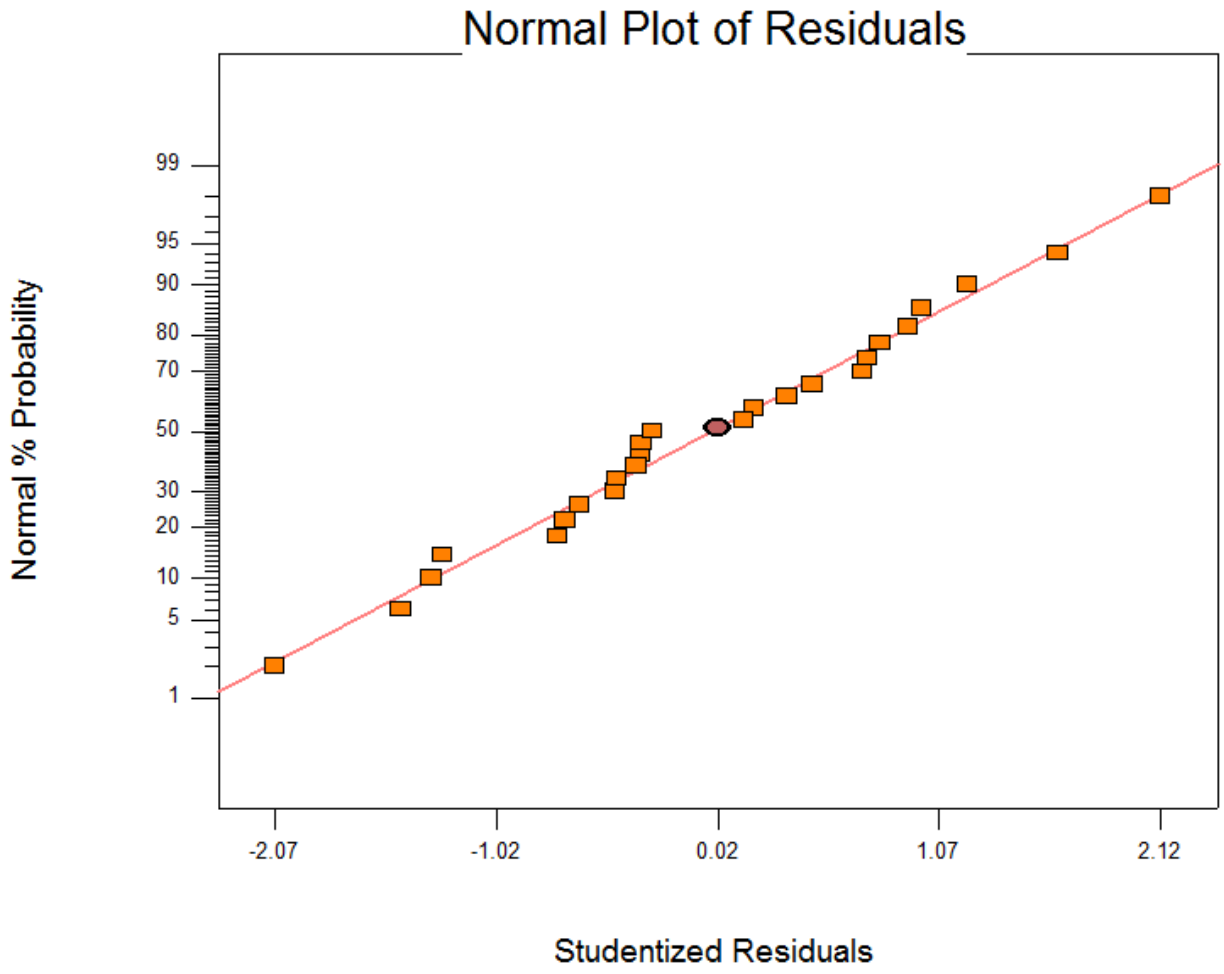

Figure 4.5 Normal plot of residuals

As it was already described in the above note, this residual analysis was necessary to confirm that whether the assumptions for the ANOVA were met and the above plot of studentized residuals showed that it was a good plot. According to [Shari Kraber., 2005], a good plot must be linear and normal.

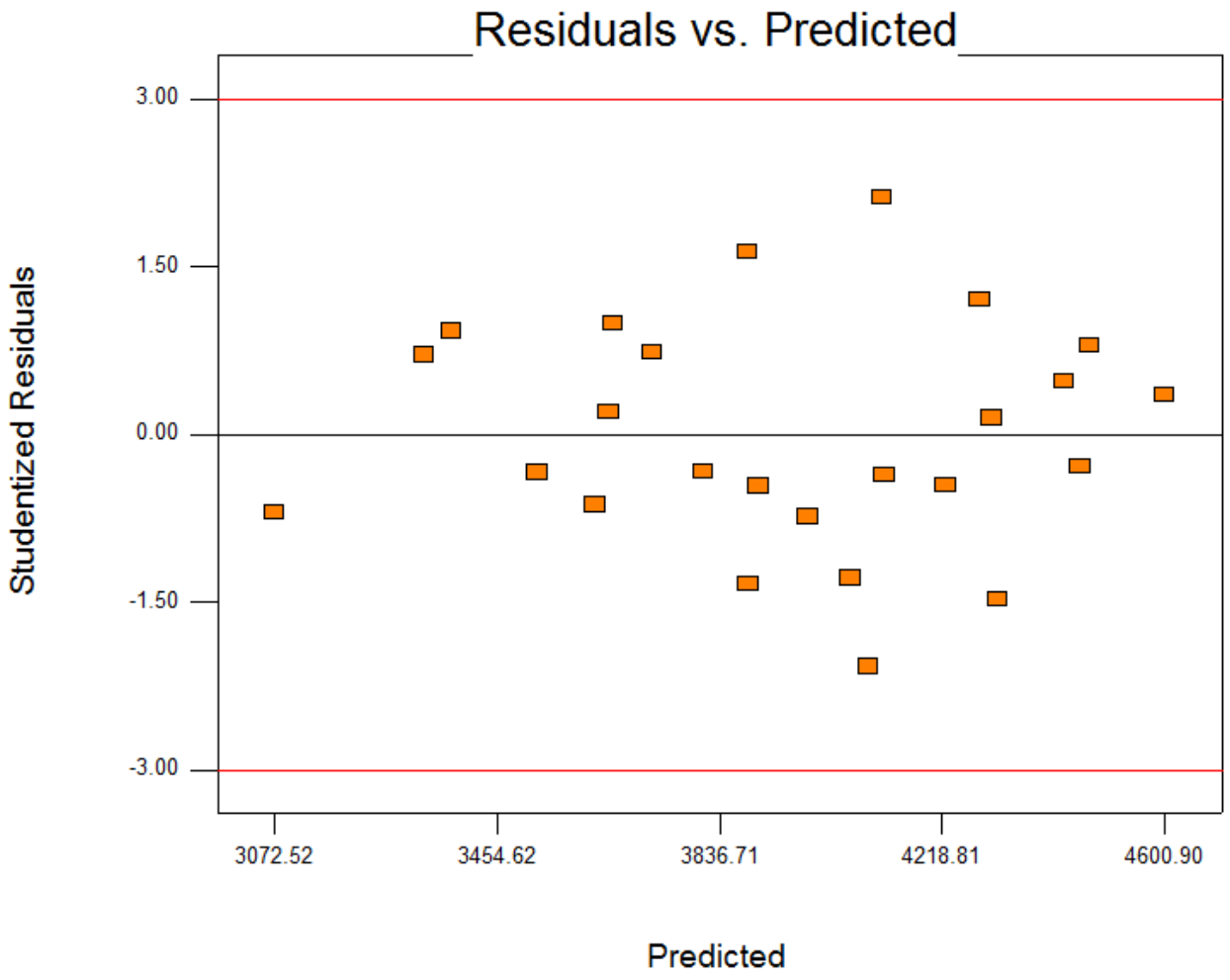

Figure 4.6 Studentized residuals versus Predicted value

According to the above plot, the points in the figure were random scatter which indicated that it was a good plot [Shari Kraber., 2005] and the assumptions for the ANOVA were met. With respect to the residual versus run number, the plot should also be in random scatter with no trends which indicated that the following plot was also a good one.

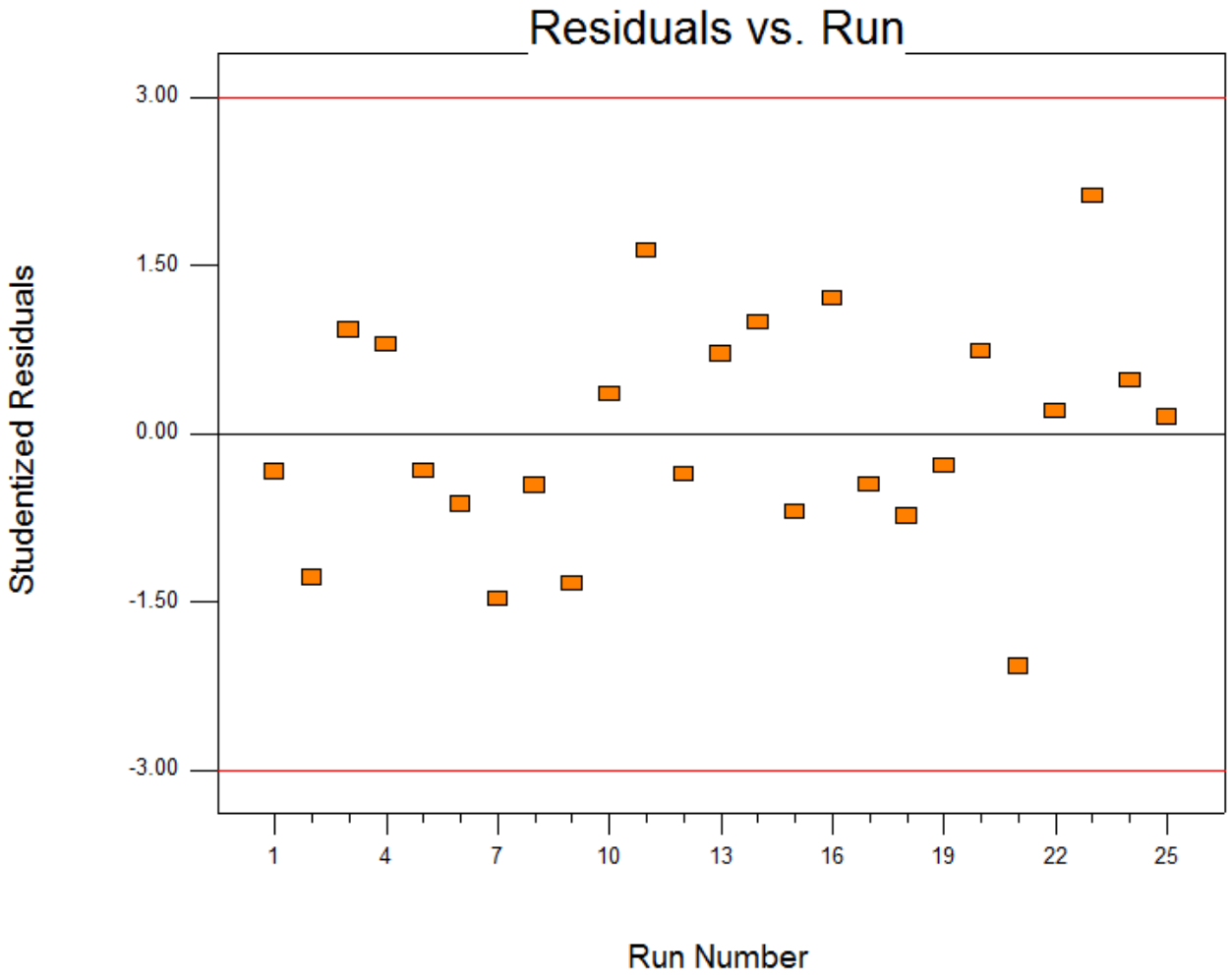

Figure 4.7 Studentized Residuals versus run number

One of the aims of statistical design is to ensure that the models make good use of all observations and are not critically dependent on just a few points. The other range for checking assumptions was predicted versus actual and with respect to the figure below, the points were randomly scattered along the 45-degree line which implied that it was a better prediction [Shari Kraber., 2005]. Groups of points above or below the line indicate areas of over or under prediction.

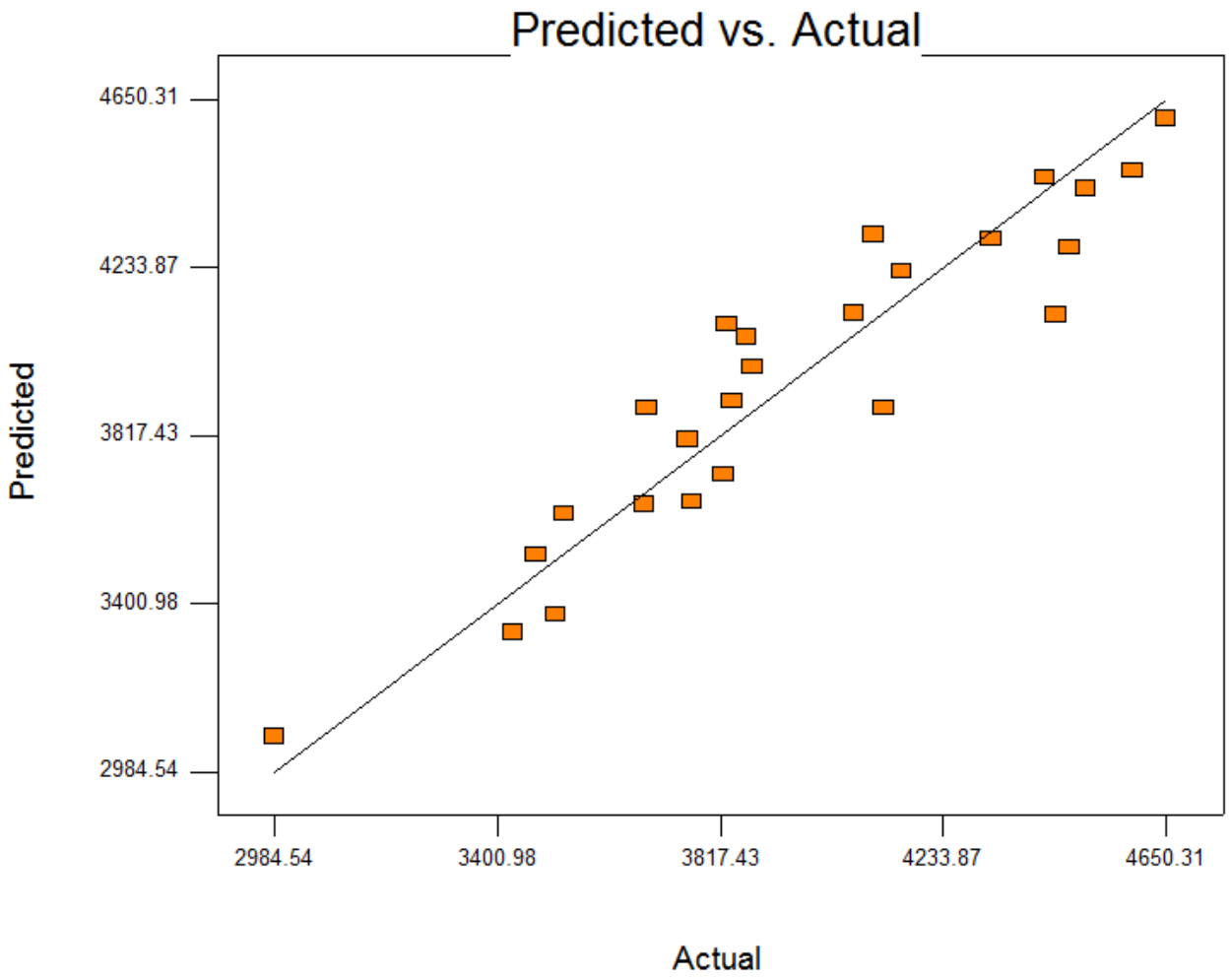

Figure 4.8 Predicted versus Actual

The contour plots in design expert are used to explore design space, slicing on the factors or components identified from the perturbation or trace plots as well as any categorical factors. The following contour plot was sliced in order to show the different points. The red points in the plot showed the design points within each of the factors.

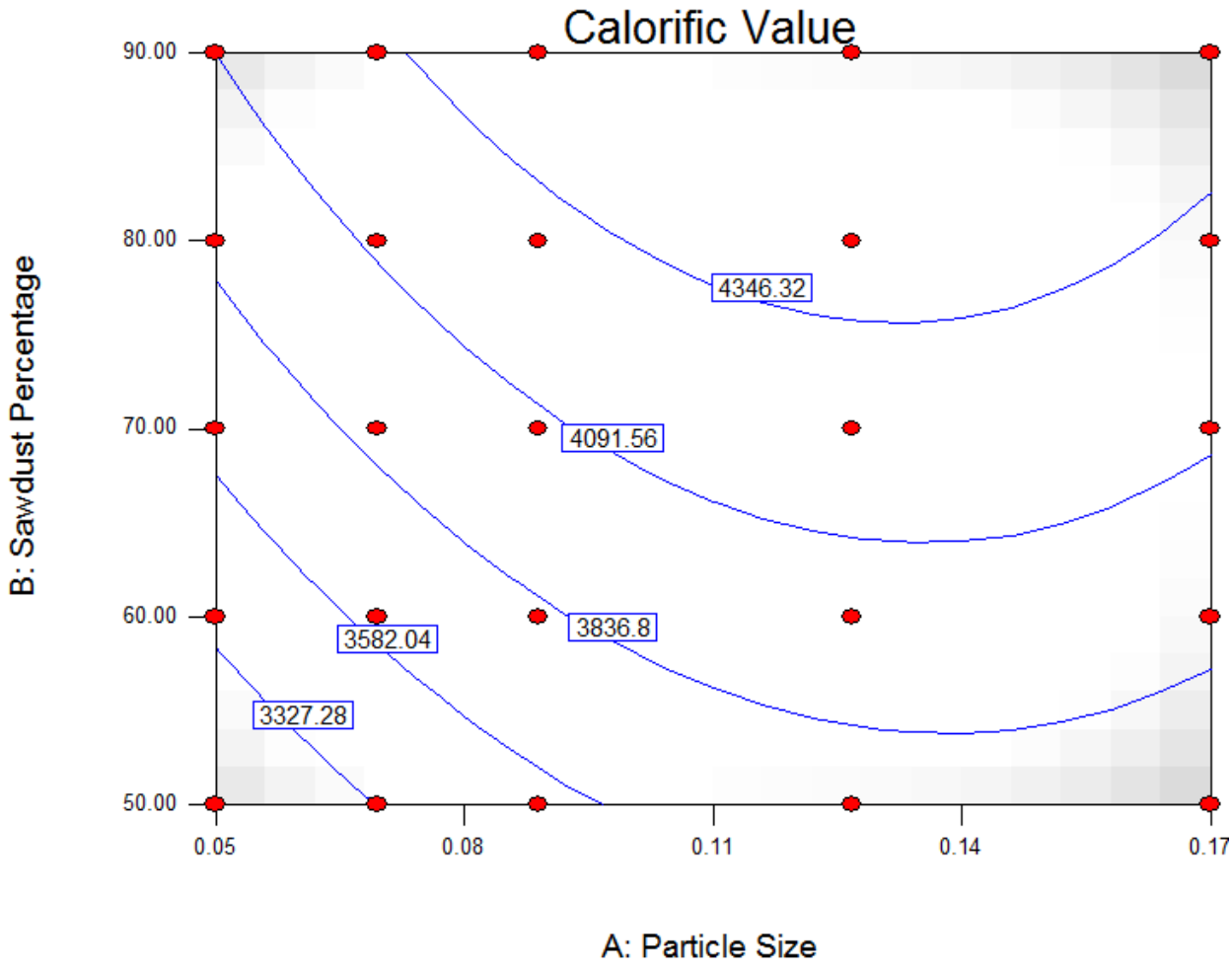

Figure 4.9 contour plot of sawdust percentage and particle size

5 Conclusion and Recommendation

5.1 Conclusion

The useful value of the sewage sludge can be improved by the admixture of other wastes so that the sludge becomes applicable in the production of energy, which also eliminates its disadvantageous consistency. The fuels can be obtained in this way which offers the pre assumed parameters (key criteria's) of alternative fuels. The parameters can also be tailored to make the fuels fit for the combustion process in the kiln.

The results of this study revealed that biomass fuel switching is possible and can be utilized in the cement industry. It was seen in the finding that the main parameter of the energy property: the calorific value of sewage sludge was increased when it was mixed with sawdust (wood waste). These components (wastes) can be converted into compacted fuels like pellets which can meet the requirements of the cement industry. That route will also make it possible to utilize the sludge as a source of energy, in an environmentally friendly way.

The selected wastes in the study have been critically analyzed on the ground of physiochemical properties and they offered the physical-chemical properties which meet the requirements of alternative fuels. The calorific values of the mixed pellet fuels fall within 12.49–19.20 MJ/kg, the lowest was obtained with an equal percentage of the mixture and with an average particle size of 0.054mm, which classified as low alternative fuels. The results on physical properties of water absorbability and strength by dropping factor indicated that the fuels should be protected against atmospheric precipitation for intermediate storage.

5.2 Recommendation

The following are some of the actions that should be taken by cement industries in Ethiopia for the beneficial use of the company as well as for a safe sound environmental and social benefit.

- The use of alternative fuels in cement kilns must be adapted in different cement industries of the country in order to decrease the environmental pollution by using 3R principle (recycle, reuse & reduce) and also to promote the sanitation of the city by developing solid waste management for the city of Addis Ababa.
- Further studies in alternative fuels especially from byproducts and wastes must be investigated for Ethiopian cement industries in order to minimize coal consumption and save foreign currency.
- Since Biomass-switching in the cement industry also has a rich pedigree in the Clean Development Mechanism (CDM). Cement industries must utilize and substitute the different biomasses and pellets produced in this mechanism for cost minimization (increased financial incentives) and most importantly for a safe environment.
- 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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Appendix

Appendix A: Laboratory work photos

Sewage sludge in drying bed

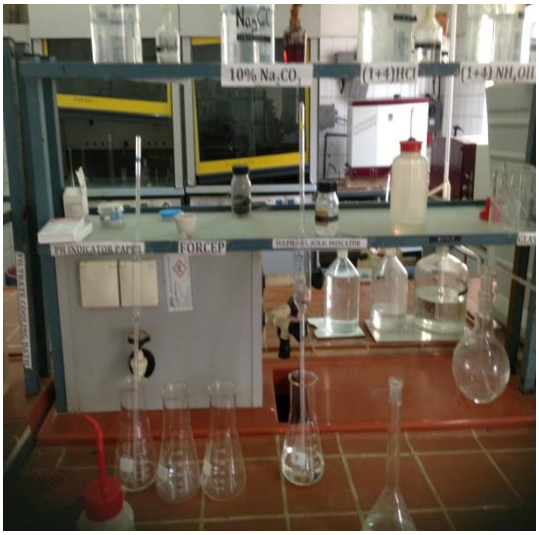
Sludge disposed and accumulated on the land

Drying Samples in oven

Ash sample for oxide analysis

Chemicals in MCF

Reagents in MCF



Preparation of solution for ash chemistry analysis

Titration using EDTA Solution

Determination of MgO

Determination of SiO_2

Laboratory Tablet Pellet Presser

Mortars for pellet preparation

SDT Q600 Thermo gravimetric analysis

Samples of different size and shape

A mixed sample pellet

Atomic Absorption spectrometer