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A

Thesis

On

Characterization of carbonized and uncarbonized bone waste: Physicochemical properties and their potential as alternative energy sources

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Abstract

One of the significant challenges facing societies today is meeting the growing energy demand for transportation, heating, lighting, and industrial processes, which have a considerable environmental impact. Population growth and urbanization have both directly and indirectly increased energy demand. This study investigates the characterization of carbonized and uncarbonized waste bone, examining their physicochemical properties and potential as alternative energy sources, particularly for use in the cement industry.

The research utilized two laboratory techniques: proximate analysis to determine the physical properties and calorific values, and ultimate (elemental) analysis to assess the chemical composition, including hydrogen, carbon, nitrogen, oxygen, and sulfur content of both carbonized and uncarbonized bones. The results indicated that the moisture content, volatile matter, and fixed carbon of carbonized and uncarbonized bones were 1.35% vs. 2%, 55.65% vs. 50.22%, and 2.55% vs. 7.72%, respectively. The calorific values were 3,212.75 kcal/kg for carbonized bones and 4,018.01 kcal/kg for uncarbonized bones.

In terms of elemental composition, carbon content was 32.46% for carbonized bones and 38.13% for uncarbonized bones, while nitrogen levels were 0.99% and 1.10%, and sulfur content was 0.18% and 0.078%, respectively. Comparative analysis of greenhouse gas emissions revealed that uncarbonized bones emitted 1.10% nitrogen, 38.13% carbon, and 0.078% sulfur, compared to 9.67% nitrogen, 58.84% carbon, and 0.25% sulfur from coal.

The study concludes that uncarbonized bones are more favorable as an alternative energy source compared to carbonized bones, as they offer comparable emissions and higher calorific values. It is recommended that partial replacement of fossil fuels with bone-derived energy could offer both environmental and economic benefits, promoting cleaner, cost-effective energy solutions.

***Keywords**: Carbonized bone, un-carbonized bones, coal, alternative energy, calorific value*

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LIST OF ACRONOMY

AEF	Alternative Energy Fuel
ANOVA	Analysis Of Variance
Ash	Ash content
ASTM	American Society for Testing and Materials,
BSE	Bovine Spongiform Encephalopathy
CV	Calorific Value
CCS	Carbon Capture and Storage
E	Energy
FC	Fixed Carbon
GW	Giga Watt
GHG	Greenhouse Gas
KW	kilo Watt
LHV	Lower Heating Value
MBM	Meat and Bone Meal
MJ/kg	Mega Joule per kilogram
MN	Moisture Content
NOx	Nitrogen oxides
PWh/y	Pico watt hour per Year
RDF	Refuse Derived fuel
RSE	Renewable Source of Energy
SPL	Spent Cell Linear
TWh	Tera Watt hour
WtE	Waste to Energy

W	Watt
VM	volatile matter

1. INTRODUCTION

1.1. Background of the Study

For socio-economic development of any country energy resources are painstaking to be the back bone and most vital instrument. The decades we are living are characterized by growth in wealth, but also by higher levels of pollution and the consequent deterioration of public health, mainly due to the increasing usage of fossil fuels for industrial and post industrial development. Fossil fuels such as coal, petroleum and natural gas provide most of the energy needs of the world today [1].

Historically, the primary fuel used in cement industry is coal. A wide range of other fuels such as gas, oil, liquid waste materials, solid waste materials and petroleum coke have all been successfully used as sources of energy for firing cement-making kilns, either on their own or in various combinations. Coal plays an important role in the security of supply in developed countries, and is a key enabler for economic growth and development in developing countries. It is the most predominantly used type of fossil fuels in industries. Coal resource exists in developing countries (including those with significant energy challenges). Therefore, coal has a key role to play in assisting the development of base load electricity where it is most needed.

Developing countries are increasingly satisfying their growing energy demands with cheap coal in order to sustain economic growth to reduce energy poverty and to achieve the United Nations (U.N.) development goals [2]. One of the most energy-intensive industrial product is production of cement. Cement is considered one of the most important building materials around the world. Cement production process consumes thermal energy of the order of 3.3 GJ/ton of clinker produced. Electrical energy consumption is about 90 – 120 kWh/ton of cement [5]. The principal fuel burned in cement kiln is Coal [6]. Since coal is carbon-enriched material, carbon dioxide is released during burning process. It is primary greenhouse gas that drives global climate change in a significant amount. To enhance the profit of the factory and to alleviate the problems caused by carbon dioxide emission by burning of coal, alternative fuel sources should be utilized. Now a day alternative fuel is used in many cement plants throughout the world [7].

The finite nature of global fossil fuel resources, high prices and most importantly, their damaging effect on the environment underscore the need to develop alternative fuels. As a result, the global society has been striving to find alternative ways for energy production. In line with that, major institutions of several countries have tried to implement a shared regulatory framework to promote renewable energies, thereby diversifying the sources of supply through replacing conventional energy resources. [1]. Increased use of renewable and alternative fuels can extend fossil fuel supplies and help resolve air pollution problems associated with the use of conventional fuels [3].

Biomass is one of the most promising renewable energy sources and it is abundant in many areas of the world. Due to its abundance, various forms in nature, its energy content and the low emissions to the atmosphere, it could play a major role in meeting world energy demand [4].
The replacement of coal by carbon dioxide neutral fuels will reduce net carbon dioxide emissions to the atmosphere, while letting the manufacturer gain economic advantages by reducing fuel costs and possibly earning carbon dioxide allowances under an Emissions Trading scheme [8].

Cement factories can potentially use alternative fuels, including biomass and biomass residues, to heat their kilns [6]. Industrialized countries have over 20 years of successful experience. The world pioneers in this practice are the Netherland and Switzerland, with national substitution rate of 83% and 48% respectively. In the U.S., cement plants usually get 20-70% of their energy input from alternative fuel [9].

The range of alternative fuels is very wide. One of the waste materials used as alternative fuels is meat and bone meal - MBM (also called animal meal) is used in several cement kilns, in particular in Western Europe. The fuel is prepared by post-treating (grinding and sterilizing) the waste materials associated with slaughtering operations. Since it contains only biogenic materials it can be categorized as 100% biomass fuel which gives no net carbon dioxide emissions during the combustion process [10].

In general, in view of this will be a positive step towards mitigating the energy environmental problems associated with the use of fossil fuels.

1.2. Statement of the Problem

One of the greatest challenges for the growing society in this century is to meet the energy demand for transportation, heating, lighting and industrial processes, which have a significant impact on the environment. World population and increased urbanization have directly or indirectly influenced the energy demand. The energy request and the development of any country are directly related, for the reason that the energy sources are considered to be the back bone and most vital instrument for the development of any country. Energy consumption and energy crisis are increasing day to day due to ever-increasing high speed of economic expansion. Messebo Cement Industry use large conservative fossil fuel energy. It is totally dependence on foreign fossil fuel. From all the fossil fuel types coal is the primary fuel burned in cement kilns. The running down and non-renewability of these fossil fuels and continuous rise in fossil fuel cost challenges the growth and profitability of the industries. In line to this the cost of cement is increasing.

The rise in fossil fuel cost and the significant contribution of coal to global warming with high emission of CO_2 and other pollutants to the environment leads the local cement industries to look for alternative renewable energy sources. Utilization of alternative fuels is going to reduce use of coal in kiln systems. Their use is likely to reduce manufacturing cost and may also give rise to environmental benefits. In Mekelle area huge amount of animal bones are being discarded without proper disposal which causes environmental and water bodies' pollution. Hence, The animal bone waste is a suitable alternative bio energy for substituting fossil fuels like crushed coal in rotary kiln burners used in cement kiln systems.

Therefore, due to the critical limitations of conventional fossil fuels like coal applications for cement industries and the potentials of bone as alternative energy source for cement industry motivated the researcher to conduct this research. Promoting such alternative fuels for meeting energy requirement is an eagerness initiative which can help to replace fossil fuel and mitigate greenhouse gas (GHG) emissions. This study has been carried out to determine physicochemical characteristic of carbonized and un-carbonized waste bone and their potential as alternative energy sources in cement industry.

1.3. Objective of the Study

1.3.1. General Objective

The general objective of the study was to investigate the physicochemical characteristics of carbonized and uncarbonized bone waste and their potential as alternative energy sources in cement industry.

1.3.2. Specific Objectives

The specific objectives of this study were;

- To determine the major elemental constituent such as C, O, N, S and H contents of carbonized and uncarbonized bones.
- To conduct the proximate analysis of carbonized and uncarbonized bones.
- To determine the heating values of carbonized and uncarbonized bones and compare it with with that of coal.
- To evaluate the potential risk of the bone on the environmental impact relative to coal.

1.4. Significance of the study

Energy consumption and energy crisis are increasing day by day due to ever-increasing high speed of economic development. This crisis of energy leads the society discoveries of other alternatives for gaining of enough energy for all activity of the development. Now a day the main energy source in the cement industry is fossil fuel, replacing partially the fossil fuel used in kiln burning process by alternative fuel such as bones can save foreign currency by replacing imported fuels;

Municipal solid waste (MSW) such as bone is one of the most occupied waste in Ethiopia and due to its unlimited resources availability, there is a high potential usage for the production which results in lower cost of manufacture**.**

Biomass is considered to be a zero-emission fuel. One of the numerous profits from the implementation of biomass like bone usage instead of fossil fuel would be the reduction of greenhouse gas (GHG) emissions. Since a proportion of using alternative fuels don't require high thermal processing and also has high efficiency of the process.

From an economic perspective, using of waste bone as energy source reduce the crisis of foreign currency of the country and needs more man power on the collecting of these bone from the field or another area. This can help farmers make extra money in addition to their farm activities.

2. LITERATURE REVIEW

2.1. Energy and Sustainable Development

Reliable energy supply is essential in all economies for lighting, heating, communications, computers, industrial equipment, transport, etc. Purchases of energy account for 5–10% of gross national product in developed economies [11]. However, in some developing countries such as Ethiopia, energy imports create economical unsustainable and an economic challenge for sustainable development. World energy use increased time to time predominantly from fossil fuels (i.e. coal, oil and gas) and with the addition of electricity from nuclear power. Due to the rising industrialization, further increases in world energy consumption can be expected. Using of the fossil fuels (i.e., coal, oil and gas) and nuclear fuels are potential climate change, and related sustainability issues, is now established as one of the major drivers of energy policy. In short, renewable energy supplies are much more compatible with sustainable development than are fossil and nuclear fuels, in regard to both resource limitations and environmental impacts. Consequently, almost all national energy plans include four vital factors for improving or maintaining social benefit from energy. These are increased harnessing of renewable supplies, increased efficiency of supply and end-use, reduction in pollution and consideration of lifestyle [11].

2.2. Global resources of energy

Unexpected high growth in the energy market especially the renewable, in terms of investment, new capacity and high growth rates in developing countries have changed the landscape for the energy sector. We have seen the growth of unconventional resources and improvements in technology evolution for all forms of energy resources. This has contributed to falling prices and the increased decoupling of economic growth and greenhouse gas (GHG) emissions. Most countries have achieved a more diversified energy mix with a growth in community ownerships and an evolution of micro grids. Considering these aims, and with the most energy-efficient modern equipment, buildings and transportation, a justifiable target for energy use in a modern society with an appropriate lifestyle is E=2kW per person [12]. Such a target is consistent with an energy policy of ‘contract and converge’ for global equity, since worldwide energy supply would total approximately the present global average usage, but would be consumed for a far higher standard of living. Is this possible, even in principle, from renewable energy? Each square meter of the earth's habitable surface is crossed by, or accessible to, an average energy flux from all renewable sources of about 500W. This includes solar, wind or other renewable energy forms in an overall estimate. If this flux is attached at just 4% efficiency, 2kW of power can be drawn from an area of 10m×10m, assuming suitable methods. Housing areas of residential towns have population densities of about 500 people per square kilometer. At 2kW per person, the total energy demand of 1000kWkm^{-2} could be obtained in principle by using just 5% of the local land area for energy production [12]. Thus, renewable energy supplies can provide a satisfactory standard of living, but only if the technical methods and institutional frameworks exist to extract, use and store the energy in an appropriate form at realistic costs. [13]

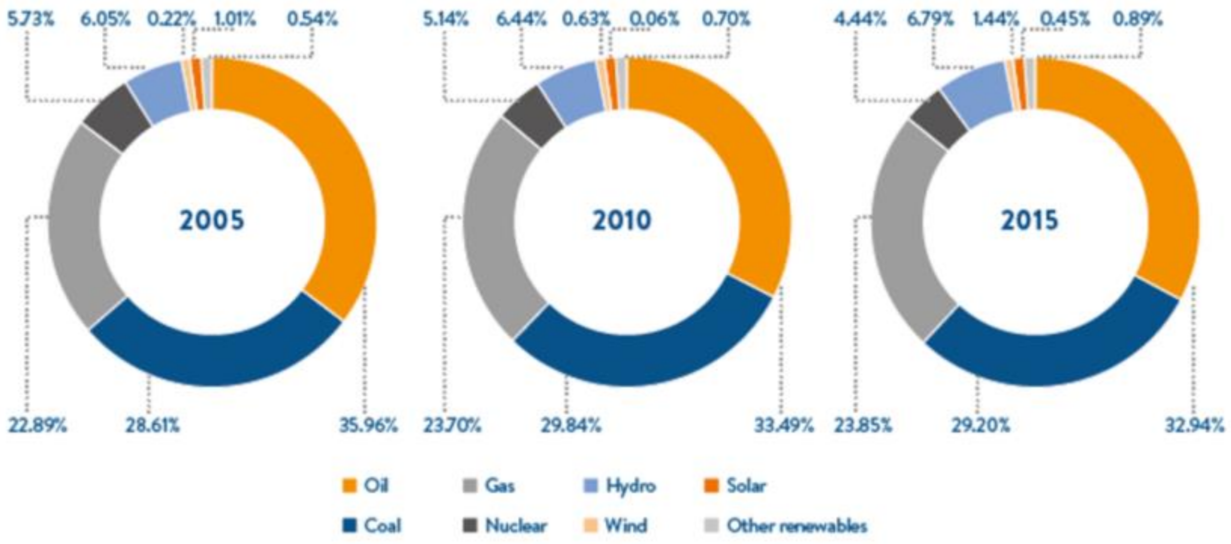

Figure .2.1.: Comparative primary energy consumption over the past 15 years

Solar: Global installed capacity for solar-powered electricity has seen an exponential growth, reaching around 227 GWe at the end of 2015, producing 1% of all electricity used globally. The total capacity for solar heating and cooling in operation in 2015 was estimated at 406 GWth. As solar PV module prices have declined around 80% since 2007 (from ~ US$4/W in 2007 to ~ US$1.8/W in 2015), the cost associated with balancing the system represents the next great challenge for the Solar PV industry [13].

E-storage: E-storage has been characterized by rapid change, driven by reduced costs (especially batteries) and increased industry requirement to manage system volatility. As of end-2015, the global installed storage capacity was 146 GW, consisting of 944 projects. There are already around 25000 residential-scale units in Germany alone. Bottom-up projections suggest a global storage market of 1.4 GW/y by 2020, with strong growth in electro-mechanical technologies in particular [13].

Marine: 0.5 GW of commercial marine energy generation capacity is in operation and another 1.7 GW under construction, with 99% of this accounted for by tidal range. The total theoretical wave energy potential is said to be 32 PWh/y, but is heterogeneous and geographically distributed, technology costs for marine energy are still very high, hindering deployment [13].

Uranium and Nuclear: Global uranium production increased by 40% between 2004 and 2013, mainly because of increased production by Kazakhstan, the world's leading producer. As of December 2015, 65 nuclear reactors were under construction with a total capacity of 64 GW. Two-thirds [14] of the units under construction are located in three countries: China, India and Russia. Currently there are more than 45 Small Modular Reactors designs under development and four reactors under construction [14].

Waste-to-Energy: Despite Waste-to-Energy (WtE) occupying less than 6% of the total waste management market, the global WtE market was valued at approximately US$25 billion in 2015 and is expected to reach US$36 billion by 2020.

Hydropower: Hydropower is the leading renewable source for electricity generation globally, supplying 71% of all renewable electricity at the end of 2015. Undeveloped potential is approximately 10 000 TWh/y worldwide. The global hydropower capacity increased by more than 30% between 2007 and 2015 accounting to a total of 1209 GW in 2015, of which 145 GW is pumped storage [13].

Oil: Oil remained the world's leading fuel, accounting for 32.9% of global energy consumption. Crude oil prices recorded the largest percentage decline since 1986 (73%). Roughly 63% of oil consumption is from the transport sector. Oil substitution is not yet imminent and is not expected to reach more than 5% for the next five years. Unconventional oil recovery accounts for 30% of the global recoverable oil reserves and oil shale contains at least three times as much as conventional crude oil reserves, which are projected at around 1.2 trillion barrels [13].

Natural Gas: Natural gas is the second largest energy source in power generation, representing 22% of generated power globally and the only fossil fuel whose share of primary energy consumption is projected to grow.

Wind: Global wind power generation reached 432 GW in 2015, around 7% of total global power generation capacity (420 GW onshore, 12 GW offshore). A record of 63 GW was added in 2015 and total investment in the global wind sector was US$109 billion in 2015 [13].

Coal: Coal production decreased with 0.6% in 2014 and with a further 2.8% in 2015, the first decline in global coal production growth since the 1990s. Coal still provides around 40% of the world's electricity. However, climate change mitigation demands, transition to cleaner energy forms and increased competition from other resources are presenting challenges for the sector. Asia presents the biggest market for coal and currently accounts for 66% of global coal consumption [13].

Carbon capture and storage (CCS): CCS is an essential element of any low carbon energy future and industrial future, but policy is the main issue, not technology. The world's first large-scale application of CO_2 capture technology in the power sector commenced operation in October 2014 at the Boundary Dam power station in Saskatchewan, Canada. There are 22 large-scale CCS projects currently in operation or under construction around the world, with the capacity to capture up to 40 million ton of CO_2 per year [13].

Geothermal: Geothermal global output is estimated to be 75 TWh for heat and 75 TWh for power, but is concentrated on geologic plate boundaries [13].

Bioenergy: Bioenergy is the largest renewable energy source with 14% out of 18% renewables in the energy mix and supplies 10% of global energy supply [13]

2.3. Overview of Alternative energy

The world we are living are characterized by growth in wealth, but also by higher levels of pollution and the consequent deterioration of public health, mainly due to the increasing usage of fossil fuels for industrial and postindustrial development. As a result, the global society has been striving to find alternative routes for energy production. Most natural and artificial materials contain some energy which can be utilized by cement industries to meet the requirement of the thermal energy. The use of alternative fuel for cement clinker production is of high importance for the cement manufacturers as well as for the environment. Alternative fuel utilization at commercial level in cement industry is as old as about 40 years now. Utilization of alternative fuels in cement kilns is still progressing. In some kilns up to100% substitution rates, while the others are facing some barriers such as environmental, social and quality issues. In any case, alternative fuel utilization requires the adaptation of the combustion process. Modern multi-channel burners and thermograph systems allow to control alternative fuel feed rate and the flame shape to optimize the burning behavior of the fuels [15].

Considering various alternative energy sources, biomass has been an indispensable part of energy debates within the policy context, strongly desired by the European Union, which has been able to transform saving and environmental protection provisions into strategic execution plans for development [15].

2.3.1. Advantages and disadvantages of the alternative energy

Advantages of the alternative energy:

- Alternative fuels are cheaper than the fossil fuels which lead the cement industries to use them in optimal proportion.
- The maximum benefit can be achieved when the alternative fuel is used with minimal preparation [16].
- The significant advantage of alternative fuel substitution is the utilization and preservation of non-renewable energy sources, conservation of environment and reduction of waste disposal sites [17].
- Alternative fuels can also supplement the raw material requirement in cement production. For instance, the steel belts in tires may be used to replace a portion of the iron required in the raw materials [18].

Disadvantages of the alternative energy:

- Switching from conventional fuels to alternative fuels presents several challenges as they have different characteristics compared to the conventional fuels.
- Poor heat distribution, unstable precalciner operation, blockages in the preheater cyclones, build-ups in the kiln riser ducts, higher SO_2, NO_X, and CO emissions, and dusty kilns are some of the major challenges which need to be addressed [19].
- One potential constraint on the implementation of alternative fuels is the final clinker composition since the combustion by-products are incorporated into clinker. If even one of these compounds/elements affects the quality of the cement, the very benefits derived may disappear [20].

Generally, the cement producers choose the alternative fuel on basis of environmental friendly. But it is also necessary to know the composition of the fuel including the fixed carbon, moisture and volatiles contents. All kinds of varieties from liquid to solids, powdered or as big lumps need to be considered when dealing with alternative fuels. It requires a flexible fuel feeding whether they are fed directly into the burning zone in the kiln itself or into the pre-heating system [18]. Thus, the fuel material should be cost effective easy to handle, easy to store, longer storage life. Alternative fuels inherently requires investment costs associated with adjustment or replacement of a burner, Implementation of alternative fuel delivery systems, new fuel storage facilities, and fuel distribution systems [22].

2.4. Classification of alternative fuel

A wide range of materials can be considered as viable alternative fuels in cement industry. [22] Have categorized alternative fuels based on their physical and chemical properties.

2.4.1. Alternative fuel options for the cement industry.

Liquid waste fuels: Industrial chemical wastes, waste solvents, used oils, paint waste, oil sludge, distillation residues, wax suspensions, tar, petrochemical waste, asphalt slurry [18].

Solid waste fuels: Used tire, paper waste, plastic residues, spent cell liner (SPL), meat and bone meal (MBM), sewage sludge, municipal solid waste (MSW), agricultural biomass (green waste, wood waste, nut shells, rice husk, etc.), refuse derived fuel (RDF), rubber residues, pulp sludge, battery cases, oil-bearing soils [18]

Gaseous waste: Landfill gas, pyrolysis gas [18]

2.4.2. Criteria of alternative fuels

By far there are no selection criteria for the alternative fuels in cement industry. The specific criteria that a material must meet in order to be considered as a fuel are typically set by the cement producers according to their own standards. The following criteria are example of few standards [7, 23]:

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

.

2.4.3. Usage of alternative fuel

The cement manufacturing industry is under increasing pressure from the environmental protection agencies to reduce the emissions. The usage of alternative fuels in cement manufacturing not only helps to reduce the emission but also has significant ecological benefits of conserving non-renewable resources [24].

2.4. Biomass production for energy

One of the mast important types of the alternative energies is bioenergy. Bioenergy is energy from organic matter (biomass), i.e., all materials of biological origin that is not embedded in geological formations (fossilized). Biomass can be used in its original form as fuel, or be refined to different kinds of solid, gaseous or liquid biofuels. These fuels can be used in all sectors of society, for production of electricity, for transport, for heating and cooling, and for industrial processes [13]. The most important biomass sources are agricultural and forestry residues (wastes from the wood processing industry such as shavings, sawdust, etc.), animal residues (livestock farms), sewage, algae, and aquatic crops. Municipal solid waste (MSW) and the waste streams originating from anthropogenic activities also fall in the biomass category; only if they are not reusable in subsequent processing [25].

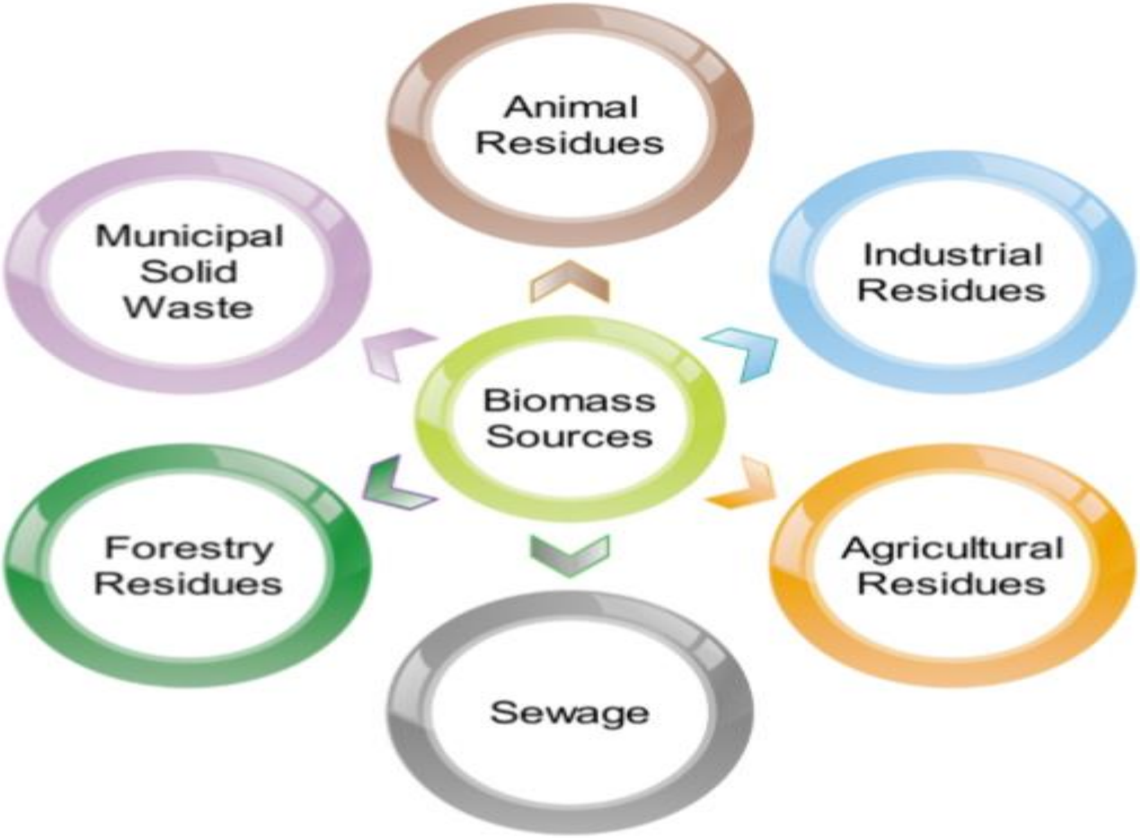

Figure 2.2.: the most important biomass sources

2.5. Wastes

Waste is an inevitable product of society, and one of the greatest challenges for future generations is to understand how to manage large quantities of waste in a sustainable way. One approach has been to minimize the amount of waste produced, and to recycle larger fractions of waste materials. However, there still is a considerable part of undesired end products that must be taken care of, and a more suitable solution than simple land filling needs to be found [13].

The waste management sector faces a problem that it cannot solve on its own. The energy sector, however, is considered to be a perfect match, because of its need to continuously meet a growing energy demand. Waste is now not only an undesired product of society, but a valuable energy resource as well. Energy recovery from waste can solve two problems at once: treating non-recyclable and non-reusable amounts of waste; and generating a significant amount of energy which can be included in the energy production mix in order to satisfy the consumers' needs.

The interaction between waste management solutions and energy production technologies can vary significantly, depending on multiple factors. Different countries across the world choose to adopt different strategies, depending on social, economic and environmental criteria and constraints. These decisions can have an impact on energy security, energy equity and environmental sustainability when looking at the future of the energy sector. If waste-to-energy (WtE) technologies are developed and implemented, while following sustainability principles, then a correct waste treatment strategy and an environment friendly energy production can be achieved at the same time, solving challenges in both the waste management and energy sectors [13].

2.5.1. Animal wastes

The application of all types of organic waste as energy materials makes it possible to lower the extent to which the limits of CO_2 emission into the atmosphere occurs and to introduce a new source of energy into the energy fuel balance. The exploitation of the environment, which is regarded as an economic expense, may be reduced significantly if the energy recycling of waste, included as renewable sources of energy (RSE), is introduced on a large scale. Therefore, nowadays, their use for limits defining the emission of solid fuel combustion products containing large amounts of carbon provides an opportunity for introduction various types of alternative energy fuels (AEF). Nowadays, the most common is the woody biomass that includes wood, agricultural waste, energy crops or wood-industry waste. The AEF can be derived from biodegradable waste, which is also regarded as biomass. The application of all types of organic waste as energy materials makes it possible to lower the extent to which the limits of CO_2 emission into the atmosphere occurs and to introduce a new source of energy into the energy fuel balance. The exploitation of the environment, which is regarded as an economic expense, may be reduced significantly if the energy recycling of waste, included as renewable sources of energy (RSE), is introduced on a large scale. Therefore, nowadays, their use for energy purposes has attracted an increasing attention. This refers mainly to the animal waste of deferent kind, including poultry waste and meat and bone meal (MBM). One of the animal wastes is bone which is the non-reusable [26].

2.5.2. Bone

Bone is very strong, so a new material based on bone structure could make a strong membrane. Unfortunately, bone is very bad at transporting ions. A bone is a rigid organ that constitutes part of the vertebrate skeleton in animals. Bones protect the various organs of the body, produce red and white blood cells, store minerals, provide structure and support for the body, and enable mobility.

Meat and bone meal (MBM) is produced in rendering plants where animal offal and bones are mixed, crushed and cooked. Tallow is extracted during the cooking process, and the remaining material is then dried and crushed. Feeding MBM to cattle, sheep or other animals was banned within the EU in 1994 and disposal to landfill is not an option since this does not destroy any potential bovine spongiform encephalopathy (BSE) pathogens (publicly known as mad cow disease) [26]. This change in legislation increased the interest in using MBM as fuel to ensure that any living organism is thermally destroyed totally and its energy potential is utilized [6]. Now a day’s most cement producers started using MBM in a large extent. In France about 45% of the annual productions of MBM were burnt in cement plants [27].

The availability of bone meal is higher than most of the other alternative fuel commonly used in cement kiln [28]. The feeding rates of bone in cement kilns vary from country to country. For example, in Spain the limit is 15% of the energy needed in the kilns, but there is no limit in Switzerland [8]. MBM has calorific value (lower heating value, LHV) of 14.47 MJ/kg [29] which is almost half of the coal. The high content of calcium in bone offers the advantage of reducing SO_2 emission as it could act to retain most of SO_2 formed during bone combustion [30].

Presence of excess amount of calcium can produce free lime while burning in cement kiln which may affect the clinker quality [31].

Table 2.1: physical and chemical properties of studies samples of bone meal derived from pigs cttle and poultry sourced from zpm"Ostrowite

Physical and chemical properties	Bone meal
Proximate analysis (% as received)	
Moisture	4.17
Ash	39.47
Volatile matter	49.08
Fixed carbon	7.28
Ultimate analysis (% daf)	
Carbon	58.84
Hydrogen	8.96
Nitrogen	9.67
Sulfur	0.25
Oxygen	22.03
Physical properties	
Apparent density, kg/m^3	606
Bulk density, kg/m^3	662
Higher heating value HHV, MJ/kg	15.75
Lower heating value LHV, MJ/kg	12.77

Compared with coal, bone has lower fixed carbon and higher chlorine. Due to higher chlorine content, there is a potential of build-up and blockages in preheater units [6]. This will reduce the efficiency of the plant. As the nitrogen content in the MBM is about 7–8 times higher than that in coal one would expect that NO_X emissions would increase. But it was observed that NO_X decreases with increasing MBM content in coal-MBM blend [26]. In contras [32] mentioned that the emission of nitrogen oxides increases during incineration of MBM using heavy fuel oil. Abad et al [33]. Reported that incineration of meat and bone meal has no impact on dioxin and furan emissions

2.6. Thermochemical conversion

Biomass is one of the first sources of energy used by mankind. It is still the major source of energy in developing countries. Nowadays there are mainly three ways frequently used to extract energy from biomass. These are: combustion, gasification and pyrolysis [34]. Combustion is the oxidation of fuel in which biomass can be completely oxidized and transferred into heat. However, efficiency of this process is only about 10% and this manner of use is a source of substantial pollution. Gasification is a partly oxidizing process that converts a solid fuel into a gaseous fuel, while pyrolysis is the first stage of both combustion and gasification processes. Therefore, pyrolysis is not only an independent conversion technology, but also a part of gasification and combustion, which consists of a thermal degradation of the initial solid fuel into gases and liquids without an oxidizing agent [35].

2.7. Proximate and ultimate analysis of Bone

2.7.1. Proximate analysis of bone meal

Determination the moisture content, volatile matter, ash content and fixed carbon in bone meal comprises its proximate analysis. Moisture content of bone refers to the weight loss when a weighed amount of bone is heated in a muffle furnace at 105-110^{0}c. Volatile matter of bone refers to the weight loss when a weighed amount of moisture free powder is heated at 950^{0}c in a muffle furnace for a certain time. The Ash content of a bone is the weight obtained after a weighed amount of bone sample is burned in an open crucible in a muffle furnace and the fixed carbon content refers to the mass of a sample after its moisture content, volatile matter and ash content are subtracted.

2.7.2. Ultimate analysis of bone meal

Ultimate analysis of bone meal refers to the determination of total carbon, hydrogen, oxygen, nitrogen and sulfur percentages in bone. Carbon and hydrogen content of the bone are determined by burning the bone in a current of dry oxygen and passing it through weighed tubes containing anhydrous calcium chloride ($CaCl_2$) and potassium hydroxide (KOH) respectively. The carbon and hydrogen of bone are combusted into CO_2 and H_2O respectively. Then the CO_2 is absorbed by KOH and H_2O is absorbed by $CaCl_2$.

$$C + O_2 \rightarrow CO_2 \ and \ H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Sulfur is determined by burning of bone in a bomb calorimeter in a current of oxygen. The ash obtained is extracted with diluted hydrochloric acid (HCl) and the acid extract is treated with barium chloride ($BaCl_2$) solution to precipitate as barium sulfate ($BaSO_4$).

$$S + HCl \overset{O_2}{\rightarrow} SO_4^{-2} \xrightarrow{BaCl_2} BaSO_{4(s)}$$

The barium sulfate obtained is then filtered, washed, dried and weighed.

Nitrogen in a bone is determined in a Kjeldahal’s flask by heating with a concentrated sulfuric acid in the presence of potassium sulfate there by converting the nitrogen of bone to ammonium sulfate. When clear solution is obtained, it is treated with 50% sodium hydroxide.

2.8. Overview of Cement Production

The production of cement consumes large quantities of raw materials and energy (thermal and electricity). The manufacturing process is very complex, involving a large number of raw materials (with varying material properties), pyro processing techniques, and a variety of fuel sources. This process requires approximately 3.2–6.3 GJ of energy and 1.7 tons of raw materials (mainly limestone) per ton (t) of clinker produced [33,36]. Being an energy intensive industry, thermal energy accounts for about 20–25% of the cement production cost [9]. The typical electrical energy consumption of a modern cement plant is about 110–120 kW h per ton of cement. In the process thermal energy is used mainly during the burning, while maximum share of electrical energy is used for cement grinding [9].

Generally fossil fuels such as coal, petroleum coke (petcock) and natural gas provide the thermal energy required for cement industry. Due to environmental concerns, many researchers tried different alternative operating option for coal fired plant. To reduce the emission from coal fired plant different CO_2 capture technology can be adopted. Among them oxy-fuel combustion could be a viable option for cement industry. In oxy-fuel combustion technique primary fuel coal is burnt in oxygen rather than air with recycled flue gas [16, 37]. Oxy-fuel combustion could potentially reduce the NO_X emission [16, 38]. But it could also present some problem regarding the quality of the clinker since the carbon content of the fly-ash may increase in this process. An increase of SO_2 in the flue gas is also reported [16].

2.8.1. **Cement manufacturing process**

The main process routes for the manufacture of cement vary with respect to equipment design, method of operation and fuel consumption [39]. The four basic processes can be classified as follows:

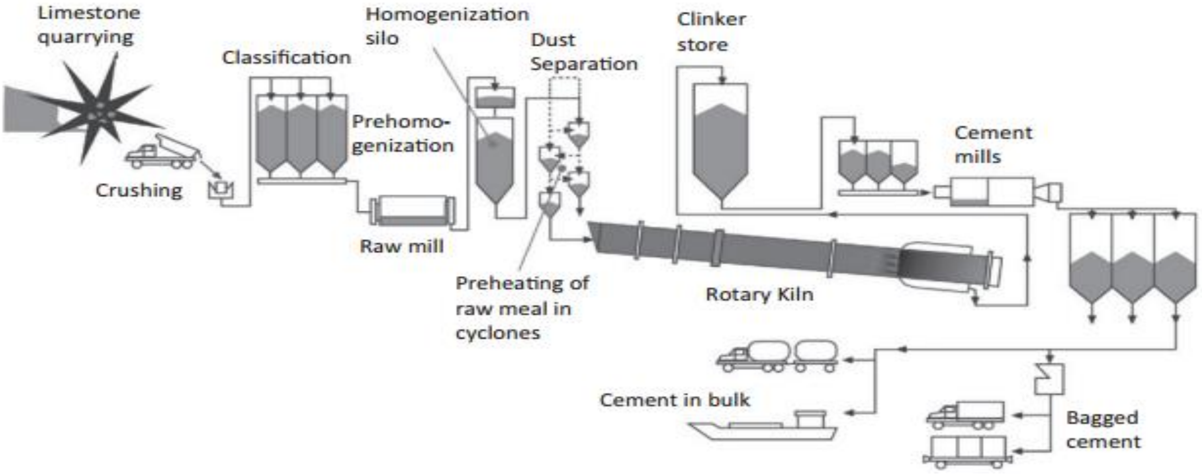

Figure. 2.3: Cement manufacturing process

- Dry process: Dry raw meal is fed to a cyclone preheater or precalciner kiln.
- Semi-dry process: Dry raw meal is pelletized with water and fed to a traveling grate preheater prior to the rotary kiln.
- Semi-wet process: Raw slurry is first dewatered in filter processes. The resulting filter cake is either extruded into pellets and fed to a traveling grate preheater or fed directly to a filter cake drier for (dry) raw meal production prior to a preheater/precalciner kiln.
- Wet process: The raw slurry is fed directly to a long rotary kiln equipped with an internal drying/preheating system [40].

Cement companies have tended to phase out older, less efficient wet and long dry kilns and replaced them with new kilns that use more efficient processes and technologies such as pre-heating, precalcining. New installations have come on stream in emerging markets, with high efficiency and high clinker–blending factors [41]. In 2012–13, precalciner kilns accounted for over 90% of total clinker production in the Australian cement industry. Vertical shaft kilns are still used in some parts of the world, predominately in China, to produce cement. A shaft kiln essentially consists of a large drum set vertically with a packed mixture of raw material and fuel traveling down through it under gravity [42].

The basic chemistry of the cement manufacturing process begins with calcination, the decomposition of calcium carbonate ($CaCO_3$) at about 900^0C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO_2). This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically $1400–1500^0$C) with silica, alumina and ferrous oxide to form the silicates, aluminates and ferrites of calcium which comprise the clinker. The clinker is subsequently ground together with gypsum and other additives to produce cement. A schematic diagram of cement manufacturing is given in Fig. 2.3 [27] which contains the processes from initial quarrying through to the shipment of the final product. Cement manufacturing in a preheater–precalciner kiln system basically includes the following steps.

1 **Quarry;** Natural raw materials such as limestone/chalk, marl, and clay/shale are extracted from quarries which, in most cases, are located close to the cement plant. After extraction, these raw materials are crushed at the quarry site and transported to the cement plant for intermediate storage, homogenization and further preparation [40].

2 **Raw material preparation:** After intermediate storage and pre-homogenization, the raw materials are dried and ground together in defined and well-controlled proportions in a raw mill to produce a raw meal for the dry process. Raw meal is stored and further homogenized in raw meal silos to achieve and maintain the required uniform chemical composition before entering the kiln system [40].

3 **Preheating and precalcining**: Preheating is adopted only in dry production process. Here the blended raw meal is passed through the pre-heater tower which consists of a series of vertical cyclone, through which the raw material is passed from the top to bottom. Hot air is driven from the bottom by a precalciner to pre heat the meal about $1000–1200^0$C [36]. To pump more heat into the pretreatment phase, additional fuel is burnt in precalciner with air from the clinker cooling stage.

4 **Kiln**: In next stage raw materials enter in the huge rotating furnace called a kiln. The rotary kiln is an inclined steel tube with a length to diameter ratio between 10 and 40. The slight inclination (2.5–4.5%) together with the slow counter-current rotation (0.5–4.5 revolutions per minute) allow for a material transport sufficiently long to achieve the thermal conversion processes required [40]. Gases and solids flow in opposite directions through the kiln, providing more efficient heat transfer. The raw meal is fed at the upper or cold end of the rotary kiln, and the slope and rotation cause the meal to move toward the lower or hot end.

The kiln is fired at the hot end, usually with coal or petroleum coke as the primary fuel. As the meal moves through the kiln and is heated, it undergoes drying and pyro-processing reactions which causes chemical and physical changes to form the clinker, consisting of lumps off used, incombustible material.

5 **Clinker cooling and final grinding**: The clinker leaves the hot end of the kiln at a temperature of about 1400^0C. It falls into a clinker cooler, typically a moving grate through which cooling air is blown. The clinker is ground with gypsum and other additives, usually in a ball mill, to produce the final product cement. The different cement types have to be stored separately in cement silos prior to bagging and dispatch.

6 **Storage and transportation**: The cement is conveyed from the finish cement mill to large, vertical storage silos in the pack house or shipping department. Usually, processed cement is transported in bulk through a heavy trucks, rails and barge. Only a small amount of cement is bagged and sent for retail sale using transport methods that are sometimes same as bulk transport [26].

2.9. Coal as energy

Source Coal has been present in the world before the beginning of human history. This rock is the remaining of organic life over the last 360 million years. It is a petrified matrix of carbon formed during the primary age of the Earth through the deposition and compaction of organic matter from prehistoric animals, forest and soils [41]. In this period of time, this material has been exposed to extreme physical processes including high pressures and elevated temperatures through compaction, resulting in significant changes in its chemical structure. Then, the material has been concentrated in deep layers underground to remain as the mineral that is today known as coal [42].

Figure 2.4: Coal formation process

2.9.1. Types of Coal

Coals are classified considering degree of metamorphism. Many chemical and physical properties change during this progression. The rank refers to the degree of carbonization undergone by the organic matter. It is determinate by evaluation of the rank parameters: moisture content, specific energy, volatile matter content [43]. Over many more millions of years, the increased temperature and pressure produced more changes in the lignite, progressively increasing its maturity and transforming it into sub-bituminous coals. As further chemical and physical changes occurred these coals became harder and more mature, to be classified as bituminous or hard coals. Under the right conditions, the progressive increase in the organic maturity continued ultimately to form anthracite [44].

Lignite: Is the lowest rank coal. It is soft, brownish-black coal and it easily burns with a long and smoky flame. It contains a high moisture and volatile matter. It is generally referred to as brown coal [43].

Sub-bituminous coal: dull, dark brown to black coal. It is soft and crumbly. It has relatively low density and high-water content. It is susceptible to spontaneous combustion [43].

Bituminous coal: dense, banded dull and glossy black coal with relatively hardness contains bitumen (tar-like substance). It contains a high percentage of volatile matter and it ignites easily with a smoky long yellow flame. It exhibits agglomerating and caking behavior, making this coal useful for making coke [44].

Anthracite: Very hard and dense coal with high Hydrogen content (between 92% and 98%) and contains the fewest impurities of all coals. Anthracite difficultly ignites an extremely hot, blue flame and very little smoke. Anthracite coal has a very low level of volatile components and a high percentage of fixed carbon [43].

2.9.2. World coal reserves

Coal is one of the most significant natural resources in the world. It has been estimated that there are over 984 billion tons of proven coal reserves worldwide. Coal is located worldwide it can be found on every continent in over 70 countries, with the biggest reserves in the USA, Russia, China and Australia. While it is estimated that there is enough coal to last almost 200 years, this could extend still further through the discovery of new reserves from ongoing and improved exploration activities and advances in mining techniques, which will allow previously inaccessible resources to be reached [44].

2.9.3. Coal occurrences and deposits of Ethiopia

The Nonrenewable energy source coal is the primary source for many technological activities of the present day. It provides the major fraction of feedstock to commercial organizations, industrial sectors, as well as household entities all around the world.

YayuBasin: Yayu is 564 km from Addis Ababa along Jimma- Bedle- Gambella road. The basin is found between 1300 and 1700 m above sea level. A total of 100 boreholes were drilled in the Yayu Basin. Ten humic coal seams are interbedded in the middle sedimentary succession, and laterally traceable throughout the basin. The coal seams attain a maximum thickness of 4 m. The middle sedimentary succession contains the main coal seams a total of 200,000,000 tons of coal deposits estimated in the Yayu Basin [9].

Delbi-Moye Basin: Delbi is 390 km west of Addis Ababa, and 48 km south of Jimma. The basin is found between 2060 and 2240 meters above sea level. A total of 25 boreholes were drilled in the Delbi-Moye Basin. The coal seams and coal-bearing sediments reach a maximum thickness

2.2 m and 278 m, respectively. The Calorific values and fixed carbon of the Moyehumic coals range from 29485190 kcal/kg and 28.1-42.2 %, respectively. The Moye coals are characterized by sub-bituminous to high volatile bituminous B coals with strong coking properties. The coal deposit of Moye area is the best type of coking coal deposit in Ethiopia [9].

Wuchale area: Wuchale is 62 km from Dessie along Addis Ababa-Mekele Road. The area is found between 2067 and 3560 m above sea level. The coal seams exposed on the southern flanks of Titito River. Two lignite seams are interbedded within 25 m thick coal-bearing sediments. The total reserve is estimated to be 3.3 million tones [45].

Mush valley: Mush Valley is situated 159 km northeast of Addis Ababa along Addis Ababa-Dessie Road. The area is found between 2600-2800 m above sea level. Two coal seams are interbedded at different levels in the coal-bearing sediments. The lower and upper coal seams attain a thickness of 1.75 m and 1.0 m, respectively. The total reserve is estimated to be 1 million tones [9].

ChilgaBasin: Chilga is located 52 km southwest of Gonder. The basin is found between 1900 and 2100 m above sea level. 12 boreholes were drilled in the central part of the basin. The coal-bearing sedimentary succession consists of coals, carbonaceous shales, clay stones, and silt stones, fine to medium-grained sandstones. The thickness of the coal seams in the Chilga Basin ranges from 0.2 to 1.25 m. The Chilga coal reserve is estimated to be 19, 700, 000 tones.

Generally, the humic coals in Yayu, Chilga, Mush Valley, Nejo and Wuchale Basins range in ash content (16.6 - 41.6%), fixed carbon (10.6 - 45.2%), volatile matter (18 - 40.6%) and calorific values (2824.5 - 4599.5 kcal/kg). These coals classified under low-medium ash content, medium volatile matter, moderate calorific values lignite to bituminous coal [9].

Table 2.2: Proximate analysis and calorific value of coal deposits in different basins [9]

Resource (%)	Moisture (%)	Volatile matter (%)	Ash content (%)	Calorific value (%)	Reserve in tone (%)
Delbi-Moye coal	4-8	25-29	11-25	2948-5190	$20*10^6$
Yayu coal	8-20	28-46	25-42	3795-5930	$200*10^6$
Chilga coal	5-10	21-31	16-41	3072-4560	$19*10^6$
Mush valley	21	31-40	19-27	2824-3568	$1*10^6$
Nejo	14-16	30-35	19-23	3400-3987	$3*10^6$
Wuchale	10-12	18-29	35-48	3700-5445	$3.3*10^6$

As the exploration advances further, the number of coal occurrences increase from time to time. The geological survey of coal is not reached its end and the reserves explored yet are not the last reserves. Some additional exploration still under way in the country has proven that there is coal and the coverage of the target area may be rationally expanding, so the mineable resources will be increased accordingly that makes the service life of the mine longer.

3. MATERIALS AND METHODOLOGY

3.1. Location/area of the study

The study area Enderta woreda and Mekelle city, Tigray ,Ethiopia. Mekelle town is located at a distance of 780 km from Addis Ababa towards North. Mekelle is located between 40°43′–41°15′E and 9°71′– 11°20′N. And Enderta woreda is also located in the Latitude: 13° 29' 59.99" N and Longitude: 39° 39' to 59.99" E.

3.2. Availability

Bone is one of the evolving alternative fuels in cement industry and their availability increases due to the restriction of their usage in other sector such as cattle feed. The availability of the material is assessed in Mekelle city and including of 20kms radius from Mekelle city which is Enderta woreda. At this mentioned area there is 560 tons of annual production.

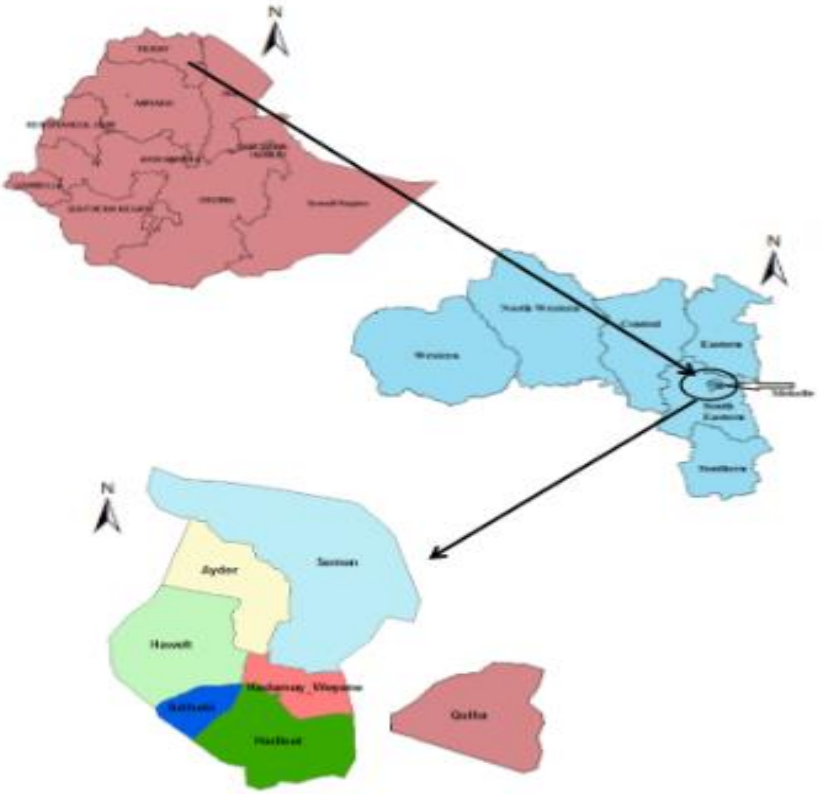

Figure 3.1: Map of study area

3.3. Materials

The main raw material, municipal waste, bone was collected from Enderta woreda and Mekelle city. The equipment used during the preparation for the experimentations were cutter, centrifugal mill, sieves, electronic balance, ceramic crucibles, oven, muffle furnace, desiccators, tubular furnace with a stainless steel, tubular reactor and bomb calorimeter.

The experiments were conducted in laboratories of two different institutions. The ultimate analysis of carbonized and uncarbonized bone sample was done at Addis Ababa University and proximate analysis of carbonized and uncarbonized bone were done at the laboratory of Messebo cement factory, and also calorific value of both samples were done at Messebo Cement Factory.

3.4. Methods

3.4.1. Sample preparation

First Raw bone was cleaned from meat, fat, soil and other contaminants collected along with it by washing and scrubbing. Next prior to grinding the collected samples were sun dried and cut manually into pieces of 10 cm length and 3-5 cm width to make suitable for subsequent crushing and carbonization process. Pieces of samples were then grinded and allowed to pass through 0.75mm of mesh or sieve.

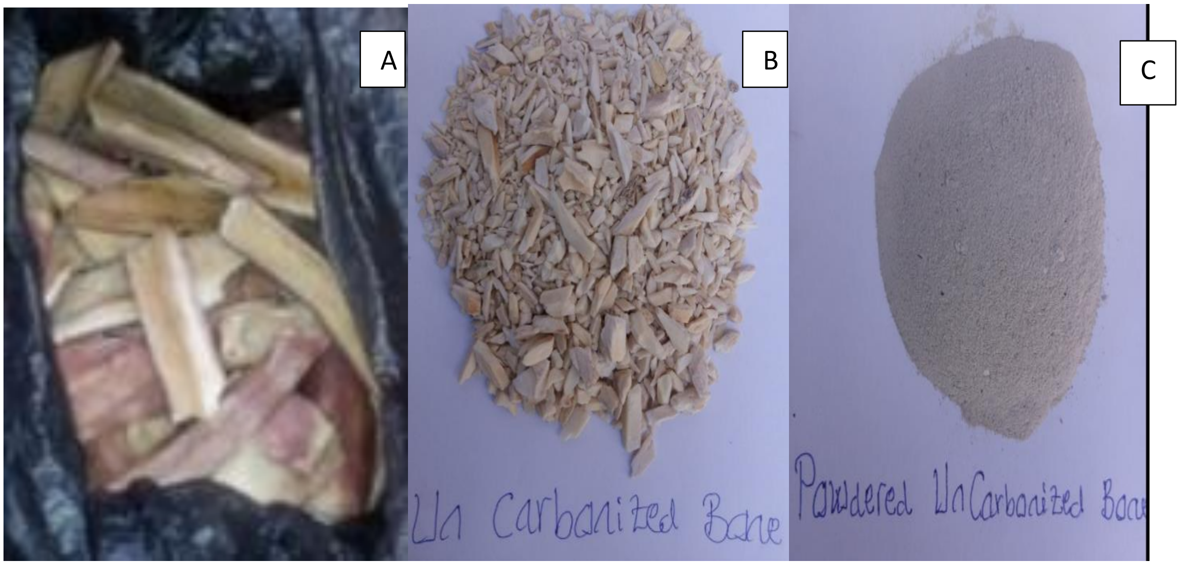

Figure 3.2: A. Collected bone from the field. B. crashed uncarbonized bone. C. Fine uncarbonized bone.

3.4.2. Carbonization of bone

The collected solid waste bone was prepared for carbonization based on the following way. The collected bone from the field was cleaned first to be free from any content of meat, fat and dusts. Then the bone was prepared by cutting in to pieces of 10 cm length and 3-5 cm width in dimension. It was placed in a container tubular reactor equipped with tubular furnace. Next, it was burned. Finally, it has cooled.

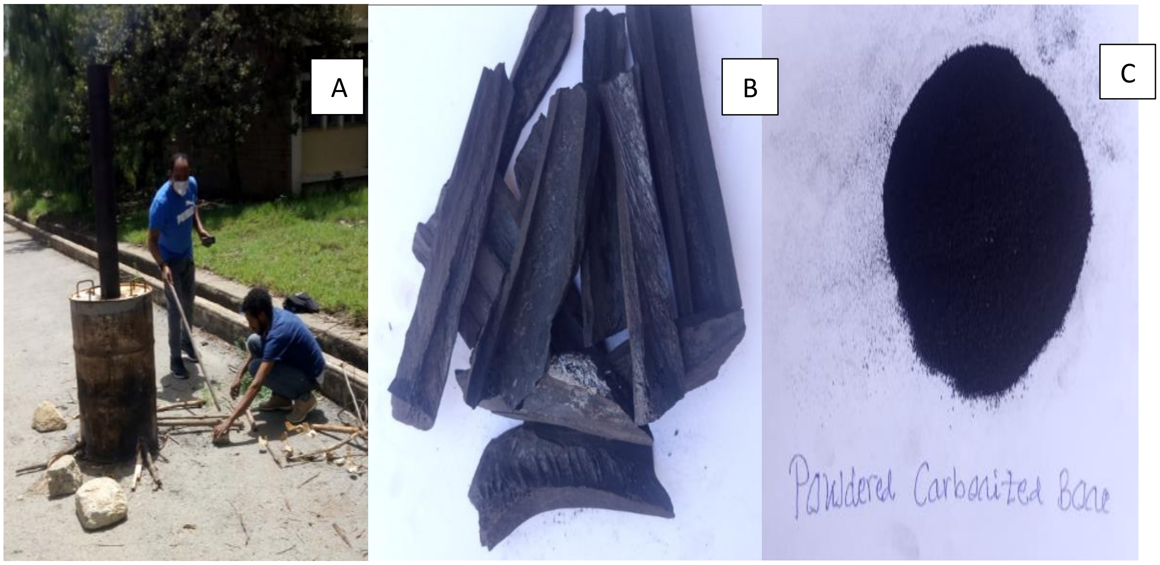

Figure 3.3: A. carbonizing of prepared sample. B. carbonized bone. C. fine carbonized bone

3.4.3. Sample characterization

Proximate analysis of bone was carried out for determination of volatile matter, fixed carbon, ash content, and calorific value in the biomass. The ASTM D 3175, ASTM D 3172, ASTM D 3174, ASTM D 3286 used for the study of mentioned parameters, respectively.

Moisture content: Moisture content of bone refers to the weight loss when a weighed amount of bone is heated in a muffle furnace at 105-110^{0}c. The moisture content of bone was measured by oven dry method. A gram of sun-dried powdered sample was taken in crucibles and kept in an oven at temperature of 105°C for 24hours. Then the crucibles were taken out of the oven and the samples were weighed. The loss in weight was expressed as moisture content in the sample. The moisture content of sample was calculated by following formula (ASTM, 1989).

Calculation:

The percentage of moisture content is given by:

$$\text{Percentage of moisture content} = \frac{loss\ in\ weight\ of\ \ bone}{weight\ of\ bone\ intially\ taken} \times 100$$

$$\%\text{moisture content} = \frac{W_{1-}W_2}{W_1} \times 100 \text{ --- } (1)$$

Where; W_1, weight of sample before drying and W_2 is Weight of sample after drying

Volatile content: refers to the weight loss when a weighed amount of moisture free powder is heated at 950^0c in a muffle furnace for a certain time. A gram of air-dried powdered sample was taken in crucible. The crucible was covered with silica lid. Then crucible was kept in a furnace for 7 min at the temperature of 925°C ± 5°C. The crucible was then taken out from the furnace and allowed to cool in air. The Percentage of volatile matter of the sample was determined by using the following formula (ASTM, 1989). The percentage of Volatile Matter is given by:

$$\text{Percentage of volatile matter} = \frac{loss\ in\ weight\ of\ moisture\ free\ bone}{weight\ of\ bone\ intially\ taken} \times 100$$

$$\%\text{volutile content} = \frac{W_{2-}W_3}{W_{2}\text{-}W_1} \times 100 \text{ -- } (2)$$

Where; W1; Weight of crucible, W2; Weight of crucible + Weight of sample and W3; Weight of crucible + residual content

Ash content: The Ash content of a bone is the weight obtained after a weighed amount of bone sample is burned in an open crucible in a muffle furnace. The ash content was determined by placing one grams of finely grounded, dried samples into a reignited and previously weighed ceramic crucible which was then placed in a muffle furnace and ignited for 2 hours at 750 ^{0}C. Then, the crucible was then taken out, cooled in desiccators and weighed. Percentage of ash was determined by using the following formula (ASTM, 1989).

The percentage of ash content is given by:

$$\text{Percentage of ash content} = \frac{weight\ of\ residue\ ash\ formed}{weight\ of\ bone\ intially\ used} \times 100$$

$$\%\text{ash} = \frac{W_3 - W_1}{W_2 - W_1} \text{ --- } (3)$$

Where; W1; Weight of crucible, W2; Weight of crucible + Weight of sample before ash and W3; Weight of crucible + ash

Fixed carbon: the fixed carbon content refers to the mass of a sample after its moisture content; volatile matter and ash content are subtracted. The residue remaining after volatile matter release has been expelled, contains the mineral matter originally present and non-volatile. The fixed carbon was thus calculated as follows (ASTM, 1989) based on equation 4.

$$\%\text{fixed carbon} = 100 - (\%\text{moisture} + \%\text{volatile matter} + \%\text{ash}) \tag{4}$$

II. Determination of calorific value

Calorific value is the quantity of heat liberated by the combustion of unit quantity of fuel. When a weighed quantity of bone was burnt in the calorimeter the heat liberated is used up in heating the calorimeter and the water in the calorimeter. Heating value of a biomass is measured experimentally in terms of the high heating value (HHV). The standard method uses a device called bomb calorimeter. The device burns a small mass of biomass in the presence of oxygen inside a sealed container (or bomb). The heat released from combustion is transferred to a mass of fluid (air or water) that surrounds the container. The heating value is calculated from the product of mass of fluid x specific heat of fluid x net temperature increase. The calculated heating value must be corrected for heat losses to the mass of container, heat conduction through the container wall, and heat losses to the surrounding of the device. In modern calorimeters the corrections are made automatically using sensors and controllers. The resulting measured heating value is considered gross heating value (high heating value) at constant volume because the biomass combustion in the container has taken place inside the fixed volume of the container. The procedure for the determination of calorific value by Bomb calorimeter used was as followed:

First a 0.5 g weighed of fuel in the silica crucible and place the crucible over the ring. Then a fine Nickel-chromo wire was stretched across the electrodes to the fuel sample and oxygen was Supplied to the bomb till a pressure of 20-25 atm is reached. The initial temperature of water was recorded in the calorimeter after thoroughly stirring and the fuel was burned in the crucible by switching ON the current. The maximum temperature recorded shown by the thermometer. Finally, the calorific value of the fuel calculated

Calculation

Calculation of the higher (gross) calorific value of the fuel

Heat gained by water = $y(t_2-t_1)$kcal

Heat gained by calorimeter =$z(t_2-t_1)$kcal

Total heat gained = $y(t_2-t_1) + z(t_2-t_1)$kcal

$$Heat\ liberated\ by\ fuel\ = Heat\ gained\ by\ water\ and\ calorimeter\ x\ C \qquad (5)$$

$$c = \frac{\frac{(y+z)*(t_2-t_1)}{x}}{m(kg)} \quad kcal \qquad (6)$$

Where x; weight of the fuel sample in the crucible kg, y; weight of the water in the calorimeter kg, z; water equivalent of the calorimeter bomb kg , t_1 ;initial temperature of water in (^{o}C) and t_2 , final - temperature of water in (^{o}C).

Ultimate analysis used to determine the elemental composition such as carbon(C), hydrogen(H), nitrogen(N), Sulphur(S), and oxygen(O) were EA 1112 Flash CHNS/O- analyzer.

Conditions: Carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900 °C and oven temperature of 75 °C.

Calibration: 6 calibration points for every component. Sample was run in duplicate and the average values are to be taken. The values of oxygen content were achieved by subtracting, as percentages, from 100% the total of C, H, N, S and ash contents.

Table 3.1 the relation between ultimate and proximate analysis

Relation between ultimate and proximate analysis.	
%C	0.97FC + 0.7(VM – 0.1A) – M(0.6 – 0.01M)
%H	0.036FC + 0.086(VM – 0.1A) – 0.0035M(1 – 0.02M)
%N	2.10 – 0.02VM
%O	100 - (%C + %H + %N +%S +%ASH)

4. RESULTS AND DISCUSSION

4.1. Characterization of bone

A proximate analysis results of uncarbonized bone and carbonized bone were shown in Table 4.1. The proximate analysis determines only the moisture content, volatile matter, ash content, and fixed carbon content.

Moisture content of uncarbonized bone was 2.00% and that of the carbonized bone was 1.35%. The values obtained were smaller in carbonized bone which can be confirmed with the fact that high moisture content lowers the calorific value of the bone.

Volatile matter content of uncarbonized bone was found to be 50.22% and that of carbonized bone was 55.65%. The results can be justified as that higher volatile content as shown in carbonized bone, is easy to ignite but may burn with a smoky flame while lower volatile content as found in uncarbonized bone, is difficult to light and burns very cleanly. The higher volatile carbonized bone is preferable for some purposes such as flame, while other utilizations as metal manufacture need charcoal with low percentage volatile matter content.

Ash content of uncarbonized bone and carbonized bone was found to be 40.06% and 40.45% respectively. The result showed that the raw uncarbonized ash was lower than the ash content of the bone in the form of carbonized. This higher amount of ash of carbonized may be considered as undesired residue. The presence of high mineral matter components in burned matter is not desirable, because they are not degraded during carbonization and they remain in charcoal as an undesirable residue which also contributes to the reduction of charcoal heating value.

Fixed carbon content was determined to be 7.72% for uncarbonized bone and 2.55% for carbonized bone. It was obtained which gives uneven estimation of the heating value of a fuel and acts as the main source of heat during burning.

The calorific values of uncarbonized bone were in the range of 4009.08 kcal/kg to 4018.10kcal/kg, which while the calorific value of carbonized bone sample was 3212.75kcal/kg. The carbonized bone is lower calorific value than the un carbonized bone, the reason may that, bone fat, this fat is available probably in un carbonized bone, then is a cause for increasing the carbon content. In addition to this bone may contain lighter hydrocarbon combustible gases emit easily.

Table 4.1: Proximate analysis

Property	Un carbonized bone	Carbonized bone
Moisture content (%)	2.00	1.35
Ash content (%)	40.06	40.45
Volatile matter (%)	50.22	55.65
Fixed carbon (%)	7.72	2.55
Calorific value(kcal/kg)	4018.10	3212.75

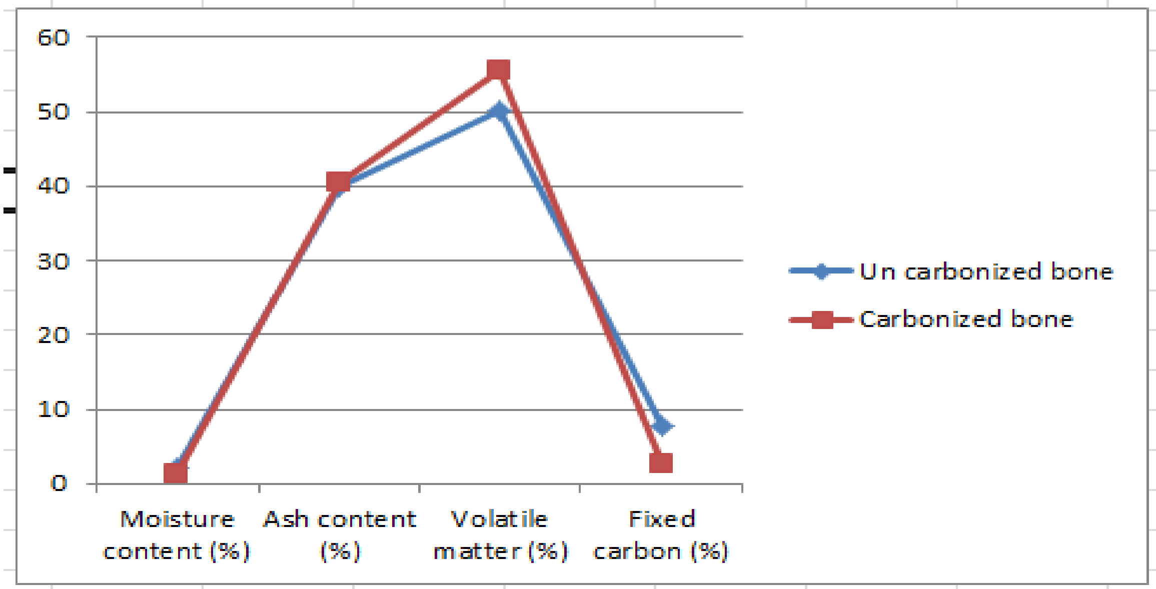

Figure 4.1: Proximate analysis of carbonized and uncarbonized bone.

4.2. Comparison of the result of proximate analysis for uncarbonized bone and coal

Moisture content: As it can be seen from table 4.2, moisture content of uncarbonized bone was 2.00% and that of the coal was 0.90%. The values obtained were very small in coal which can be confirmed with the fact that high moisture content lowers the calorific value of the bone.

Volatile matter content: As it can be seen from table 4.2, Volatile matter content of uncarbonized bone was found to be 50.22% and that of coal was 24.92%. This indicates that high volatile content as shown in uncarbonized bone, is easy to ignite but may burn with a smoky flame while low volatile content as found in coal, is difficult to light and burns very cleanly.

Ash content: By way of it can be understood from table 4.2, the ash content of uncarbonized bone was found to be 40.06% while coal was 13.73%. The result showed that the raw uncarbonized ash was higher than the ash content of the coal. This higher amount of ash in the uncarbonized bone may be considered as undesired residue. The bone may presence of high mineral matter components in burned matter is not necessary.

Fixed carbon content: fixed carbon content was obtained which gives uneven estimation of the heating value of a fuel and acts as the main source of heat during burning. From table 4.2 fixed carbons content uncarbonized bone was determined to be 7.72% for coal was 60.40%.Fixed carbon content was obtained which gives rough estimation of the heating value of a fuel and acts as the main source of heat during burning. Due to this coal is much higher calorific value.

Calorific value: The calorific values of uncarbonized bone were in the range of 4018.10kcal/kg, which while the calorific value of coal was 6404kcal/kg. The coal has higher calorific value than the bone.

Table 4.2: Proximate analysis comparison of uncarbonized bone and coal

Property	Un carbonized bone	Coal
Moisture content (%)	2.00	0.90
Ash content (%)	40.06	13.73
Volatile matter (%)	50.22	24.97
Fixed carbon (%)	7.72	60.40
Calorific value(kcal/kg)	4018.10	6404

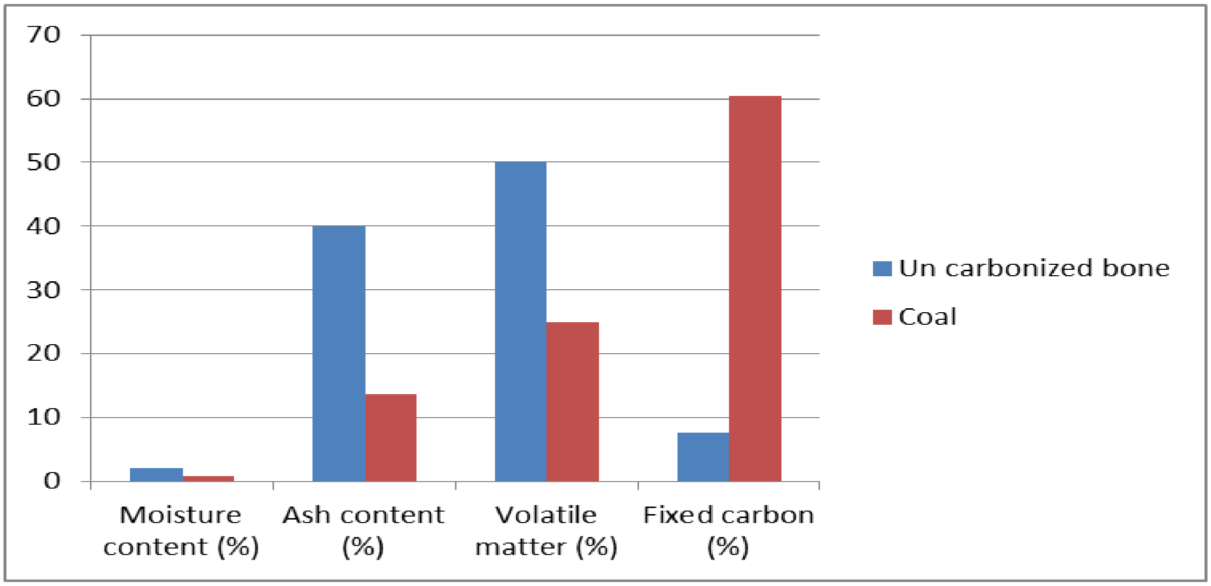

Figure 3.5: Proximate analysis comparison of uncarbonized bone and coal

4.3. Statistical data analysis

4.3.1. Analysis of variance (ANOVA)

All data were statistically analyzed by evaluating the mean, percent standard deviation and variance (at 95% confidence level). For the statistical analysis tools like, micro soft excel 2010, and IBM SPSS statistics version 20, were used. In this study, one way analysis of variance (one way ANOVA) and multivariate comparisons were done. All the samples have significant difference at ($p \leq 0.05$) level except MC in uncarbonized and cool as well as Ash in carbonized and uncarbonized samples.

Table 4.3: Multiple comparison of data using one way ANOVA

Multiple Comparisons							
Dependent Variable			**Mean Difference (I-J)**	**Std. Error**	**Sig.**	**95% Confidence Interval**	
						Lower Bound	**Upper Bound**
MC	Carbonized	Uncarbonized	-0.88*	0.12	0.00	-1.25	-0.52
		Coal	-0.89*	0.12	.001	-1.25	-0.53
	Uncarbonized	Carbonized	0.88*	0.12	.001	0.52	1.25
		Coal	-0.01	0.12	.998	-0.37	0.35
	Coal	Carbonized	0.89*	0.12	.001	0.53	1.25
		Uncarbonized	0.01	0.12	.998	-0.36	0.37
VM	Carbonized	Uncarbonized	5.44*	0.14	.000	5.00	5.8843
		Coal	20.87*	0.14	.000	20.43	21.3143
	Uncarbonized	Carbonized	-5.44*	0.14	.000	-5.88	-5.00
		Coal	15.43*	0.14	.000	14.99	15.8709
	Coal	Carbonized	-20.87*	0.14	.000	-21.31	-20.43
		Uncarbonized	-15.43*	0.14	.000	-15.87	-14.99
Ash	Carbonized	Uncarbonized	0.42	0.18	.135	-0.14	0.98
		Coal	30.20*	0.18	.000	29.64	30.76
	Uncarbonized	Carbonized	-0.42	0.18	.135	-0.98	0.14
		Coal	29.79*	0.18	.000	29.23	30.35
	Coal	Carbonized	-30.20*	0.18	.000	-30.76	-29.64
		Uncarbonized	-29.79*	0.18	.000	-30.35	-29.23
FC	Carbonized	Uncarbonized	-4.98*	0.10	.000	-5.27	-4.68
		Coal	-50.19*	0.10	.000	-50.48	-49.89
	Uncarbonized	Carbonized	4.98*	0.10	.000	4.68	5.27
		Coal	-45.21*	0.10	.000	-45.50	-44.92
	Coal	Carbonized	50.19*	0.10	.000	49.89	50.48
		Uncarbonized	45.21*	0.10	.000	44.92	45.50
CV	Carbonized	Uncarbonized	-803.71*	2.67	.000	-811.90	-795.51
		Coal	-3649.63*	2.67	.000	-3657.82	-3641.43
	Uncarbonized	carbonized	803.71*	2.67	.000	795.51	811.90
		Coal	-2845.92*	2.67	.000	-2854.11	-2837.72
	Coal	carbonized	3649.62*	2.67	.000	3641.43	3657.82
		Uncarbonized	2845.92*	2.67	0.00	2837.72	2854.12

***. The mean difference is significant at the 0.05 level.**

4.4. Ultimate analysis of uncarbonized bone and carbonized bone

An ultimate analysis of uncarbonized bone and carbonized bone were shown in Table 4.4. The ultimate analysis represents the elemental composition of the organic material in the uncarbonized bone and carbonized bone in terms of carbon, hydrogen, nitrogen, sulfur, and oxygen. The current practice in most coal and fuel laboratories is to determine carbon, hydrogen, nitrogen, and sulfur using instrumental methods.

Hydrogen content: As it can be seen from table 4.4, the hydrogen content of uncarbonized bone was 5.249% and the carbonized was 4.470%. The values obtained were smaller in the carbonized than the uncarbonized bone which can be confirmed with the fact that higher hydrogen content lowers the calorific value of the bone.

Carbon content: From table 4.4 Carbon content of uncarbonized bone was found to be 38.127% and that of carbonized bone was 32.465%. The results can be justified as that high carbon content as shown in uncarbonized bone, is easy to ignite burns very cleanly and gives high calorific value. While low carbon content as found in carbonized bone, is difficult to light and may burn with a smoky flame. In addition to this the highest elemental percentage distribution recorded is carbon with 38.127% found in un carbonized bone higher potential as an energy feedstock, but the low carbon content in carbonized bone indicates its low potential as an energy feedstock.

Oxygen content: As it can be seen from table 4.4, the oxygen content of uncarbonized bone and carbonized bone was found to be 55.446% and 61.898% respectively. The result showed that the raw uncarbonized bone oxygen content was lower than the oxygen content of the bone in the form carbonized bone. This higher amount of oxygen may be considered as undesired residue which also contributes to the reduction of bone heating value.

Nitrogen content: from table 4.4, the nitrogen content of uncarbonized bone and carbonized bone was found to be 1.10% and 0.987% respectively. The result showed that the raw uncarbonized bone was higher nitrogen content than the nitrogen content of the bone in the form of carbonized bone. This higher amount of nitrogen may be considered as unwanted residue. In line to this it contributes more in the production of NO_x gas.

Sulfur content: As it can be seen from table 4.4, the sulfur content of uncarbonized bone and carbonized was found to be 0.078% and 0.18% respectively. Higher amount of sulfur on the carbonized may be considered as unnecessary remainder and also contributes more in the production of environmentally polluted gases.

Table 4.4: Ultimate analysis uncarbonized and carbonized bone

Sample	Un carbonized	Carbonized	Remark
Hydrogen(%H)	5.249	4.470	Laboratory
Carbon(%C)	38.127	32.465	Laboratory
Nitrogen(%N)	1.100	0.987	By relation
Oxygen (%O)	55.446	61.898	By relation
Sulfur(%S)	0.078	0.180	Laboratory

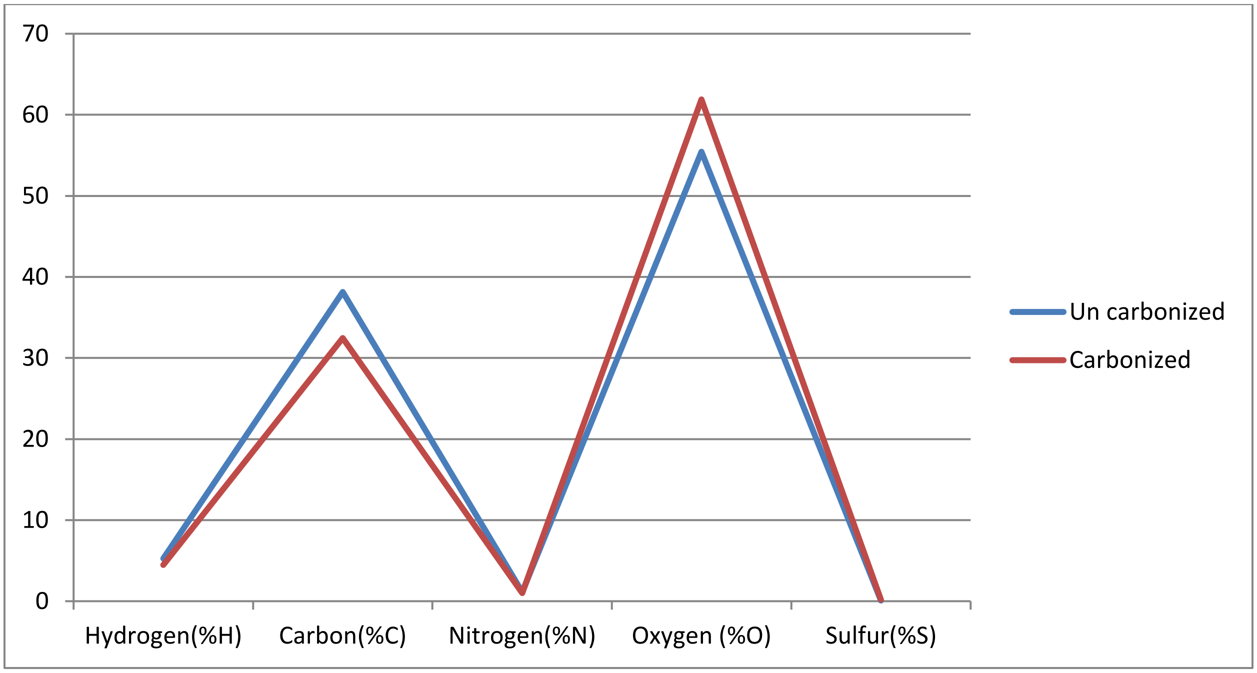

Figure 3.6: Comparison of elemental analysis for carbonized and uncarbonized bones

4.5. Comparison of the result of ultimate analysis for uncarbonized bone and coal

Hydrogen content: As it can be seen from table 4.5 the hydrogen content of uncarbonized bone was 5.249% and the coal was 8.96%. The values obtained were very small in the uncarbonized that can be confirmed with the fact that high hydrogen content lowers the calorific value of the bone, but at this point is the inverse, this is due to the higher content of carbon in coal.

Carbon content: from table 4.5, Carbon content of uncarbonized bone was found to be 38.127% and that of coal was 58.84%. The results can be justified as that high carbon content as shown in coal, is easy to ignite burns very cleanly and gives high calorific value.

Oxygen content: The oxygen content of uncarbonized bone and coal referred from table 4.5 was found to be 55.446% and 22.03 % respectively. The result showed that the raw uncarbonized bone oxygen content was higher than the oxygen content of the coal. The high content of oxygen in the uncarbonized bone is a cause for lowering the calorific value.

Nitrogen content: As it can be seen from table 4.4 the nitrogen content of uncarbonized bone and coal was found to be 1.10% and 9.67% respectively. Higher amount of nitrogen on the coal, it contributes more in the production of NO_x gas which is environmentally polluted gas.

Sulfur content: from table 4.5, the sulfur content of uncarbonized bone and coal was found to be 0.078% and 0.25% respectively. Higher amount of sulfur on the coal may be considered as unwanted residue. In addition to this it also contributes more in the production of GHG emission.

Table 4.5: Comparison of the result of ultimate analysis for uncarbonized bone and coal

Sample	Un carbonized	Coals	Remark
Hydrogen(%H)	5.249	8.960	Laboratory
Carbon(%C)	38.127	58.840	Laboratory
Nitrogen(%N)	1.100	9.670	By relation
Oxygen (%O)	55.446	22.030	By relation
Sulfur(%S)	0.078	0.250	Laboratory

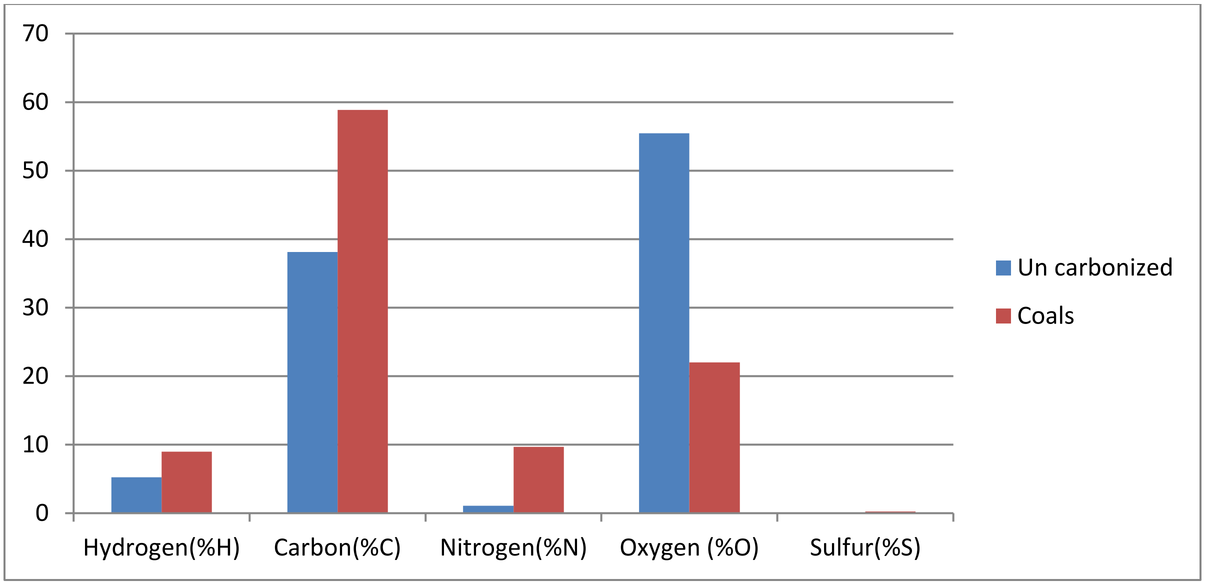

Figure 3.7: Comparison of the result of ultimate analysis for uncarbonized bone and coal

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study analyzed the physicochemical properties of carbonized and uncarbonized waste bone and evaluated their potential as alternative energy sources for the cement industry. The following key conclusions were drawn:

- **Calorific Value and Efficiency:**
  Although uncarbonized bone has a higher moisture content than carbonized bone, it exhibits a higher calorific value. This is attributed to the higher fixed carbon content in uncarbonized bone, which makes it a more efficient energy source. Therefore, using uncarbonized bone as an alternative energy source is more effective in terms of energy production.
- **Hydrogen Content:**
  The hydrogen content in both carbonized and uncarbonized bones is nearly identical. However, the higher energy content in uncarbonized bone makes it a more viable option for energy generation. As a result, uncarbonized bone is recommended for use as a partial energy source in the cement industry.
- **Environmental Impact and Greenhouse Gas Emissions:**
  The use of coal as an energy source in the cement industry significantly contributes to greenhouse gas emissions, particularly nitrogen and sulfur compounds. Mixing small amounts of uncarbonized bone with coal can reduce these emissions, making it a more environmentally friendly alternative. The findings suggest that uncarbonized bone helps decrease greenhouse gas emissions compared to carbonized bone, highlighting its potential as a sustainable energy source.
- **Calorific Value and Fixed Carbon Content:**
  The study reveals that uncarbonized bone can produce a higher calorific value than carbonized bone. Additionally, the fixed carbon content is also greater in uncarbonized bone. While carbonized materials typically have higher heating values, the inverse was observed in this study, likely due to the fat content in uncarbonized bone and its higher volatility. The volatility of carbonized bone causes lighter hydrocarbon gases (C1-C2) to combust easily, which may reduce its overall calorific efficiency compared to uncarbonized bone.

In conclusion, uncarbonized bone presents a promising alternative energy source for the cement industry, offering both higher energy content and lower environmental impact in terms of greenhouse gas emissions. The findings support the potential of using uncarbonized bone as a partial substitute for traditional fossil fuels, contributing to more sustainable and cost-effective energy solutions in industrial applications.

5.2 Recommendation

- **Investigation of Process Parameters:**

  Future studies should focus on exploring the effects of key process parameters such as temperature, pressure, and particle size on the performance of carbonized and uncarbonized bones as alternative energy sources. Understanding these factors will help optimize their energy output and improve their overall efficiency in industrial applications.

- **Promotion of Bone-Derived Energy:**

  Replacing fossil fuel-based energy sources with bone-derived energy carriers could lead to numerous benefits, including economic, environmental, and health improvements. It is essential to raise awareness about the potential of bone as a renewable energy source. Further research and public education on the advantages of utilizing bone for energy production could encourage widespread adoption and stimulate the development of sustainable energy practices.

- **Encouraging Bone Utilization in the Cement Industry:**

  To mitigate the negative environmental and health impacts associated with fossil fuels, the cement industry should consider integrating bone-derived energy as a viable alternative. This could be achieved by collecting bones from various regions, which would not only help reduce waste but also create new job opportunities in the process. Establishing a supply chain for bone collection and distribution to cement factories could contribute to both environmental sustainability and local economic growth.

- **Further Studies on Social and Environmental Impact:**

  Given that bones are widely available in many regions, further research is recommended to assess the broader social and environmental impacts of using bone as an alternative energy source. Studies should also explore the feasibility and rates of fossil fuel replacement with bone-derived energy to ensure a balanced and sustainable transition.

By addressing these areas, the cement industry can take significant steps toward reducing its reliance on fossil fuels, while also contributing to environmental preservation, economic development, and public health.

6. REFERRENCES

[1] Lauri, P. (2014) *Woody Biomass Energy Potential in 2050. Energy policy*; 2014. 66, 19-31

[2] European Cement Association. *(1997) Alternative fuels in cement manufacturing*: *Technical and environmental Review*. Brussels. p.5.

[3] Moses P. M. (2010) *Alternative Fuels in Cement Manufacturing*. November 18th 2010 Reviewed: May 24th 2011Published: August 9/ 2011.

[4] Khardiwar, A. D. (2014) Performance *of Open Core Gasifier with Briquette of different Crop Residues* International Journal of Engineering Sciences & Research Technology, 833840.

[5] Chinyama, M. P. M. (2011) *Alternative Fuels in Cement Manufacturing, Alternative fuel*; 2011.

[6] Mokrzycki, E.& Uliaszbochen, A. (2003) Use *of Alternative Fuels in the Polish Cement Industry. Applied Energy*; 2003.74, 101-111.

[7] European Commission. (N.d.) Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 Establishing a Scheme for Greenhouse Gas Emission Allowance Trading Within the Community and Amending Council Directive 96/61/EC 2003.

[8] Ahmed, W. (2008) *Fossil Fuel Energy Resources of Ethiopia*. International Journal of Coal Geology, Chemical Society of Ethiopia, 22(1), pp.67-84.

[9] Murray, A & Price, L. (2008) *Use of Alternative Fuels in Cement Manufacture*. Chinese Cement Sector, U.S. Environmental protection Agency.

[10] John, T. and Tony, W.T. et al. (N.d.) Renewable *Energy Sources*. Second edition, &Francise group, London and New York.

[11] Boyle, G. (2004,) *Renewable Energy.* Oxford University Press. Excellent introduction for both scientific and non-scientific readers.2nd ed.

[12] World Energy Council (2016) *World Energy Resource*.

[13] Sørensen, B. (2004,) *Renewable Energy*. Academic Press, London. Outstandingly the Best Theoretical Text at Postgraduate Level, Considering Energy from the Environment to Final Use.3rded.

[14] Schneider,M. et.al.(2011)*Sustainable Cement Production: Present and Future*. CemConcr Res 2011; 41(7):642–50.

[15] Burhenne, L. et al. (2013) *Effect of Feedstock Water Content and Pyrolysis Temperature on the Structure and Reactivity of Spruce Wood Char Produced in fixed Bed Pyrolysis.* Fuel 2013.

[16] Yang, YB. Et.al. (2003) *Effects of Fuel Devolatilisation on the Combustion of Wood Chips and Incineration of Simulated Municipal Solid Wastes in a Packed Bed*. Fuel 2003; 82:2205–21.

[17] DiBlasi, C. et al. (2001) *Pyrolytic behavior and products of some wood varieties*. Combust Flame 2001; 124: pp.165–77.

[18] Demirbas, A. (2004) *Combustion Characteristics of Different Biomass Fuels*. Progr Energy Combust Sci 2004; 30:219-30.

[19] Magdziarz, A. et al. (2017) *Combustion Process of Torrefied Wood Biomass aKinetic Study*. J Therm Anal Calorim2017; 127:1339-49.

[20] Jia,L& Anthony, EJ.(2011) *Combustion of Poultry-Derived Fuel in a Coal-fired Pilot-Scale Circulating fluidized Bed Combustor*. Fuel Process Technol2011; 92:2138–44.

[21] Wilk, M. et. al. (2017)*Combustion and Kinetic Parameters Estimation of Torrefied Pine, Acacia and MiscanthusGiganteus Using Experimental and Modelling Techniques*. BioresourTechnol2017; 243:304-14.

[22] Madlool, NA. et al. (2011) *A Critical Review on Energy Use and Savings: In the Cement Industries.* Renew Sustain Energy Rev2011; 15(4):2042-60.

[23] Trezza, M.A. &Scian A.N. (2000) *Burning Wastes as an Industrial Resource: Their Effect on Portland cement Clinker*. CemConcr Res 2000; 30(1):137–44

[24] Kaltschmitt, M. (2013) *Renewable Energy from Biomass: Introduction,* in: Kaltschmitt, M. et al. (Eds.): Renewable Energy Systems. Springer, New York.

[25] Gulyurtlu, I. et.al. (2005) *Co-Combustion of Coal and Meat and Bone Meal*. Fuel 2005; 84: pp.2137-48.

[26] Deydier, E. et al. (2005) Physical *and chemical characteristics of crude meat and bone meal combustion residue*: ''*waste or raw material*?''. JHazard Mater; 121(1-3):pp.141-8.

[27] Kowalski, Z. &Krupa,Z. K.(2007) *A Model of the Meat Waste Management*. Pol J Chem Technol 2007; 9(4): pp.91-7.

[28] Senneca. O. (2008) *Characterizationof Meat and Bone Mill for Coal Co-Firing.* Fuel2008; 87(15 16):3262-70.

[29] Karol, D.&Poskrobko, S. (2016) *High-Methane Gasification of Fuels fromWaste: Experimental Identification*. Energy 2016; 116:592-600.

[30] Ariyaratne,W.K.H. (2009) *Alternative Fuels in Cement Kilns: Characterization and Experiments*. A MSc. Thesis. Telemark University College, Norway.

[31] Denafas, G. et al. (2004) *Meat and Bone Meal Incineration in Terms of Industrial and Energetic Infrastructure in Lithuania*: *Energetic and Environmental Aspects.* Environ Res, Eng Manage;30(4): pp.36-48.

[32] Abad, E. et.al. (2004) *Polychlorinated Dibenzo-P-Dioxin/ Polychlorinated Dibenzofuran Releases into The Atmosphere from The Use of Secondary Fuels In Cement Kilns During Clinker Formation.* Environ SciTechnol2004; 38(18):4734-8.

[33] Frassoldati, A. et al. (200*0) Detailed Kinetic Modeling of Thermal Degradation of Biomasses.* In Proceeding of the 29th Meeting on Combustion. Napoli, Italia.

[34] Gronli, M., et al. (2002) *Thermo gravimetric Analysis and Devolatilisation Kinetics of Wood.* Ind. Eng. Chem, pp.4201-4208.

[35] Aarsen, F. C. et al. (1985) *Wood Pyrolysis and Carbon Dioxide Char Gasification Kinetics In :A Fluidized Bed, Fundamentals Of Thermochemical Biomass Conversion*, 691-715.

[36] Cascaras, E. e al. (2011) *Co-Gasification of Meat and Bone Meal with Coal in a fluidised Bed Reactor*. Fuel 2011.

[37] Cembureau the European Cement Association. (1999) *Best available techniques for the cement industry*. pp. 15-43.

[38] European Commission. (2001) *Reference Document on the Best Available Techniques in the Cement and Lime Manufacturing Industries.* BAT Reference Document (BREF). European IPPC Bureau, Seville, Spain.

[39] Font-Palma C. (2005) *Characterization, Kinetics and Modeling of Gasification of Poultry Manure and Litter: An Overview.* Energy Converse Manag2005; 25: pp.511-8.

[40] Fryda, L.et al. (2006) *Experimental Investigation of fluidised Bed Co-Combustion of Meat and Bone Meal with Coals and Olive Bagasse*. Fuel 2006; 85:1685–99.

[41] Grammelis, P. et al. (2009) Pyrolysis *Kinetics and Combustion Characteristics of Waste Recovered Fuels*. Fuel 2009; 88: pp.195-205.

[42] Suarez Ruiz, I. (2007) *Applied Coal Petrology: The Role of Petrology in Coal Utilization*. Oxford.

[43] Garcia Cortes C. E. T. (2009) *Technologies for Coal Based Hydrogen and Electricity Coproduction Power Plants with* Co_2 *Capture. European Commission Joint Research Centre. Institute for Energy.*

[44] Morris, L. (1997) *Coal Power for Progress the New Zealand Coal Industry.* New Zealand: world coal institute.

[45] Getaneh, A. &Saxena, G.N. (1984) *Energy Exploration and Exploitation*.

[46] Ariyaratne,W et al.(2010) *Meat and Bone Meal as a Renewable Energy Source in Cement Kilns*: *Investigation of Optimum Feeding Rate* In: International conference on renewable energies and power quality (ICREPQ'11), Spain.

7. Appendix


Waste Bone


Clean crashed bone


Un carbonized bone


Carbonizing of bone

Calorimeter

Milling Machine