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Preparation of Prosopis juliflora Charcoal and the study of its use as energy mix in cement industries

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ACRONYMS

AF	Alternative fuel
ANRS	Afar National Regional State
DSC	Differential scanning calorimetry
EDTA	Ethylenediaminetetraacetic acid
FC	Fixed carbon
HFO	Heavy Fuel Oil
MC	Moisture content
Mt	Million Metric Tons
SNNP	Southern Nations Nationalities and Peoples
TEA	Triethanolamine
TGA	Thermogravimetric analysis
VM	Volatile matter

ABSTRACT

Cement manufacturing is a high energy consuming and heavy polluting process. To reduce the energy and environmental costs cement producers are currently using a blend of alternative fuels with conventional fossil fuels. The research was conducted to investigate the potential of Prosopis juliflora charcoal as energy mix in cement industries. Proximate analysis and calorific value of Prosopis juliflora wood and laboratory scale carbonized Prosopis juliflora were done by standard procedure and compared with traditionally produced Prosopis juliflora charcoal. The results showed that ash chemistry for Prosopis juliflora wood and laboratory scale carbonized Prosopis juliflora were performed in order to determine the amount of different oxides present such as SiO_2, Fe_2O_3, Al_2O_3, CaO & MgO and sulfur were 4.14%, 1.21%, 0.79%, 43.64%, 6.27%, 0.18% and 4.43%, 2.41%, 0.93%, 43.39%, 7.31% & 0.11% respectively. The pyrolysis process of Prosopis juliflora was investigated using a thermogravimetric analyzer. Thermo-chemical decomposition behavior of Prosopis juliflora was carried out over a temperature range of 25 -700°C at the heating rate of 20°C /min under nitrogen.

Two response variables; charcoal yield and calorific values were analyzed by varying carbonization temperature (350, 450, 550 and 600°C) and holding time (60, 120, 180, 240 minutes). The maximum charcoal yield was found to be 75.83% at 350°C and 60 minutes of holding time while the minimum charcoal yield was 31.13% at 600°C for 240 minutes of carbonization time. On the other hand, the maximum calorific value 6620 kcal/kg was obtained at 600°C and 240 minutes of holding time and the minimum calorific value was 4196 kcal/kg at 350°C and 60 minutes. All experimental data were analyzed and modeled using Design-Expert version 6.0.8 software and significance was accepted at 0.05 level of probability ($p<0.05$).

1. INTRODUCTION

1.1. Background

Cement has played a key role as a construction material throughout the history of civilization. Cement production is an energy-intensive process consuming thermal energy of the order of 3.3 GJ/tonne of clinker produced. Electrical energy consumption is about 90 – 120 kwh/tonne of cement (Cembureau, 1997). Coal is the predominant fuel burned in cement kilns (Chinyama, 2011). 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 alleviate the problems caused by CO_2 emission by burning of coal, alternative fuel sources should be utilized. Now a days alternative fuels are used in many cement plants throughout the world (Mokrzycki & Uliaszbochen, 2003).

Coal is classified into three major types namely anthracite, bituminous, and lignite. However, there is no clear demarcation between them and coal is also further classified as semi- anthracite and semi-bituminous. Anthracite is the oldest coal from geological perspective. It is a hard coal composed mainly of carbon with little volatile content and practically no moisture. Lignite is the youngest coal from geological perspective. It is a soft coal composed mainly of volatile matter and moisture content with low fixed carbon (Garcia, 2009).

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 form in nature, its energy content and the low emissions to the atmosphere, it could play a major role in meeting world energy demand (Khardiwar, 2014).

Cement factories can potentially use alternative fuels, including biomass and biomass residues, to heat their kilns (Chinyama, 2011). 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 (Ashley & Lynn, 2008).

Messebo Cement Factory is working to partially replace its fuel consumption with biomass (sesame husk), which has been considered as waste and burnt at farmlands in Woreda Kafta Humera. Therefore, the use of biomass as an energy source is believed to contribute to reduce CO_2 emission, increase energy security, and support sustainable development.

Among the wide range of biomass species Prosopis juliflora is a tropical and subtropical tree and shrub, mainly found in the arid and semi-arid regions of the world and it is one of the alien invasive species that cause detrimental effect in the world (Pasiecznik et al., 2001).

In Ethiopia, the socio-economic and ecological impacts of Prosopis juliflora are becoming serious. Nevertheless, since its introduction to Ethiopia there is no strong controlling or eradication measures taken by the government, and non-governmental organizations. Prosopis species produce high quality charcoal depending on the type of species. The wood does not spit, spark, or emit much smoke and thus, it is called wooden anthracite. Moreover, the durability, strength, less shrinkage, less cracking and hardness make the wood of Prosopis juliflora more useful for many purposes (Victor, 2007).

Generally, in view of energy & environmental problems associated with the use of fossil fuels, attempts must be made to develop an alternative source of energy for cement industries. This will be a positive step towards mitigating the environmental problems associated with the use of fossil fuels.

1.2. Statement of the Problem

The large conventional fossil fuels demand of all Ethiopian cement industries; local industry's total dependence on foreign fossil fuel such as coal and heavy petroleum oil; the depletion and non-renewability of these fossil fuels; time to time rise in fossil fuel cost and the significant contribution to global warming with high emission of CO_2 and other pollutant to the environment compel the local cement industries to look for alternative renewable energy sources.

Prosopis juliflora has been introduced in many parts of the world (Africa, Asia and Australia) during the last 100-150 years. The species is now established in Africa; including Ethiopia, Kenya, Eritrea and Sudan (Pasiecznik et al., 2001). When, from where and how Prosopis was introduced in Ethiopia is not well documented and there are different narrations on its arrival and spread. Some believe that the Ministry of Agriculture introduced the species during the 1970's indiscriminately to both degraded and high quality pastures, including those in the Afar National Regional State (ANRS), to serve as a shade tree and wind breaker for plantations, and for land reclamation (Dubale, 2008). Others, however, contend that the introduction of the species to the ANRS, the most invaded part of the country is done by foreigners working in the area in the late 1970's and 1980's. The spread of the species was also facilitated later by the Food for Work Program between 1986 and 1988 (Sertse, 2005).

The effect of Prosopis juliflora to the biodiversity depends on the ecosystem to which it spread, and the economic damage and benefit depends on the socio-economic environment of the invaded land and its potential alternative use. In terms of coverage, the areas most adversely affected are the Afar and Somali Regions in the east and southeast of the country and the areas around Dire Dawa City. There are also moderately affected areas in Amhara, Oromia, Southern Nations Nationalities and Peoples (SNNP) and Tigray Regions that is in the mainly dry lands of Central, East and North Ethiopia (Steele et al., 2009).

Prosopis juliflora takes over pasture lands and irrigable areas; people and livestock suffer from mechanical injuries by sharp and poisonous Prosopis juliflora thorns; indigenous trees and pasture species are lost due to the invasion; access roads are blocked; challenge from predators increases; unrestricted livestock feeding on pods poses health problems; agro pastoralists spend large amounts of money to clear Prosopis juliflora from their farmlands; and malaria cases increased due to the favorable microclimate created due to the invasion (Greesing and Khawlani, 2004).

Prosopis juliflora germinates easily and once it has settled in an area it is difficult to get rid of it. It takes over the natural vegetation, does not allow undergrowth and hence greatly reduces the grazing value of land. It also tends to creep into waterways including dry riverbeds choking them in the process and causing flood rivers to run wild (Steele et al., 2009).

Therefore, the abovementioned critical limitations of conventional fossil fuels (coal and heavy petroleum oil) for cement industries and the above mentioned potential to utilize this plant as alternative energy source for cement industry, for the reason that utilizing such alternative fuels for meeting energy requirement is a sustainable initiative which can not only help to save fossil fuel and mitigate greenhouse gas (GHG) emissions, but also eradicating invasive weed biomass therefore, presents a win-win situation for a country like Ethiopia which has a strategic plan of climate resilient green economy.

1.3. Objectives of the study

1.3.1. General objective

The objective of this study is preparation of Prosopis juliflora charcoal and the study of its use as energy mix in cement industries.

1.3.2. Specific objectives

The specific objectives of this study are:

- Characterization of Prosopis juliflora wood using proximate and ultimate analysis
- Determination of calorific value of Prosopis juliflora wood
- Conduct proximate and ultimate analysis of Prosopis juliflora charcoal
- Investigation of the effects of carbonization time and temperature on charcoal yield and calorific value
- To compare the proximate analysis and calorific value of Prosopis charcoal produced in the laboratory with the traditional Prosopis juliflora charcoal

1.4. Significance of the research

This research gives a safe solution for society, the environment and the cement industry. Replacing partially the fossil fuel used in kiln burning process by alternative fuel can save foreign currency by replacing imported fuels.

Providing energy security for land locked countries such as Ethiopia and hedges against volatile global energy market this indicates Prosopis juliflora is one of the most invaded species 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.

It has global benefits from the implementation of biomass usage instead of fossil fuel would be the reduction of greenhouse gas (GHG) emissions. Provided the biomass or biomass residues are sourced sustainably, biomass is considered to be a zero-emission fuel. Since a proportion of using alternative fuels don't require high thermal processing and also has high efficiency of the process, CO_2 emission per tonne cement produced is reduce.

2. LITERATURE REVIEW

2.1. Overview of Cement Production

In 2010, 8 cement plants operated in Ethiopia, while 12 cement facilities were under construction. The new plants are expected to become operational during the period 2012-2016. Currently new entrants are coming into the cement manufacturing sphere in Ethiopia in addition to the existing large-scale cement industries such as Mugher cement, Derba Cement and National Cement factory. Based on the survey, the actual 2010 cement and clinker production was estimated at 2.0 Mt and 1.7 Mt, resulting in a clinker-cement-ratio is expressed as clinker production divided by cement production of 0.85(Tesema & Worrell, 2015).

The production process of cement starts with raw material supply, which involves such activities as blasting of rocks, transporting the raw material from quarries by dump trucks, crushing the rock on site and transporting it to the cement plant by conveyer belts. The raw material transported to the plant is stored and homogenized at the plant storage facilities. Raw meal is obtained by grinding the homogenized raw material. The raw meal is pre heated in cyclone heaters, calcined and sent to the kiln (Seboka et al., 2009).

The kilns used in cement production are of two types. These are the small scale vertical type of kilns that are predominantly used in developing countries and the large size horizontal rotary type of kilns widely used in industrialized countries. Large scale rotary kilns are more energy efficient. In the kiln, a flame of 2,000°C heats the raw material to about 1,500°C. After air cooling, clinker is obtained. Clinker is the principal ingredient in cement production and is a mixture of approximately 80% limestone and 20% clay. The clinker formation process has four stages (Karstensen, 2006):

- Stage 1: Drying and pre-heating, which releases free and chemically bound water, takes place in a temperature range of 20-900°C.
- Stage 2: Calcination, which is the stage of CO_2 release in the initial reactions associated with formation of clinker minerals and the intermediate phase. This stage occurs in a temperature range of 600-900°C.
- Stage 3: Sintering or clinkerisation, which is essentially the stage of formation of calcium silicates and the liquid phase. This stage takes place in a temperature range of 1,250–1,450°C.
- Stage 4: Kiln internal cooling, in which crystallisation of calcium aluminates and calcium ferrite occurs in the temperature range of 1,350-1,200°C.

2.2. 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 (Crelling, 1980).

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 (Suarez-Ruiz, 2007).

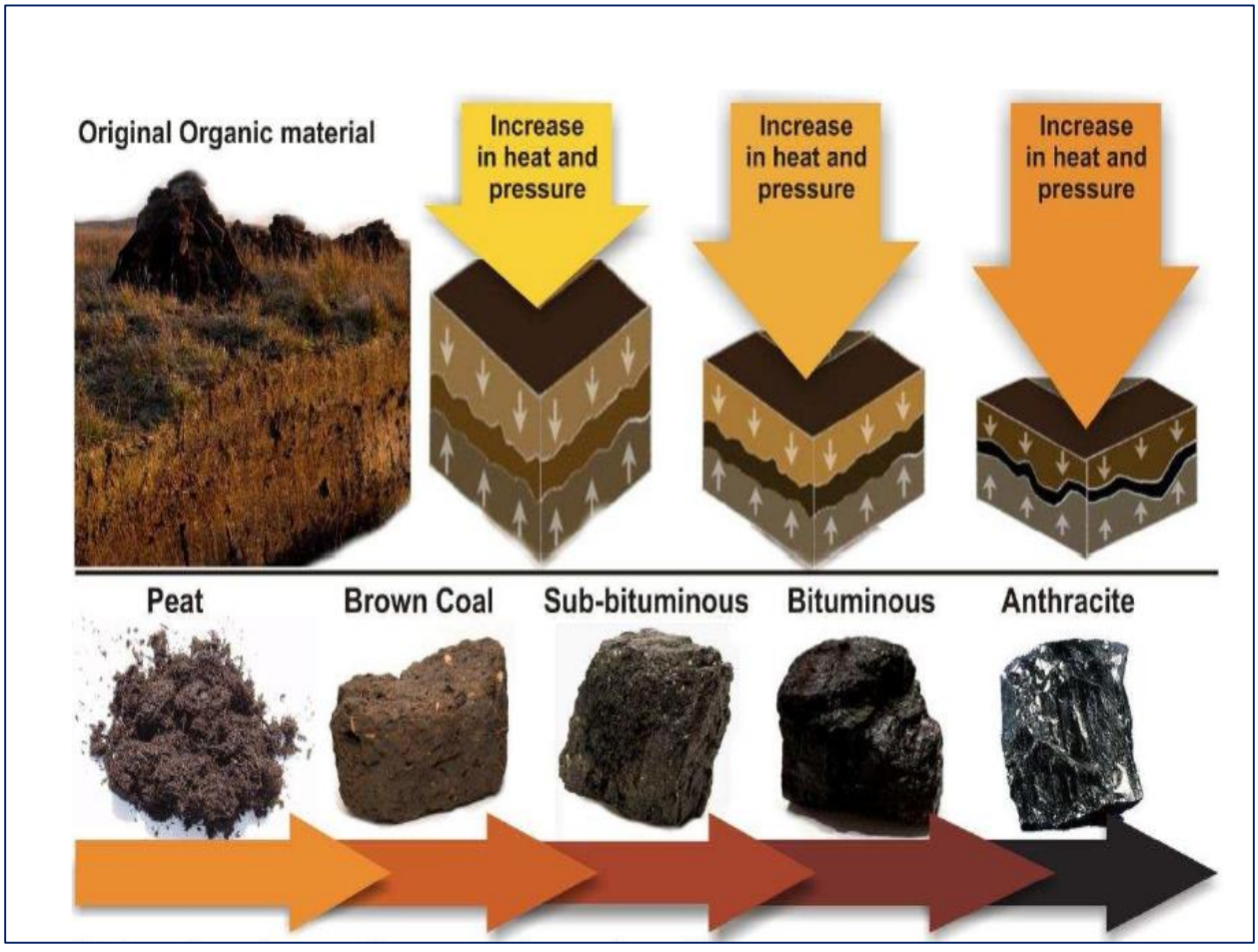

Figure 2.1: Coal formation process (Crelling, 1980 & Suarez-Ruiz, 2007)

2.2.1. 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 (Garcia, 2009). 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 (Morris, 1997).

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. (Garcia, 2009).

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 (Garcia, 2009).

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 (Morris, 1997).

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 (Garcia, 2009).

2.2.2. 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 (Morris, 1997).

2.2.3. 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.

Yayu Basin

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 (Ahmed et al., 2008).

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 Moye humic coals range from 2948-5190 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 (Ahmed et al., 2008).

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 (Getaneh & Saxena, 1984).

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 (Ahmed et al., 2008).

Chilga Basin

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, siltstones, 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 (Ahmed et al., 2008).

Table 2.1: Proximate analysis and calorific value of coal deposits in different basins (Ahmed et al., 2008)

Resource	Moisture (%)	Volatile matter (%)	Ash content (%)	Calorific value (Kcal/Kg)	Reserve In tones
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.

2.3. Alternative fuels

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 30 years now. In calciner lines, close to 100% alternative fuel firing at the precalciner was achieved at very early stage. Use of AFs in rotary kilns is still in progress. Reports show that in some kilns up to 100% substitution rates have been achieved, while others are facing some limitations regarding environmental, social and product quality issues. In any case, AF utilization requires adaptation by the cement industry. Modern multi-channel burners and thermograph systems are in use these days which help in controlling the AF feed rate and the flame shape to optimize the burning behavior of the fuels (Rahman et al., 2013).

Fossil fuels are most commonly used in the cement industry due to their availability and price. In recent years, due to increasing prices and concerns over climate change, industry has been looking at alternative fuel sources which may be able to partially or totally replace fossil fuels.

Biomass is one of the most extensively used alternative materials in the cement industry because of its diversity and volume. The major restrictions to the use of biomass in cement manufacturing are linked to economic factors, the necessity of pre-treatment stages, and the local availability of the resources and transport costs. A wide array of different types of biomass is used in combustion or gasification processes, for example, sawdust or wood, straw, agriculture and forest wastes, almond shells, and olive residues. In spite of this wide diversity of biomass types, wood and other waste from agriculture and forest processes are some of the most common types of biomass processed by combustion or gasification (Caballero et al., 1997).

Biomass additions can replace a portion of the traditional fuel use. Although replacement ratios approximately 20% are recommended to maintain a stable combustion process and the quality of the clinker, higher values have been used with very satisfactory results (Murray, 2008).

2.3.1. Criteria of alternative fuel

There are no set criteria for selection alternative fuels today. The specific criteria that a material must meet in order to be considered as a fuel is typically set by the individual cement producer according to their own needs. Alternative fuels are generally a mixture of various wastes and therefore consistency in their composition cannot be guaranteed. There is a need for ensuring the chemical contents of the alternative fuel that meets regulatory requirements for environmental protection (Mokrzycki & Uliaszbochen, 2003). The following properties are expected to be considered as alternative fuels: physical state of the fuel (solid, liquid, gaseous), composition and content of ash, moisture and content of volatiles, calorific value over 3343 kcal/kg, sulfur content less than 2.5%, physical properties (scrap size, density, homogeneity), grinding properties, proportioning technology, emissions released, cement quality and alternative fuels availability must be economically viable (Madlool et al., 2011).

2.3.2. Prosopis juliflora

Prosopis juliflora (mesquite) is a tropical and subtropical tree and shrub, mainly found in the arid and semi-arid regions of the world (Pasiecznik et al., 2001). The historical contexts of Prosopis and different opinions have led to the present position with two widely held points of view. There is one argument for further planting and improved management of Prosopis juliflora while the other one supports eradication and control. (Magid et al., 2014). Prosopis is native to arid and semi-arid zones of South Americas, Central America, Africa and Asia. Recently, the plant has been introduced and naturalized in many countries. In America, it has been introduced to Brazil, Hawaii, and in some Caribbean islands. In Oceania, it has been introduced to Australia, New Guinea. In Asia, it has been observed in Jordan, Saudi Arabia and Bahrain, United Arab Emirates, Pakistan, Iraq, Kuwait, Iran, India, Thailand, Vietnam, Indonesia, Philippines and in many arid and semiarid African countries (Pasiecznik et al., 2003).

Prosopis juliflora is one of the alien invasive species that cause detrimental effect in most African countries. The plant was introduced in 25 countries in the continent including Sudan, Ethiopia, Eritrea, Kenya, Tanzania in East and Horn of Africa, Namibia, Zimbabwe, South Africa, Morocco, Algeria, Tunisia, Libya, Egypt in North Africa, Cape Verde, Senegal, Gambia, Mauritania, Mali, Burkina Faso, Niger, Ghana and Guinea-Bissau and Nigeria in West Africa (Pasiecznik et al., 2003). In Ethiopia, the aggressive invasion of Prosopis juliflora in pastoral areas is displacing native trees and reducing grazing potential (Pasiecznik et al., 2001).

Over 700,000 hectares of prime grazing land and cultivable land following the Awash River is currently either invaded or at risk of invasion from Prosopis in the Afar Region (Dubale, 2008). Despite the negative impact and different perceptions among the large part of the community (farmer and pastoralist), Prosopis juliflora has become an income source for the livelihood of part of the community including daily laborers and fuel wood and charcoal producers.

Similarly, it is indicated that Prosopis juliflora was introduced 25 years ago to provide fuel and fodder, but has since become an invasive weed, threatening rather than improving local livelihoods. It is now being turned into a valuable resource and is starting to provide the rural poor with a ready cash income and numerous indirect benefits. At early stage, expensive eradication and biological control of Prosopis was considered the best option (Pasiecznik et al., 2003).

2.3.3. Benefit of Substituting Conventional Fossil Fuel in Ethiopia

In recent years the use of biomass as a source of energy became of great interest in Ethiopia. The use of biomass for energy production (biofuels) has been increasingly proposed as a substitute for fossil fuels. Biomass can also offer an immediate solution for the reduction of the CO_2 content in the atmosphere. It has three other main advantages: firstly, its availability can be nearly unlimited; secondly it is locally produced; and thirdly the fact that it can be used essentially without damage to the environment. In addition to its positive global effect by comparison with other sources of energy, it presents no risk of major accidents, as nuclear and oil energy do (Ahmed, 2010).

Alternative fuels are generally cheaper than the fossil fuels. A mixture of fossil fuels and AF in optimal proportion is used to produce the thermal energy required in cement industry. The significant advantage of AF substitution is the preservation of non-renewable energy source (Trezza & Scian, 2000).

2.4. Thermogravimetric Analysis

Thermogravimetric analysis is a technique used to determine the weight loss of a material at a specific temperature or when it is subjected to a specific heating pattern. The technique is performed with a thermogravimetric analyzer (TGA). The degradation process that occurs could be a pyrolysis or combustion process, depending on the atmosphere in which it occurs. Multiple studies have been performed to determine weight loss of many types of biomass under inert conditions (Zhaosheng & Xiaoqian, 2008).

This pyrolysis process can be used to predict the different components of the biomass such as moisture, hemicellulose, cellulose, and lignin content (Carrier et al., 2011). The output data from TGA are normally used to construct a thermogravimetric (TG) curve, from which the mass losses versus temperature or time can be observed.

2.5. 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 (Frassoldati, et al., 2006).

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 (Gronli et al., 2002).

2.5.1. Pyrolysis

Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into solid charcoal, liquid (bio-oil) and gas. Pyrolysis is considered to be an industrial realized process for biomass conversion. Each component of lignocellulosic (cellulose, hemicelluloses and lignin) biomass is pyrolysed at different rates by different mechanisms and pathways. Lignin decomposes over a wider temperature range compared to cellulose and hemicelluloses which rapidly degrade over narrower temperature ranges. Hence there is an apparent thermal stability of lignin during pyrolysis (Chhiti & Kemiha, 2013).

Thermogravimetry analysis (TGA) testing of biomass shows that there are three stages for a typical biomass pyrolysis process. The first stage, pre-pyrolysis, occurs between 120 and 200°C with a slight weight loss, when some internal rearrangements, such as bond breakage, the appearance of free radicals and the formation of carbonyl groups take place, with a corresponding release of small amounts of water (H_2O), carbon monoxide (CO) and CO_2 (Chhiti & Kemiha, 2013).

The second stage is the main pyrolysis process, during which solid decomposition occurs, accompanied by a significant weight loss from the initial biomass. The last stage is the continuous char devolatilization, caused by the further cleavage of C-H and C-O bonds. Depending on the reaction temperature, heating rate and residence time, pyrolysis can be classified into slow pyrolysis (intermediate pyrolysis) fast pyrolysis and flash pyrolysis (Chhiti & Kemiha, 2013).

Slow Pyrolysis

Slow pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal. In slow pyrolysis, biomass was typically heated at about 500 ºC at slow heating rates (10 - 20°C/min). The vapour residence time varies from 5 to 30 minutes. Thus, the components in the vapour phase continue to react with each other, as solid char and liquid are being formed. The main product charcoal can be used in a wide range of areas from domestic cooking and heating to metallurgical or chemical use as the raw material for production of chemicals, activated carbon, fireworks, absorbents, soil conditioners and pharmaceuticals (Chhiti & Kemiha, 2013).

Flash Pyrolysis

The flash pyrolysis of biomass is a promising process for the production of solid, liquid and gaseous fuel from biomass which can achieve up to 75% of bio-oil yield. This process can be characterized by rapid devolatilization in an inert atmosphere, high heating rate of the particles, high reaction temperatures between 450 °C and 1000 °C and very short gas residence time (less than 1 second) (Aguado, 2002).

Fast Pyrolysis

In the fast pyrolysis process, biomass is rapidly heated to a high temperature in the absence of oxygen. Typically, on a weight basis, fast pyrolysis produces 60% – 75% of oily products (oil and other liquids) with 15% – 25% of solids (mainly biochar) and 10% – 20% of gaseous phase depending on the feedstock used. The production of liquids is usually yielded from biomass in a low temperature, high heating rate and short resident time environment. The basic characteristics of the fast pyrolysis process are high heat transfer and heating rate, very short vapour residence time, rapid cooling of vapours and for high bio-oil yield and precision control of reaction temperature (Demibas & Arin, 2002).

Fast-pyrolysis technology is receiving incredible popularity in producing liquid fuels and commodity chemicals. This liquid product can be easily and economically transported and stored, thereby de-coupling the handling of solid biomass from utilization. It also has potential to supply a number of valuable chemicals that aerosol offer the attraction of much higher added value than fuels. Fast pyrolysis technology can have relatively low investment costs and high energy efficiencies compared to other processes, especially on a small scale. (Brammer et al., 2006).

2.6. Influence of process parameters on products of pyrolysis

Although the three fractions (solid, liquid, gas) are always present as a result of the pyrolysis process, the increase of yield to one of them in relation to others is possible by selecting the appropriate pyrolysis technology and process conditions.

The main variables that affect the mechanism of reaction are:

- the final temperature of the reaction
- the heating-rate
- the residence time of the material
- the size and shape of biomass to be treated
- pressure
- moisture
- the chemical composition of biomass

Carbonization Temperature

The temperature at which biomass material is pyrolyzed is very important and the final temperature is one of the major determinants in the thermal process. For example, at low temperatures below 150°C, tar formation usually does not take place. However, as temperature increases, formation of char begins to take place, which in turn results in higher yields of gaseous products and lower yields of char. This is due to greater decomposition of the biomass and this also leads to decrease in liquid products resulting in increase in gas production apparently due to devolatilization of the cellulosic and hemi-cellulosic materials (Oladeji et al., 2015).

Char yield decreases steadily with temperature to an almost constant value above about 650°C when devolatilization is almost complete. The carbon content of the char, however, increases sharply with increasing temperature while that of H and O decrease. High pyrolysis temperatures decline solid yield of char, but increase higher heating value, carbon and ash content (Pach, 2002).

Pressure

Higher pressure increases the residence time of the volatiles in the reaction zone, resulting in increased yield of low molecular weight gas and decreased tar and liquid products due to cracking reactions. Also, at higher temperatures, gas-solid reactions occur with product gases. At low pressures, and hence short residence times, tar molecules and heavy liquid products will escape before undergoing further decomposition. Product gases will also escape before reacting with the solid residue char (Ward, 1985).

Carbonization Time

Carbonization Time has an impact on solid char yield, higher heating value and carbon content. Increase in holding time decrease the yield of solid char. The yield of solid char observed to be approximately 13 % higher in holding time of one hour than three hours in temperature of 280 °C. Holding time has a slight positive impact on higher heating value and carbon content (Pach , 2002).

Heating rate

The product yields of pyrolysis including char, liquid and gas to certain extent depends on the applied heating rate. Rapid decomposition gives a lower yield of charcoal but greater yield of gases. Effects of prevailing pressure in the process to decomposition of wood have been studied. The studies have shown that pressures above atmospheric pressure effects to exothermic reaction and reaction becomes very violent producing a slight increase in charcoal and gas volume. Length of heating and its intensity affect the rate and extent of pyrolytic reactions, the sequence of these reactions, and composition of the resultant products.Pyrolytic reactions proceed over a wide range of temperatures; hence, products formed earlier tend to undergo further transformation and decomposition in a series of consecutive reactions (Scott et al., 1988).

The main products of biomass pyrolysis are char, tar, pyroligneous acid, and gas. At low temperature, char is the dominant product followed by H_2O. The yield of volatile products gases and liquids increases with increasing heating rate while solid residue decreases. The effect of heating rate can be viewed as the effect of temperature and residence time. As the heating rate is increased, the residence time of volatiles at low or intermediate temperatures decreases. Most of the reactions that favor tar conversion to gas occur at higher temperatures. At low heating rates, the volatiles have sufficient time to escape from the reaction zone before significant cracking can occur.

Heating rate is a function of the feedstock size and the type of pyrolysis equipment. (Aarsen et al., 1985) reported that the pyrolysis of 1 μm wood particles in a fluidized bed at 800°C is nearly complete within 2 seconds. They estimated the heating rate to be about 500°C/s. Small quantities <10% of char were produced.

2.7. Proximate and ultimate analysis wood and coal

Wood as an energy source is the focus of a renewed interest in developed countries. In the European Union, wood energy shares grew from 3% to 3.2% of the total energy consumption in 2003. Wood cannot totally replace fossil fuels. However, it may be a partial answer to the problems of CO_2 emissions and oil dependency. Wood is a CO_2 neutral fuel, provided trees are grown as much as they are burned, and wood is available in almost all countries. The characteristics of biomass are very different from those of coal. The content of volatile matter in wood based biomass is generally close to 80%, whereas in coal it is around 30%. Wood char is highly reactive, which results in complete combustion of wood fuels in fluidised bed combustion. Nitrogen and Sulphur contents of wood are low. This implies that blending wood biomass with coal lowers emissions simply because of dilution. Further, one important difference between coal and biomass is the net calorific value. Biomass fuels often have high moisture content, which results in a relatively low net calorific value (Lourtau et al., 2015).

Table 2.2: Typical properties of wood and coal (Bellais, 2007)

	Wood	Coal
Density (dry fuel) (Kg/m^3)	~570	~1500
Higher heating value(KJ/g)	19.4-22.3	23-34
Volatiles (wt % of dry fuel)	81-87	16-35
Particle size	~3 mm	~100 μm
Ash (wt % of dry fuel)	0.2-1.35	6-23.3
C (wt % of dry fuel)	49-52	65-85
H (wt % of dry fuel)	5.4-7	3.1-5.6
O (wt % of dry fuel)	40-44	3.4-13.8
N (wt % of dry fuel)	0.00-0.35	0.9-1.6
S (wt % of dry fuel)	0.00-0.07	0.4-4.3

Wood is a cleaner fuel compared to coal. It has low Sulphur content. There is usually no need for denitrification treatment of the flue gas in wood combustion. The fuel bound nitrogen is typically, 1% in coal and the combustion temperature is also lower due to a lower HHV, which reduces the fuel and thermal NOx formation (Bellais, 2007).

2.8. Batch and continuous process and kiln types

Carbonization technologies can be divided based on the feeding system into batch and continuous process or based on the heating method as internal, external or circulation gas.

Charcoal production technologies can be divided to continuous and so called batch method techniques according to the operational base. In the batch method, feedstock is charged in the beginning of the reaction. After carbonization retort is discharged and charged again with raw wood. During the carbonization, retort is not charged or discharged. Continuous kiln is charged and discharged continuously (Ciolkosz, 2011). Kiln types can be separated into traditional and more advanced kiln types. Traditional kiln types are simple, easy to build and maintain. Typical for traditional kiln types is that kilns are grouped together to improve labour productivity. In traditional kiln types by products are not recovered and exploited (Trossero, 2008).

In more advanced kiln types, like Carbo Twin Retort and Lambiotte Retort, emissions are controlled. There is difference also in the oxygen contact between traditional and advanced kiln types. In more advanced kiln types or retorts oxygen contact with the biomass is prevented to ensure high yield of charcoal. In traditional kilns, air intake is controlled but not prevented. In more advanced kiln types at least combustion gases are reclaimed but also liquids, and the process is semi continuous or continuous. Retorts are used in more advanced kiln types and among industrial charcoal manufacturing (Trossero, 2008).

Table 2.3: Types of installations for charcoal production (Trossero, 2008)

Types of installations	Yield (%)
Batch process	
Earth pits and mounds	>10
Brick, concrete and metal kilns	20-25
Retorts	30
Continuous process	
Retorts and lambiotte retorts	30-35
Multiple hearth reactors	25-30

2.9. Release and Chemical Reactions of Ash-Forming Matter

When a fuel is burned, the ash-forming elements that are released from the fuel undergo different reaction paths. After entering the furnace, fuel particles will heat up rapidly and dry at first. After this the pyrolysis will start, that is, organic volatile species will be released from the fuel and will burn with a visible flame. During this stage some reactive ash-forming elements will be released together with the gases. Hereafter char burning will begin. Most of the ash-forming elements will end up in the residual ash in the case of burning coal by the coalescence of the fused included minerals in coal during char burnout (Zevenhoven et al., 2009).

The particle size of the residual ash depends on many factors. A single fuel particle may fragment during combustion and each fragment may produce an ash particle. The size of the ash particle will depend on the initial fuel diameter, its mineral content, the uniformity of its distribution, and the number and size of fragments produced during combustion. As reactions occur in depth within the porous char, a point is reached where the pores merge and undermine segments of the partially burned char, which are then released as fragments. This description of the formation of ash is also valid for biomass fuels (Zevenhoven et al., 2009).

When burning biomasses or wastes of various kinds the ash forming matter is released and it reacts with the flue gas components and with each other. The fly ash formed this way becomes a complex mixture of compounds (Zevenhoven et al., 2009). Ash is the incombustible solid mineral matter in the fuel. It mainly contains silica (SiO_2), Alumina (Al_2O_3), Iron oxides (FeO, $Fe_2O_{3)}$, CaO and MgO.

Silicon

Silicon is present as silica (SiO_2) or various silicate minerals. These are non-soluble in the selective leaching analysis, and will be in the rest fraction. They are relatively inert under combustion conditions. During combustion, most often the various metals connected to the silicate stay in the silicate matrix. Silicates as such are seldom a problem in fluidized beds (FB) combustion. The ash formed from them is mostly high melting and at FB conditions most silicate ashes stay in crystalline form. This kind of crystalline silicate ash does not cause slagging, fouling, sintering, or corrosion problems (Zevenhoven et al., 2009).

During combustion these silicates easily react with each other and form low melting potassium silicates that may cause major sintering and fouling problems in fluidized beds. While being quite inert in their own behavior in combustion silica and their silicates may influence the chemistry of other ash-forming elements, especially K, Na, and Ca, by secondary reactions, thus influencing indirectly the fouling–corrosion properties of fly ash (Patel & Gami, 2012).

Aluminum

Aluminum is present in many forms in biofuels and wastes. Organically bound Al or precipitated Al salts are found in the acid-soluble fractions of the leaching. In the furnace processes they all form alumina, Al_2O_3. This is a solid, non-reactive compound that does not significantly participate in the ash chemistry of fluidized bed systems (Zevenhoven et al., 2009).

In some biomass fuels Al may be present as silicates. This is the case when for instance clay or other impurities have contaminated the fuel. In the leaching tests this part of aluminum stays in the insoluble rest. In some cases, such aluminum silicates are used as bed materials. Aluminum silicates are not very reactive but they may react with alkali vapors, thus influencing the flue gas alkali chemistry. Metallic Al has a low melting point around 600°C and it will easily form agglomerates and deposits on tube surfaces in the furnace or super heaters (Patel & Gami, 2012).

Iron

Iron is present in various forms in the biomass fuels. It is especially abundant in Finnish peat, where its concentration may exceed several percent of the fuel dry solids. Iron compounds can form first deposits on furnace wall tubes in pulverized fuel boilers, where furnace gas temperatures are high (Patel & Gami, 2012).

Calcium and Magnesium

Calcium is the element present in the highest concentration in woody biomasses. It is partially organically bonded and thus exchangeable in the ammonium acetate leaching. It is also present as crystalline salt particles, mostly calcium oxalate especially in biomasses having a high content of Ca, such as bark. This fraction of Ca is found mainly in the acid-soluble fraction of the leaching test. The organic calcium compounds will be converted into calcium oxide. Calcium oxide has a low vapor pressure and a high melting point. Consequently, organic calcium in biomass is released in combustion as small solid particles, CaO (Zevenhoven et al., 2009).

Magnesium is chemically similar to calcium. It is also present as natural element in many biomasses, but in much lower concentrations than calcium. The combustion chemistry of magnesium is less lively than that of calcium. The reactions that take place with calcium do also take place with magnesium but typically at lower temperatures, often so low that they do not really have significance in combustion systems. In most cases MgO can be treated as an inert compound in combustion. One exception is a low temperature corrosion additive containing magnesium. At low temperature conditions below 200°C MgO can react, selectively, with SO_3 and thus reduce the so-called acid due point corrosion (Patel & Gami, 2012).

Sulfur

Sulfur is present in biomasses as both inorganic sulfate anions and as organic sulfur. According to recent studies roughly 3/4 of the sulfur in woody biomasses is organically bound and 1/4 as soluble alkali sulfates. The organic sulfur will be fully released in combustion primarily as H_2S and other reduced gaseous species that then oxidize to SO_2. most of the sulfur in fuels will be released in combustion and finally yield SO_2 (Zevenhoven et al., 2009).

2.10. A comparison of the ash composition between different coal and biomass

Biomass typically has a lower inorganic content than coal, the biomass ash has a very different chemical composition from coal ash, the alkalis in the biomass could change the properties of mainly aluminosilicate coal ash (Vassilev et al., 2010).

Table 2.4: Chemical composition of woody biomass ash and coal ash (wt. %) (Johnson et al., 2010 and Vassilev et al., 2010)

Ash Type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Wood(range)	2 - 68	0.1 – 15	0.4 - 10	6 - 83	1 - 15	0.4 - 12
Coal(range)	32 - 68	11 – 35	0.8 - 16	0.4 - 28	0.3 - 4	0.3 - 14
Coal(avg)	54.1	23.2	6.9	6.6	1.8	3.5
Lignite(avg)	44.9	17.1	10.8	13.1	2.5	8.6
Subbituminous(avg)	54.7	22.9	5.3	7.1	2.1	4.1
Bituminous(avg)	56.1	24.8	6.7	4.9	1.6	2.2

2.11. Previous Works on Prosopis juliflora

Researchers conducted several researches to utilize Prosopis juliflora. Physical and chemical analysis of Prosopis juliflora was also done (Jothiprakash & Palaniappan, 2014). According to their work Prosopis juliflora has the following characteristics

Table 2.5: Proximate analysis and calorific value of Prosopis juliflora (Jothiprakash & Palaniappan, 2014)

Parameters	(Jothiprakash & Palaniappan, 2014)	
	Biomass	Charcoal
Moisture content (%)	7.29	1.4
Ash content (%)	4.42	3.85
Volatile matter (%)	59.57	43.5
Fixed carbon (%)	28.72	51.25
Calorific value(kcal/kg)	4348	6753

The Prosopis juliflora biomass and charcoal mentioned in table 2.5 do fulfill the minimum calorific value requirement which is 3343 kcal/kg set by the most experienced cement industries using alternative fuels such as Lafarge (Madlool et al., 2011).

3. MATERIALS AND METHODS

3.1. Materials

The main raw material, Prosopis juliflora was collected from Gewane, Afar regional state of Ethiopia. Gewane Wereda is located in the Middle Awash Valley Zone III of the Afar national regional state located at a distance of 370 kms from Addis Ababa towards East along the main road that connects Addis Ababa to port Djibouti. It is also located between degrees 40°43′– 41°15′E and 9°71′– 11°20′N. The temperature varies from mean monthly minima of 14.8 to 23.6 ºC to mean monthly maxima of 31.3 to 37.5 ºC. Mean relative humidity varies from 38.9 % to 59.3%.

The equipments used during the experimentations were cutter, centrifugal mill, sieves, electronic balance, ceramic crucibles, oven, muffle furnace, desiccators, tubular furnace with a stainless steel tubular reactor, thermogravimetric analyzer, bomb calorimeter.

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

The experimental work was began in December 2015 and ended in May 2016. Experiment were conducted in laboratories of three different institutions. Thermogravimetric analysis of Prosopis juliflora wood sample was done at Leather Industry Development Institute, located in Addis Ababa. Proximate analysis and carbonization process was done at School of Chemical and Bio-Engineering laboratory, AAiT, and also calorific value and ash chemistry of Prosopis juliflora wood and carbonized charcoal were done at Dangote Cement Factory.

3.2. Methods

3.2.1. Sample preparation

Raw Prosopis juliflora was cleaned from leaves, soil and other contaminants collected along with it. Prior to grinding the collected samples were sun dried to remove the moisture hence it helped crushing easy. The dried Prosopis juliflora were cut manually into pieces of 3 cm height, 3 cm length and 3 cm width to make suitable for subsequent pulverization and carbonization process. Pieces of samples were then grinded and allowed to pass through 0.75mm of mesh in order to obtain uniform particle sizes for TGA analysis.

3.2.2. Sample characterization

Proximate analysis of Prosopis juliflora wood 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 were used for the study of mentioned parameters, respectively.

I. Moisture content

The moisture content of Prosopis juliflora wood was measured by oven dry method. One 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).

$$\%\text{Moisture content} = \frac{W1-W2}{WI} * 100 \quad \ldots\ldots 3.1$$

Where; W_1 = Weight of sample before drying

W_2 = Weight of sample after drying

II. Volatile content

One 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 minute 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).

$$\%\text{Volatile content} = \frac{W2-W3}{W2-WI} * 100 \quad \ldots\ldots 3.2$$

Where; W_1 =Weight of crucible

W_2 = Weight of crucible + Weight of sample

W_3= Weight of crucible + residual content

III. Ash content

Ash content was determined by placing one grams of finely ground, dried samples into a pre-ignited 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).

$$\%\text{Ash content} = \frac{W3-W1}{W2-WI} * 100 \quad \ldots\ldots 3.3$$

Where; W_1=Weight of crucible

W_2 = Weight of crucible + Weight of sample before ashing

W_3= Weight of crucible + ash

IV. Fixed carbon

The residue remaining after volatile matter release has been expelled, contains the mineral matter originally present and nonvolatile. The fixed carbon was thus calculated as follows (ASTM, 1989).

%FC = 100 - (Ash +volatile content + MC) 3.4

Where; FC=fixed carbon

MC =moisture content

3.3. Determination of Ash Chemistry

Ash Chemistry of Prosopis juliflora wood and charcoal were also performed in order to determine the amount of different oxides present such as SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO and sulfur.

3.3.1. Determination of oxides

Oxides determination were done by measuring 0.5gm of Prosopis juliflora wood and charcoal which were dried at 105 ^{0}C in to the silver crucible separately and burn it in high temperature furnace with 650 ^{0}C for 30 min. remove and cool it down to room temperature. Then 6gm of NaOH pellet was put in the muffle furnace at 650^{0}C for 20 min. cool the crucible with its content by rinsing with little distilled water on its outside, 100 ml of boiling water was added in to 300 ml beaker then, Remove the beaker from the stove, 25ml of concentrated HCl was added. While stirring, the crucible was washed with 1:5 HCl and added to solution till the crucible is free, then, 1 ml nitric acid was added into the crucible. The procedure followed in determination of oxides includes (ASTM, 2002).

- ✓ **Determination of Fe_2O_3 in the solution**

25 ml of solution was dilute up to 150ml with distilled water in 300 ml beaker. drops of NH_3OH (1 gm/l) was added to the solution and pH adjusted to 2 and heated. Then, end point determination was obtained by adding 10 drops of Sulfo salicylic acid indicators. The reddish color of the solution changed in to yellow when it was titrated by EDTA (0.015 mol/l).

The formula which was used to determine Fe_2O_3

$$\% Fe_2O_3 = \frac{TFe2O3*VEDTA}{M} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 3.5$$

- ✓ **Determination of SiO_2 in the solution**

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

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

$$\% SiO_2 = \frac{vNaOH*T\ SiO2*0.5}{M} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 3.6$$

Where

M=mass of the ash

V=volume of the solution

- ✓ **Determination of Al_2O_3 in the solution**

After the Fe_2O_3 was finished 15 ml EDTA was added to the solution and pH adjusted to 4.3 and heated. While stirring, 10 drops PAN indicator were added to the solution which was titrated by $CUSO_4$ (0.015 mol/l). Finally end point determination was obtained changing the color from yellow in to violet.

The formula which was used to determine Al_2O_3

$$\% Al_2O_3 = \frac{\frac{20}{15}-(KVCuSO4)*TAl2O3}{M} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 3.7$$

Where; K= excess EDTA + consumption of CuSO4

- **Determination of CaO in the solution**

25 ml of solution was pipetted in to a 300 ml beaker.10 ml of KF (20 g/l) was added to the solution and wait for 5 minutes. The solution was diluted up to 200 ml. To deactivate the Fe_2O_3 and Al_2O_3, 5 ml of TEA (triethanolamine), 5 drops of MP indicator and 20 ml of KOH 200g/l were added to the solution and pH was adjusted to 10.2 finally, the green color of the solution was changed in to red color when it was titrated by EDTA. The formula which was used to determine CaO was;

$$\% \text{ CaO} = \frac{vEDTA * TCaO}{M} \quad \ldots \quad 3.8$$

Where, EDT= ethylenediaminetetraacetic acid

- **Determination of MgO in the solution**

25 ml of solution was pipettes in to a 300 ml beaker.15 ml of KF (20 g/l) was added and wait for 5 minutes and diluted with 200 ml of distilled water then, 1 ml of potassium sodium tartrate, 5 ml of TEA, 20ml of ammonia hydroxide (pH adjusted to 12. 5) and 6 drops of KB indicator were added. The brown color of the solution changed in to blue color when it was titrated by EDTA. The formula which used to determine MgO was;

$$\% \text{ MgO} = \frac{(vMgO * VCaO) * TMgO}{M} \quad \ldots \quad 3.9$$

- **Determination of Sulphur**

1 gram of Prosopis charcoal sample was dried at 105 ^{0}C in to the ceramic crucible. 2 grams of reagents (mass ratio MgO: Na_2O_3 2:1) were mixed carefully, and then covered with l gram of MgO and NaCO3 mixed reagent. and burn it in high temperature furnace with 815 ^{0}C for 3 hours. After three hours it was removed and cooled down at room temperature. The solution was boiled until it got pumped, and was filtered using filter paper and the paper was washed by using hot water up to mark 200ml. 3 drops of methyl red indicator (2g/l) and 2ml of HCl were added until it gets pink in colour and heated. 10 ml of $BaCl_2$ was added and cooled then; the solution was filtered by filter paper using warm water then, the filter paper was transferred in to ceramic crucible and put in to the stove until the black carbon was finished, then it was ignited in high temperature furnace with 950 ^{0}C for 30 min and cooled and weighed the solution. The formula which was used to determine Sulfur (ASTM D 3177).

$$\text{Sulfur(S)} = \frac{(M2 - M1) * 0.1373}{M} * 100 \quad \ldots \quad 3.10$$

Where; M_1= mass of the crucible before burning

M_2= mass of the crucible after burning, M=mass of the Prosopis sample

3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a SDT Q600. To maintain pyrolysis conditions, the sample was analyzed by purging with Nitrogen at a flow rate of 2 ml/min and a sample size of 27.611mg. The sample was allowed to be heated from 25˚C to 700˚C at 20˚C/min. The pulverized particle sizes of 0.75mm samples were loaded to platinum pans located in an auto sampler tray, which was controlled from a remote desktop that was also used to control the heating programs and record the weight of the sample as a function of temperature. Approximately 27.611 mg of sample was placed in the platinum crucibles then it was run using a software controlled program.

3.5. Determination of Calorific value of Prosopis juliflora

The energy content of the biomass was measured with a bomb calorimeter. The samples were milled and 0.5 grams of sample were taken in clean crucible. The crucible was then supported over the ring. A fine Nickel wire, touching the fuel sample, was then stretched across the electrodes. The bomb lid was tightly screwed and bomb filled with Oxygen at 25atmospheric pressure. The bomb was then lowered into copper calorimeter, containing a known mass of water. The stirrer was worked and initial temperature of the water was noted. The electrodes were then connected to 6-volt battery and circuit was completed. The sample was burnt and heat was liberated. Uniform stirring of water was continued and the maximum temperature attained was recorded. The heat produced after combustion of the sample was recorded and converted into KCal/kg. The calorific value of the Prosopis juliflora was determined by using the following formula (ASTM, 3286).

$$Q = \frac{E * \Delta T - 40}{m} * 4.185 \quad \text{3.12}$$

$$E = \frac{26463 * 4.185 * m2 + 40}{\Delta T} \quad \text{3.13}$$

Where; m=mass of the sample, m_2=mass of the Benzoic acid table

3.6. Carbonization of Prosopis juliflora wood

Prosopis juliflora wood pieces of 3 cm height, 3 cm length and 3 cm width in dimension were placed in a horizontal stainless steel tubular reactor equipped with tubular furnace, temperature controller and inert atmospheric nitrogen flow gas. Carbonization experiments were carried out by taking initially weighted Prosopis juliflora wood pieces into the tubular furnace. While carbonization was conducted two parameters were controlled to see their effect on carbonization pattern. Temperature effect was considered at four different levels of 350, 450, 550 and 600°C with a corresponding time level of 1, 2,3 and 4 hours under a slow heating 10°C min^{-1}.

After cooling, the carbonized samples were weighed at room temperature to determine the percentage charcoal yield. The charcoal yield for each run of experiments was calculated using the following equation:

Charcoal yield = (A / B) * 100... ... ...3.11

Where, A = weight of charcoal after pyrolysis

B = fresh biomass before pyrolysis

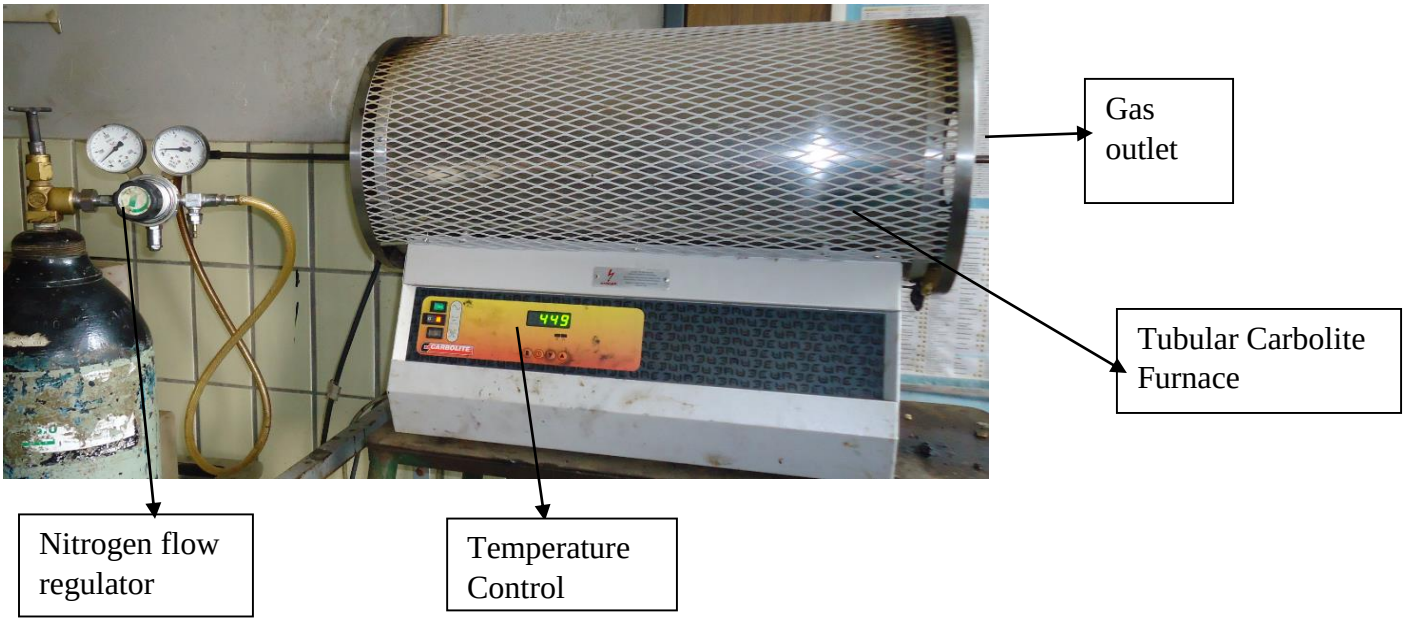

Figure 3.1: Carbonization process equipment set up

3.7. Characterization of traditionally produced Prosopis juliflora charcoal

Required amount of traditionally produced Prosopis juliflora charcoal was bought from farmers in Gewane, Afar regional state of Ethiopia. The charcoal was characterized to determine its volatile matter, fixed carbon, ash content and Calorific value based on the respective ASTM standards. The aim of doing this was to compare its values with laboratory scale carbonized Prosopis juliflora at controlled parameters of temperature and time.

3.8. Experimental Design

The full factorial design has been used throughout to design the experiment run. The data that are to be analyzed are processed and manipulated with the help of Design Expert 6.0.8 software.

The experiment was designed to investigate the effects carbonization temperature and time on charcoal yield and calorific value. Therefore, this study was employed full factorial design which is the general factorial design. Here the effects of these two factors varied in four levels are to be determined.

4. RESULT AND DISCUSSION

4.1. Characterization of Prosopis juliflora

A proximate analysis of Prosopis juliflora wood and charcoal were shown in Table 4.1. The proximate analysis determines only the volatile matter, ash content, moisture content and fixed carbon content.

As it can be seen from table 4.1, moisture content of Prosopis juliflora wood was 7%. The values obtained was very small which can be confirmed with the fact that high moisture content lowers the calorific value of wood (Patel & Gami, 2012).

Volatile content of Prosopis wood was found to be 75.81% and that of Prosopis charcoal was 45.88%- 70.9%. The results can be justified as that high volatile content as shown in Prosopis wood, is easy to ignite but may burn with a smoky flame while low volatile content as found in Prosopis charcoal, is difficult to light and burns very cleanly. These conditions are well described by Kazeem that high volatile charcoal is preferable for some purposes such as barbecue, while other utilizations as metal manufacture need charcoal with low percentage volatile matter content (Kazeem, 2014).

Ash, content of Prosopis wood and charcoal was found to be 2.37% and 0.14 – 1.59% respectively. The result showed that the raw Prosopis wood ash was higher than the ash content of the wood in the form of charcoal. This higher amount of ash may be considered as undesired residue according to (Bárbara et al., 2013).He also described that the presence of high mineral matter components in wood 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.

Furthermore, fixed carbon content was obtained which gives a rough estimation of the heating value of a fuel and acts as the main source of heat during burning. From table 4.1 fixed carbon content was determined to be 14.82% for Prosopis wood and 28.91%-52.53% for prosopis charcoal. The calorific values of charcoals were in the range of 4213 kcal/kg to 6620 kcal/kg, which while the calorific value of wood sample was 4068 kcal/kg. Fuwape verified that to enhance the energy in the biomass; the biomass can be converted into charcoal (Fuwape, 1996).

Table 4.1: Proximate analysis

Sample	Prosopis juliflora dried wood	Prosopis juliflora charcoal
Moisture content (%)	7	0
Ash content(%)	2.37	0.14 - 1.59
Volatile matter(%)	75.81	45.88 - 70.9
Fixed carbon(%)	14.82	28.91 - 52.53
Calorofic value(kcal/kg)	4068	4213 - 6620

Proximate analysis of charcoal was carried out at different time interval of 1, 2, 3 and 4 hours with correspond to 350, 450, 550 and 600^0C. The experimental results at fixed temperature of 350^{o}C indicated that fixed carbon was in the range of 28.91% - 30.36%, ash content was in the range of 0.19- 0.46% and volatile matter was from 69.2% - 70.9%. On the other hand, charring process was observed to be completed in about 4 hours.

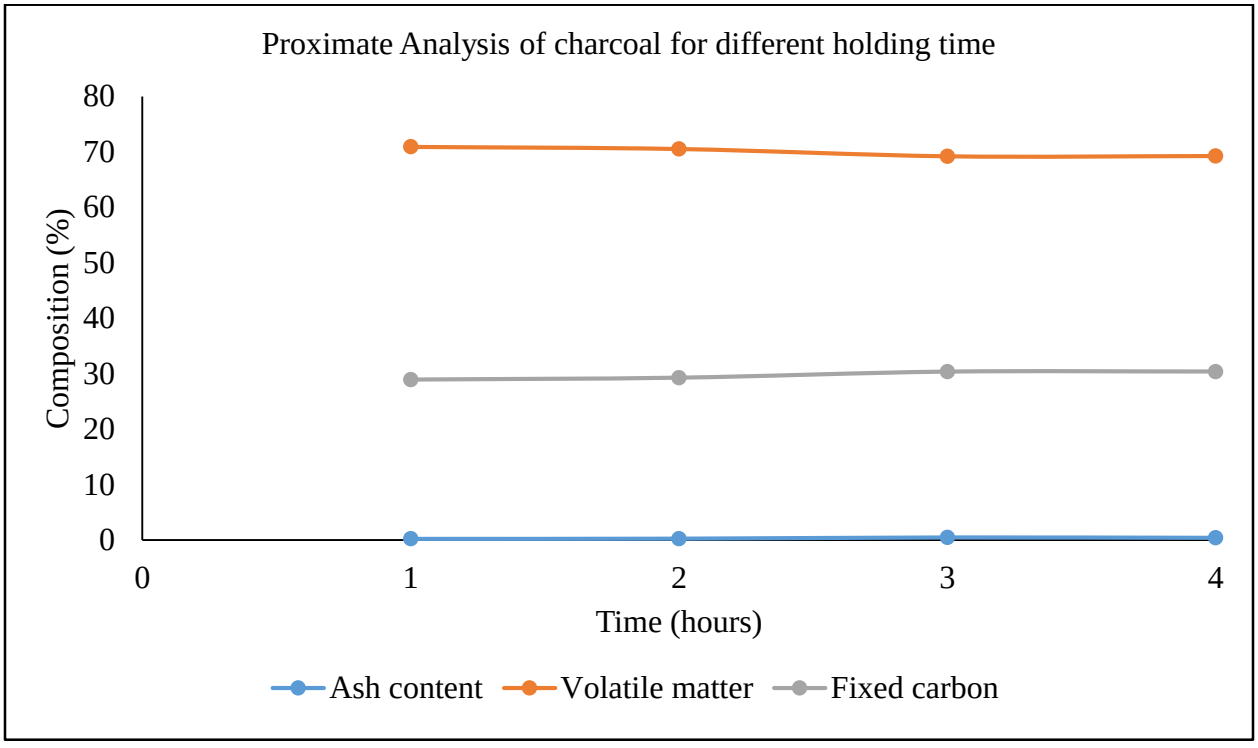

Figure 4.1: Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 350^{o}C

The experimental results from figure 4.2 show that fixed carbon, ash content and volatile content were found to be in the range of 34.17% -38.45%, 0.18%- 0.56% and 61.37% – 65.59% respectively.

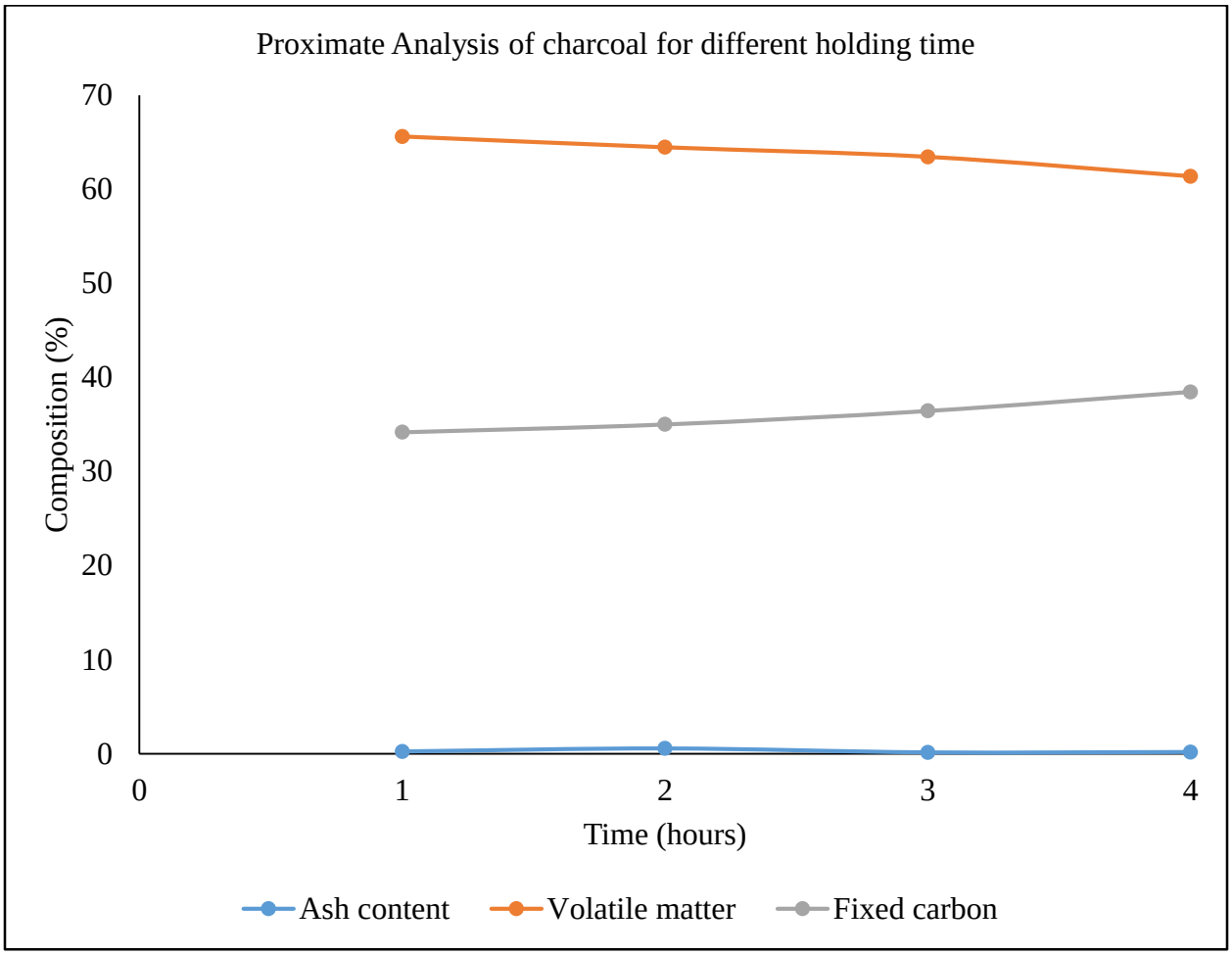

Figure 4.2: Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 450^{o}C

The experimental results from Figure 4.3 show that fixed carbon of Prosopis were in the range of 42.7% -44.46%, ash content were in the range of 0.75% -1.27% and increased with increasing carbonization temperature whereas volatile matter decrease from 56.55% - 54.27%.and also Charring process were observed to complete in about 4 hours.

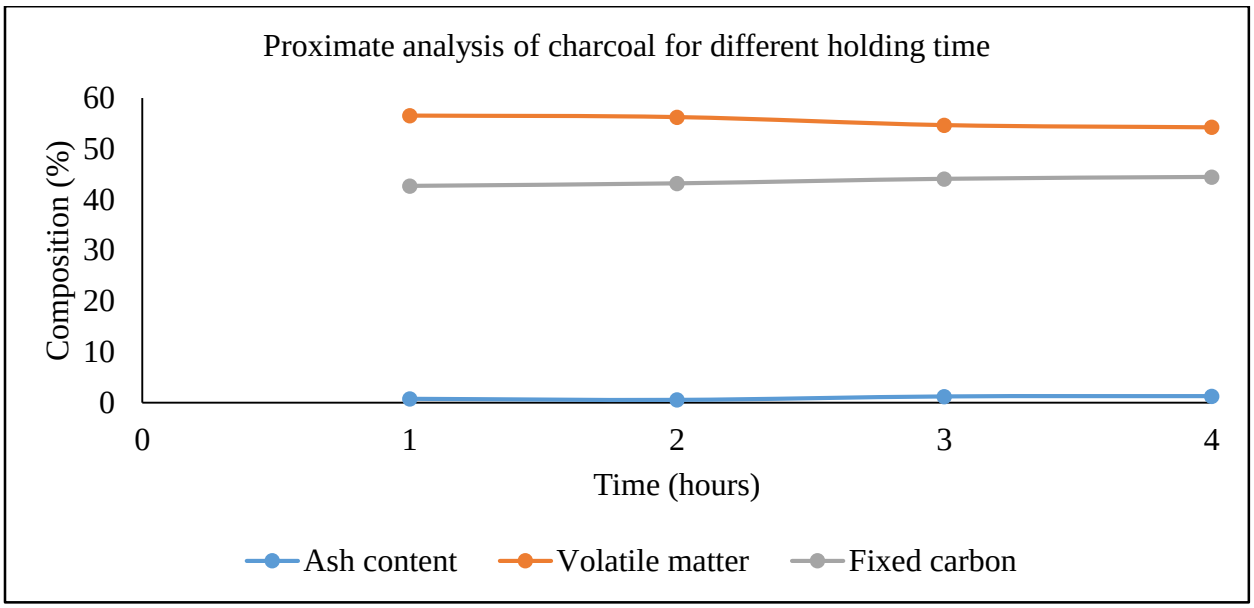

Figure 4.3: Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 550^{o}C

At 600^{o}C, proximate analysis results were showed over a charring process of about 4 hours. The of result values of fixed carbon, ash content, and volatile matter were within the range of 48.18% -52.53 %, 1.25%-1.59% and 45.88%–50.59% respectively.

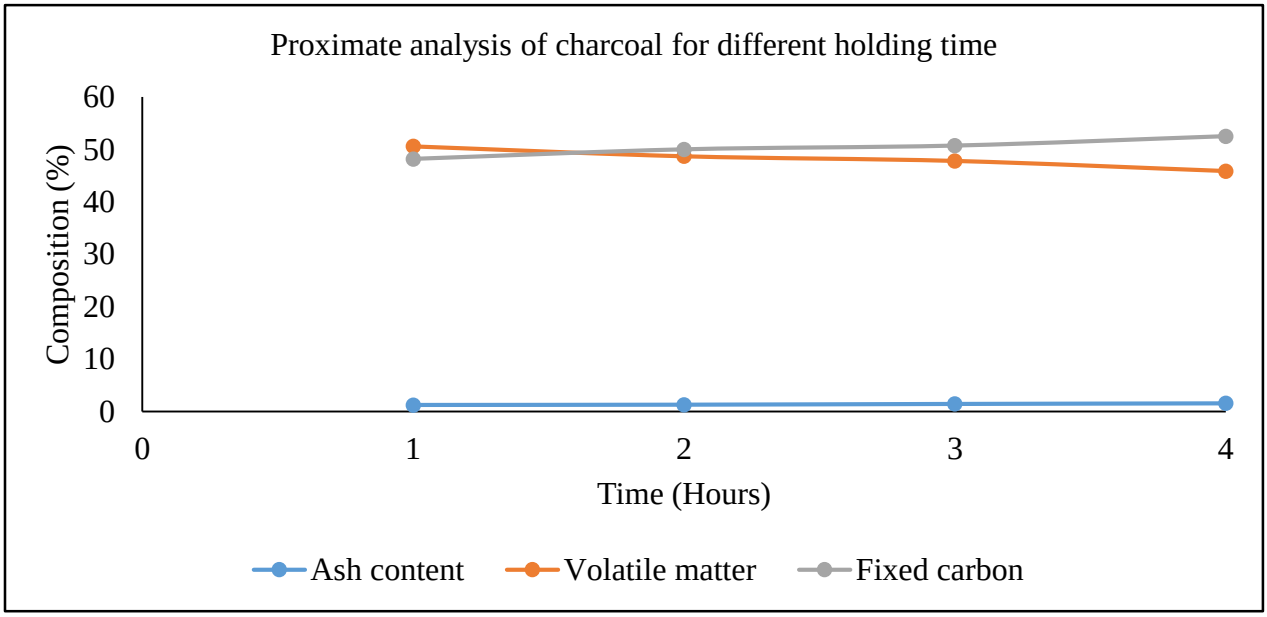

Figure 4.4: Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 600^{o}C

Generally, the results showed that Prosopis juliflora charcoal possessed a very low ash, appreciable calorific value and high fixed carbon content. The results revealed that carbonized Prosopis juliflora can be used as an alternative fuel to partially substitute the existing imported coal in the cement industries.

4.2. Ash Chemistry of Prosopis wood and charcoal

From the result of table 4.2 ultimate analysis, for Prosopis juliflora wood, the percentages of calcium oxide, magnesium oxide, iron oxide, aluminum oxide, silicon oxide, Sulphur were 43.64%, 6.27%, 1.21%, 0.79%,4.14% ,0.18 % respectively, while the corresponding values for Prosopis juliflora charcoal were 43.39%, 7.31%, 2.41%, 0.93%, 4.43%, 0.11% respectively.

The results were obtained from the residue ash of the proximate analysis by wet analysis. As it is known that chemical composition of ash is determinant factor to thermo-chemical conversion and the availability of metals in ash can cause corrosion and fouling problem. The results of ash chemistry for Prosopis juliflora revealed that it has low amount of metal oxides compared with coal as mentioned in the literature. So, Prosopis juliflora was not significant effect for fouling and corrosion problem and provides better thermal conversion.

Since Sulphur content is one of the elements to be studied in coal, it was important to identify its value and it was found to be 0.18% and 0.11% for prosopis wood and prosopis charcoal respectively. This result confirmed with the statement of Cortés that low Sulphur content varies from 0.1 to 1.0 % wt, medium content values are between 1% and 3% and over 3% of Sulphur, coals are considered to have a high content of Sulphur (Cortés et al., 2009). From the results of the two conditions above, their sulfur contents were found between 0.1 to 1% which was categorized as low sulfur content.

Table 4.2: ultimate analysis

Sample	Prosopis juliflora dried wood	Prosopis juliflora charcoal
CaO (%)	43.64	43.39
MgO (%)	6.27	7.31
Fe_2O_3(%)	1.21	2.41
Al_2O_3(%)	0.79	0.93
SiO_2(%)	4.14	4.43
Sulphur (%)	0.18	0.11

4.3. Thermo-Gravimetric Analysis

Thermogravimetric Analyzer (TGA) was used to measure weight changes in a material as a function of temperature under a controlled atmosphere.

It is expected that increasing amounts of energy will be generated from the direct combustion of biomass residues. However, biomass combustion processes are known to produce large amounts of bottom ash, resulting in ash storage and disposal problems. The presence of unburned carbon in some bottom ash suggests its potential for beneficial uses, such as an energy source.

The TGA analyses showed that the mass of Prosopis juliflora decreased as temperature increased. The weight loss occurred due to the removal of specific components of the sample such as water, carbonates, aluminates, silicates, oxides, organic carbon and other components under thermal degradation (Kumar A., 2008).

As shown from figure 4.5 the first weight loss was seen between 25 – 110^{o}C as a result of removal of moisture from the sample. Further mass loss up to 270 ^{o}C was observed due to the removal of remaining moisture, carbon monoxide, and volatiles such as tars and other organic carbons. Significant amount of mass loss due to the available organic carbon (char) was seen between the temperatures of 270 to 640^{o}C. The decomposition of mineral components such as carbonates ($CaCO_3$) and some of the other metal carbonates and oxides present in the sample may occur during this phase. Further mass losses did not occur above 640 ^{o}C.

From TGA result it can be concluded that organic carbon or char of Prosopis juliflora was found at carbonization temperatures of 270 to 640^{o}C after extensive amount of moisture removal. Beyond carbonization temperature of 640^{O}C all available organic carbon was degraded.

Figure 4.5 shows that Prosopis juliflora yielded the most intense DSC signal at carbonization temperature of 350^{o}C. This result attributed to the fact that the higher DSC peak is related to the energy density of the sample due to its higher Carbon content. Further increase in temperature beyond 350^{o}C showed the decrease in DSC curve due to degradation of Prosopis juliflora organic content.

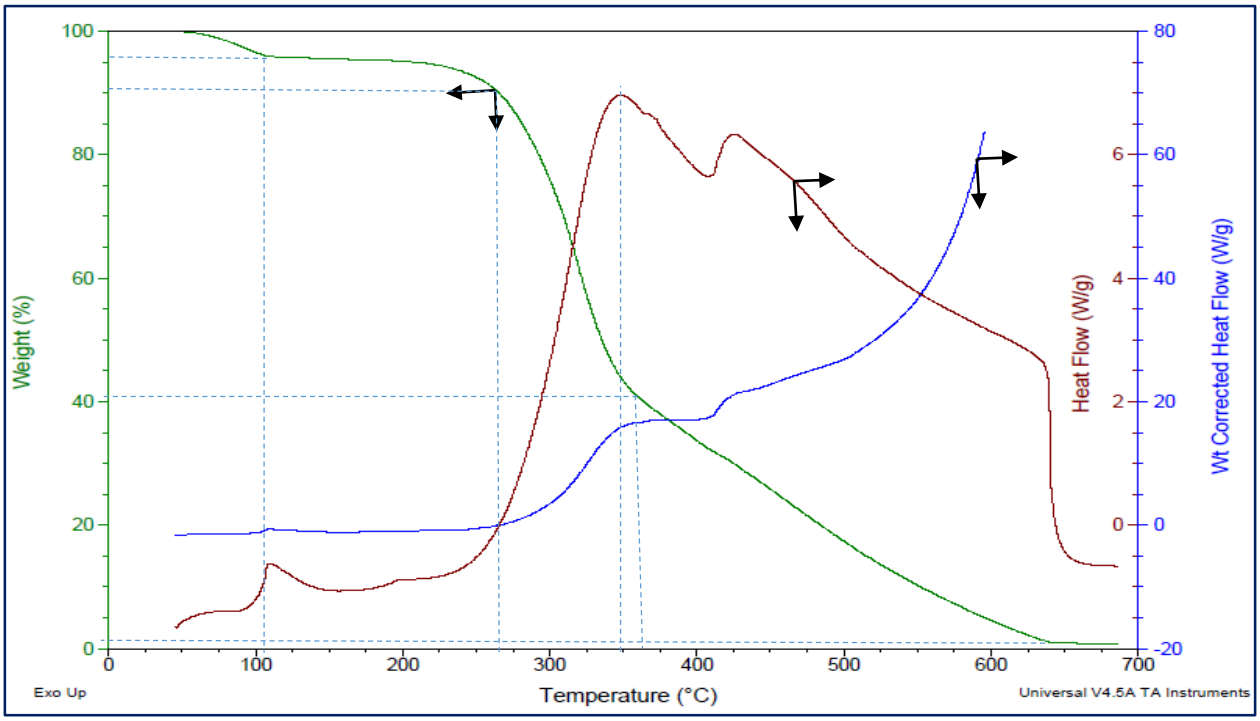

Figure 4.5: DSC-TGA

Table 4.3: Charcoal yield and calorific value of Prosopis juliflora charcoal

	Factors			
Run number	Temperature (^{0}C)	Time (minutes)	Charcoal yield (%)	Calorific value (Kcal/Kg)
1	350	60	75.83	4196
2	350	60	74.21	4234
3	350	60	75.35	4211
4	450	60	58.57	5438
5	450	60	58.43	5321
6	450	60	56.26	5414
7	550	60	41.07	5728
8	550	60	43.02	5625
9	550	60	39.23	5795
10	600	60	36.42	6261
11	600	60	38.57	6223
12	600	60	38.24	6185
13	350	120	70.43	4434
14	350	120	69.23	4325
15	350	120	67.21	4493
16	450	120	50.32	5478
17	450	120	53.23	5424
18	450	120	49.21	5486

19	550	120	35.71	5846
20	550	120	36.24	5860
21	550	120	35.34	5835
22	600	120	35.24	6335
23	600	120	34.23	6266
24	600	120	35.24	6362
25	350	180	63.55	4520
26	350	180	64.65	4596
27	350	180	64.36	4549
28	450	180	48.57	5412
29	450	180	46.32	5486
30	450	180	49.21	5428
31	550	180	35.31	6149
32	550	180	33.24	6055
33	550	180	32.23	6247
34	600	180	33.21	6589
35	600	180	32.11	6576
36	600	180	34.21	6524
37	350	240	60.21	4655
38	350	240	57.42	4697
39	350	240	59.34	4632
40	450	240	44.16	5689
41	450	240	43.24	5523
42	450	240	41.16	5560
43	550	240	32.85	6198
44	550	240	33.54	6258
45	550	240	31.21	6269
46	600	240	32.14	6598
47	600	240	31.13	6633
48	600	240	31.67	6629

The results were replicated three times to improve reliability of the data. The maximum charcoal yield obtained was 75.83% at 350 ^{0}C temperature and 60 minutes of holding time and also the minimum charcoal yield 31.13% was found at 600^{0}C for 240 minutes.

The maximum calorific value obtained was 6620 kcal/kg at 600^{0}C temperature and 240 minutes of holding time and also the minimum calorific value 4196 kcal/kg at 350^{0}C for 60 minutes.

4.4. Energy content of Prosopis juliflora charcoal

Prosopis juliflora wood was carbonized at various temperature range of 350-600^{0}C with correspond to carbonization time of 1-4 hours. For each conditions initially 80g of raw Prosopis juliflora wood was fed to the tubular furnace. After each carbonization time the mass loss, specific calorific value and amount of energy were determined. As it can be seen from table 4.4 the maximum amount of energy was found to be 255.08kcal at carbonization time and temperature of 180 minutes and 350^{0}C respectively. As temperature increased from 350 to 600^{0}C and time rises from 1-4 hours the mass of carbonized Prosopis juliflora decreased due to the removal of more volatile matters which resulted also in decrease of amount of energy. This result indicates that the lower mass of charcoal obtained at a higher temperature was caused by a much larger release of volatile matters, thus giving the lower content of volatile matters in the derived char.

Table 4.4: Energy content of Prosopis juliflora charcoal

Temperature (^{0}C)	Time (minutes)	Mass (kg)	Calorific value (Kcal/Kg)	Total amount of energy (Kcal)
350	60	0.06	4213	252.78
350	120	0.057	4417	251.76
350	180	0.056	4555	255.08
350	240	0.047	4661	219.07
450	60	0.046	5391	247.99
450	120	0.04	5462	218.48
450	180	0.038	5442	206.79
450	240	0.034	5590	190.06
550	60	0.032	5716	182.91
550	120	0.028	5847	163.71
550	180	0.027	6150	166.05
550	240	0.025	6241	156.02
600	60	0.03	6223	186.69
600	120	0.027	6321	170.67
600	180	0.026	6563	170.64
600	240	0.024	6620	158.88

4.5. Effect of parameters on carbonization of charcoal

4.5.1. Effects of carbonization temperature on charcoal yield

The effect of carbonization temperature was analyzed on the percentage of charcoal yield. The temperature range was identified to be 350-600 ^{o}C which is found between 270-640^{o}C as obtained from TGA analysis. As shown from figure 4.5 carbonizing Prosopis juliflora at 350^{o}C yields maximum pick value of energy content. From this result, temperature effect was observed by further increasing of pyrolysis temperatures from 350 up to 600^{o}C. As it can be shown from the figure 4.6, percentage yield of charcoal decreased gradually as carbonization temperature was increased. The maximum charcoal yield was obtained at carbonization temperature of 350^{0}C while the smallest yield was obtained at carbonization temperature of 600^{0}C. This decrease in charcoal yield was more rapid up to temperature of 600°C at which most of the volatile matter was removed. From figure 4.6, charcoal yield decreased from 75.83% to 31.13% as temperature was increased from 350 to 600^{0}C. The results obtained revealed that carbonization of Prosopis juliflora provided maximum charcoal yield at lower pyrolysis temperature. At high pyrolysis temperature charcoal yield was low due to thermal degradation of carbon content of Prosopis juliflora. So, it is better to carbonize Prosopis juliflora at 350^{O}C to obtain maximum charcoal yield.

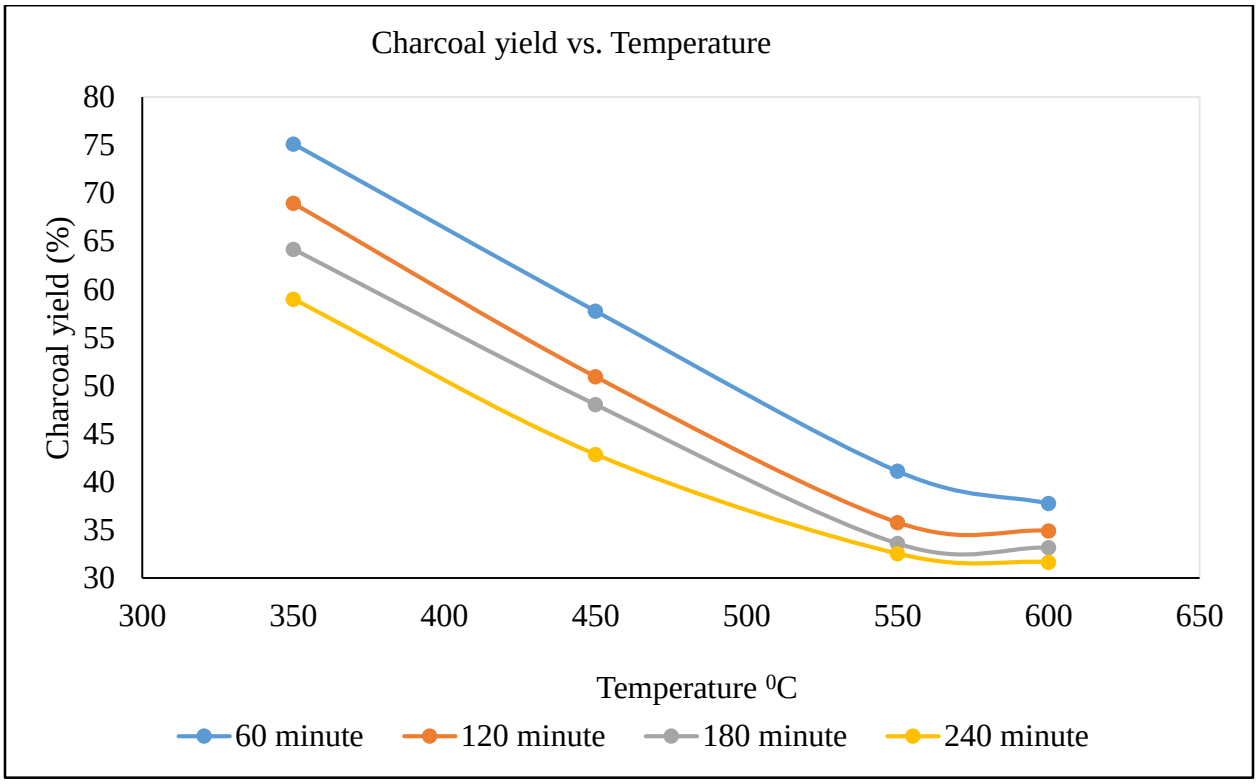

Figure 4.6: Effects of carbonization temperature on charcoal yield

4.5.2. Effects of time on Charcoal yield

The effect of carbonization time was also investigated on the yield of charcoal with its different levels. It was presented in figure 4.7 that with an increased in carbonization time from 1 to 4 hour, charcoal yield decreased from 75.83% to 31.13%. It may be due to the removal of more volatile matter over a long range of carbonization time. High amount of charcoal was obtained at 60 minutes, whereas low amount of charcoal was collected at 240 minutes. It can be interpreted as that an increment of time beyond one hour with a combination of different temperature levels of 350, 450, 550 and 600°C resulted to the loss of volatile matter. As the results suggested that pyrolysis time chosen to be is one hour, beyond which loss of volatile matter and destruction of Carbon content would be resulted.

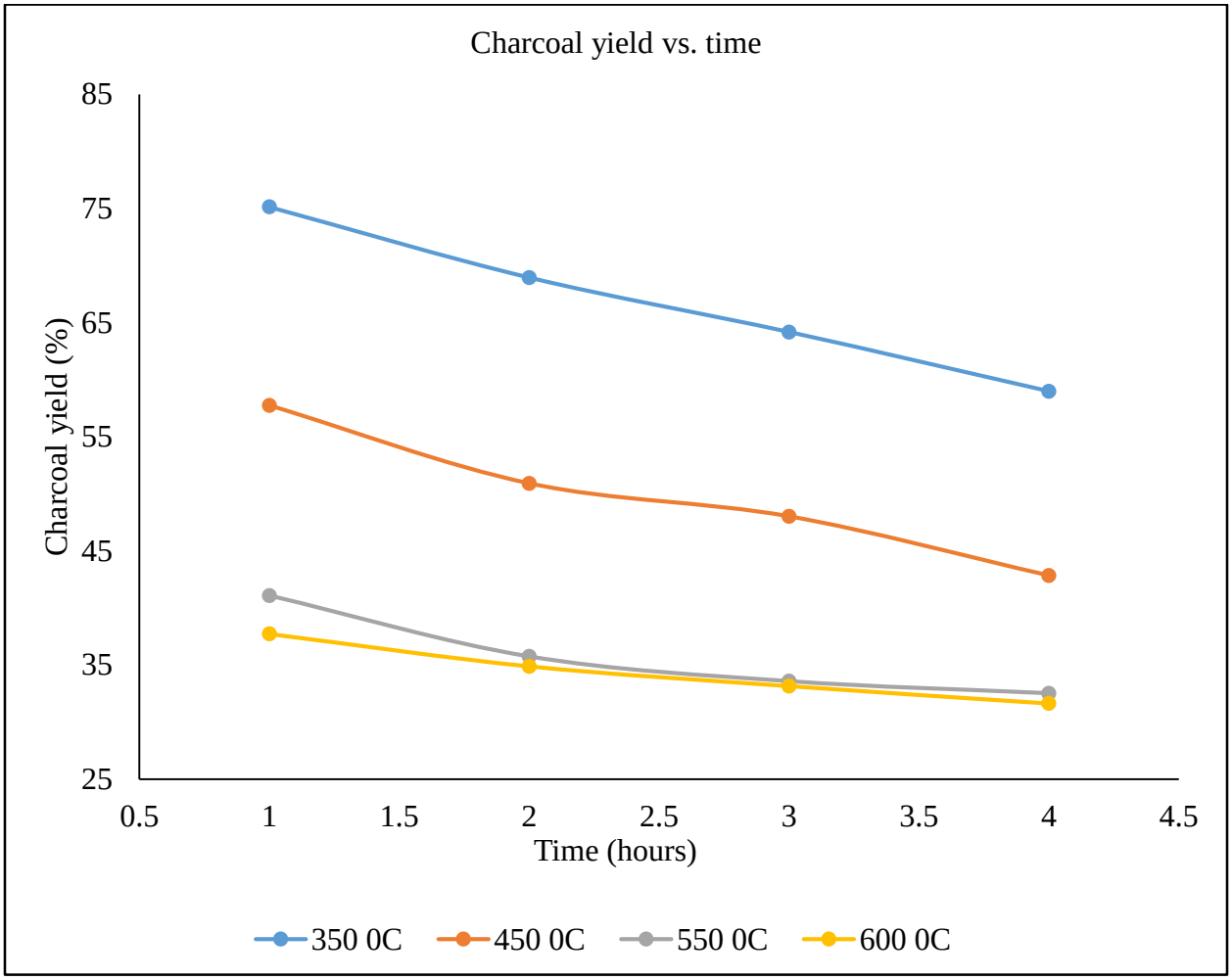

Figure 4.7: Effects of time on charcoal yield at different carbonization temperature

4.5.3. Effects of time on Calorific value

The Calorific value of Prosopis charcoal depends on the holding time. The calorific value of Prosopis was determined at a time interval of 1-4 hours with respect to different carbonization temperatures. At 350, 450, 550 and 600 ^{0}C, the calorific values were in the range of 4213 – 4661, 5391- 5590, 5716 – 6241 and 6223-6620 kcal/kg with correspond to carbonization time of 1, 2, 3, and 4 hours respectively. The difference in results depends on the holding time which is from 1 to 4hours. The maximum calorific value of Prosopis obtained was 6620 kcal/kg at 600 ^{0}C and 240 minutes while the minimum calorific value was 4196 kcal/kg at 350 ^{0}C and 60 minutes. The results revealed that maximum calorific value of Prosopis juliflora charcoal was found at 4 hours. This attributed to the fact that as time increased it provided high energy due to complete burning of charcoal. Further increment of burning time would bring insignificant change in calorific value.

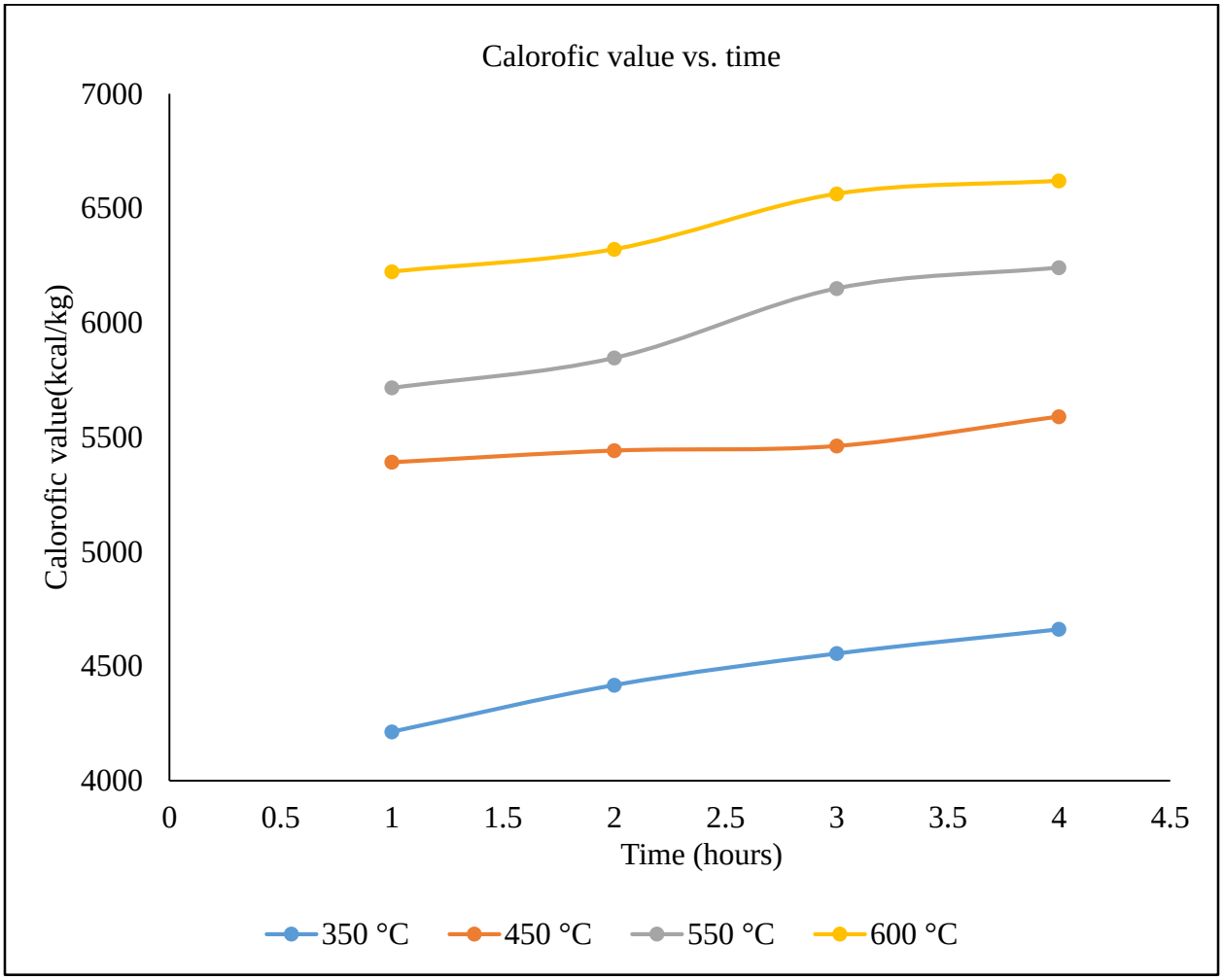

Figure 4.8: Effects of time on calorific value at different carbonization temperature

4.5.4. Effects of carbonization temperature on calorific value

Calorific value can be increases with the increase in temperature. Heating value of Prosopis wood is 4068kcal/kg whereas calorific value of Prosopis charcoal increases from 4213 kcal/kg - 6620 kcal/kg with in carbonization temperature of 350 ^{O}C - 600 ^{O}C. Since Carbonization improved the calorific value. The calorific value of Prosopis charcoal at 350 ^{0}C is 4213 kcal/kg-4661 kcal/kg, depending on the holding time. In holding time of 4 hours the higher heat was 4661 kcal/kg, at 450 ^{O}C (5391-5590 kcal/kg), at 550 ^{O}C (5716 kcal/kg-6241 kcal/kg) and at 600 ^{O}C (6223 kcal/kg-6620 kcal/kg). The results revealed that maximum calorific value of Prosopis juliflora charcoal was found at 600 ^{O}C. This attributed to the fact that as temperature increased it provided high energy due to complete burning of charcoal. Further increment of burning temperature would bring insignificant change in calorific value.

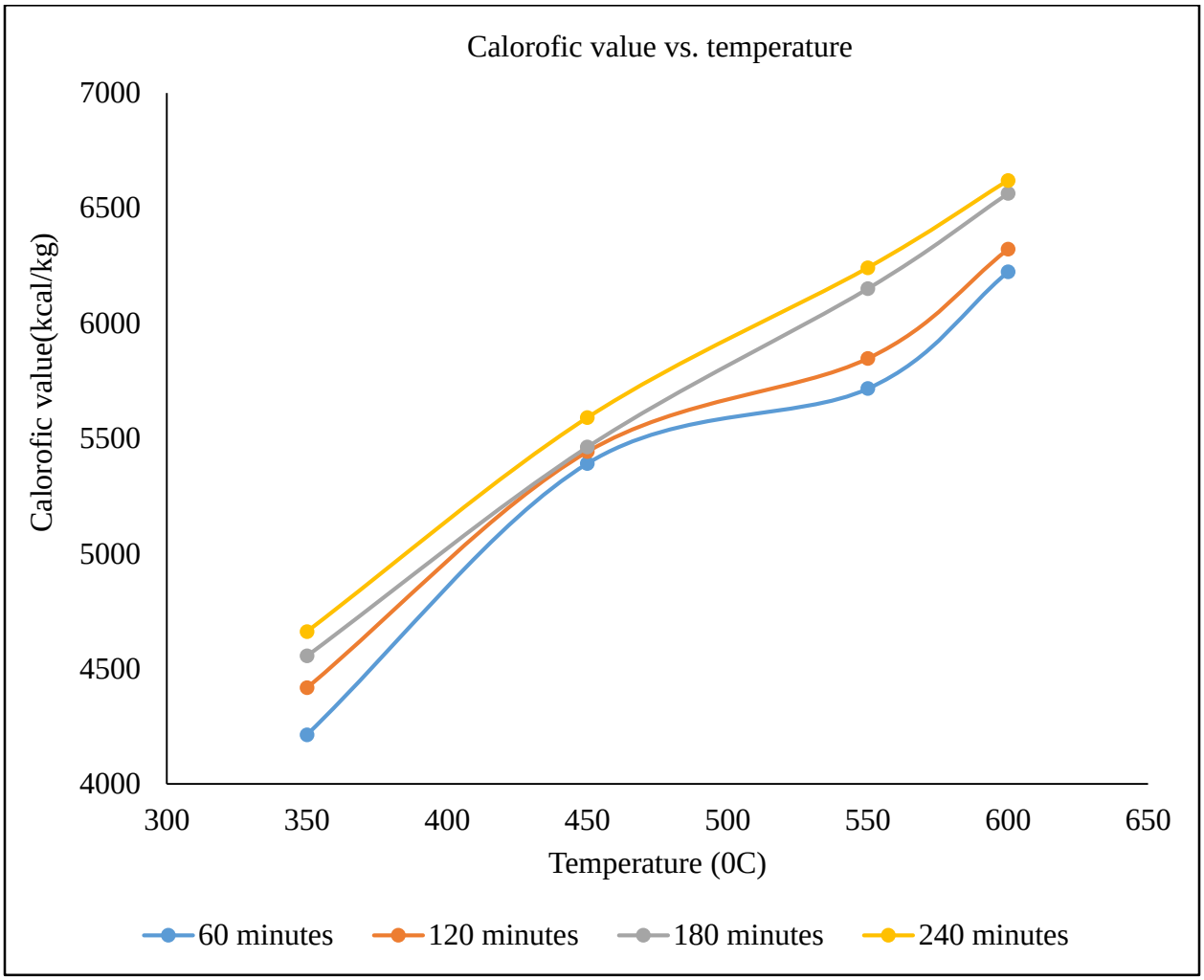

Figure 4.9: Effects of carbonization temperature on calorific value at different holding time

4.6. Comparison of parameters for Laboratory and traditionally produced Prosopis charcoal

The performance of laboratory scale carbonized Prosopis juliflora at controlled parameters of temperature and time was compared with traditionally produced Prosopis charcoal. Prosopis charcoal produced in the laboratory and traditional charcoal were shown in table 4.5. The fixed carbon content and calorific value of laboratory scale carbonized Prosopis juliflora was higher than traditionally produced Prosopis juliflora charcoal. This may be attributed to the fact that earth pits and mounds do not have good insulation, as a result large heat loss occurs during long period of operation, Long process time and poor process control (Nahayo et al., 2013).

Table 4.5: Comparison of traditional Prosopis juliflora charcoal with laboratory scale carbonized Prosopis juliflora

	Traditional system	Laboratory work
Volatile matter (%)	59.01	45.88 - 70.9
Ash content (%)	1.24	0.14 - 1.59
Fixed carbon (%)	39.75	28.91 - 52.53
Calorific value(kcal/kg)	4120	4213 - 6620

4.7. Application of Prosopis juliflora Charcoal as fuel for Cement industry

The results of this study revealed that Prosopis juliflora Charcoal has a good potential for utilization of cement industries as a fuel source. Its general physico-chemical properties were compared with the two coal types obtained from South Africa and Delbi-Moye coal from Jimma, Ethiopia. As it can be shown from table 4.6 the main determinant variables from proximity analysis were appreciable for Prosopis juliflora Charcoal and its energy content was more comparable with the imported coal which is currently utilized as energy source for many cement industries in Ethiopia including Dangote Cement factory. Finally, from the results, it can be suggested that Prosopis juliflora Charcoal can substitute coal by blending it partially. However, its energy content was equivalent to coal, fully substitution may result loss of biomass over short period of times unless it is re-cultivated the plant for energy purpose.

Table 4.6: Comparison of proximate analysis and calorific value results of South Africa and Delbi-Moye coal

	South Africa coal	Delbi- Moye coal
Moisture content (%)	6	8
Volatile matter (%)	28.32	32.12
Ash content (%)	11.04	19.85
Fixed carbon (%)	54.64	40.03
Calorific value(kcal/kg)	6490	4271

4.8. Data analysis using Design Expert 6.0.8 software

The following effects were considered carbonization temperature and time on charcoal yield and calorific value of Prosopis charcoal has been discussed. Initially two factors and four levels were selected to give a total experimental runs of 16 with two response variables. The results were replicated three times to improve reliability of the data and that resulted to perform 48 experiments. Then here, the resulted data is going to be analyzed to determine the significant factors of experimental work using Design Expert 6.0.8 software.

The factorial design results for two response variables also confirmed in the ANOVA analysis given by p value. The p values for factor A and B are 0. 0001 as shown from table 4.7 values of "prob > F" less than 0.0500 indicate model terms are significant. In this case A(temperature), B(time), A*B (temperature and time) are significant model terms.

A part of study is also to generate a model that fits experimental data Using the results of experimental design study, the predictive capability of the model was also studied figures (4.10 – 4.11) for the two response variables considered, the relationship between actual values and predicted values showed that the actual values are distributed relatively near to the straight line, indicating good fitness of the model.

The differences between the experimental and the predicated values for two responses charcoal yield and calorific value were also determined and are shown in figures (4.12 – 4.13) and contour plots for two variables were also generated in figures (4.14 – 4.15) these graphs shows that for the first response variable (charcoal yield),there is interaction between the two factors and also for the second response variable (calorific value), the interaction between two factors is significant indicating that the two factors are dependent.

Table 4.7: Analysis of variance (ANOVA) for the response charcoal yield and calorific value of Prosopis juliflora

a) Charcoal yield (R=0.9942), b) Calorific value (R =0.9965)

a)						
Source	Sum of squares	Degree of Freedom	Mean square	F Value	Prob > F	
Model	9207.756715	15	613.850448	362.54222	< 0.0001	significant
A	8242.008373	3	2747.33612	1622.5863	< 0.0001	
B	846.2607063	3	282.086902	166.60151	< 0.0001	
AB	119.4876354	9	13.2764039	7.8410906	< 0.0001	
Error	54.18186667	32	1.69318333			
Total	9261.938581	47				
b)						
Source	Sum of squares	Degree of Freedom	Mean square	F Value	Prob > F	
Model	27132049.31	15	1808803.288	604.605492	< 0.0001	significant
A	25851814.9	3	8617271.632	2880.38494	< 0.0001	
B	1111930.229	3	370643.4097	123.890222	< 0.0001	
AB	168304.1875	9	18700.46528	6.25076485	< 0.0001	
Error	95734.66667	32	2991.708333			
Total	27227783.98	47				

A= temperature and B= Time

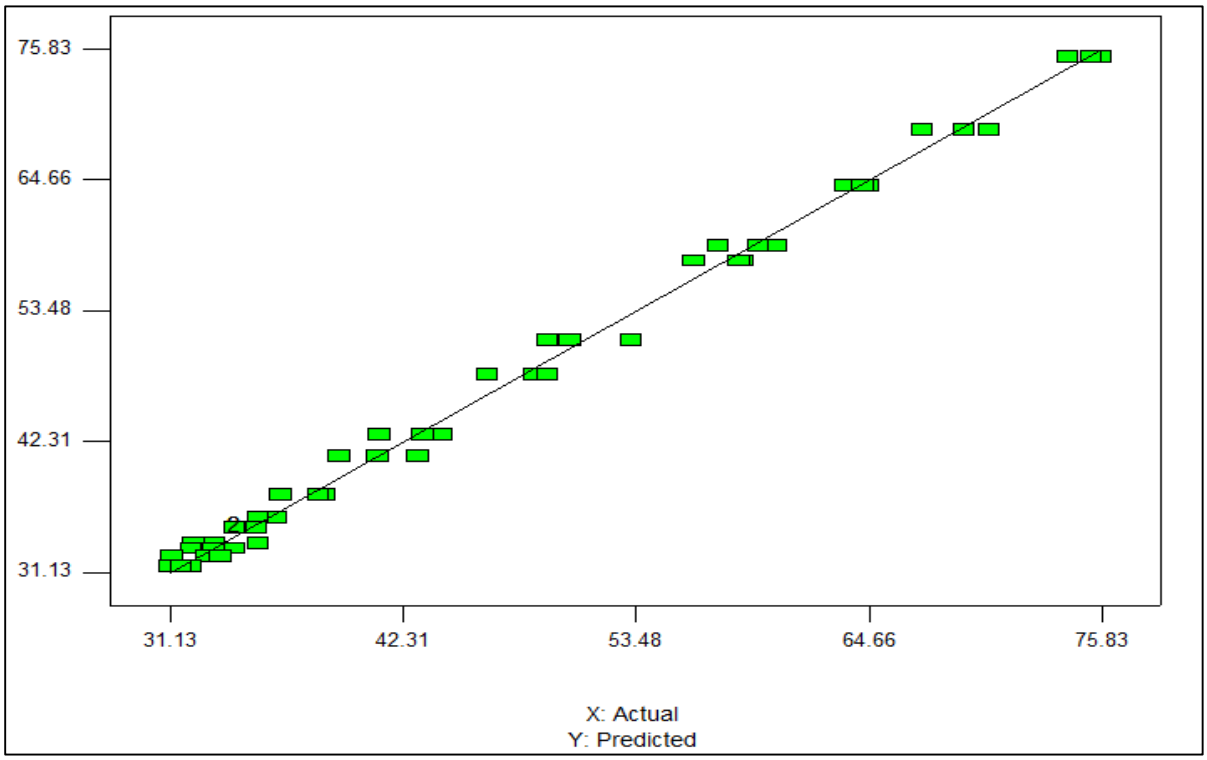

Figure 4.10: Charcoal yield (Actual and Predicted)

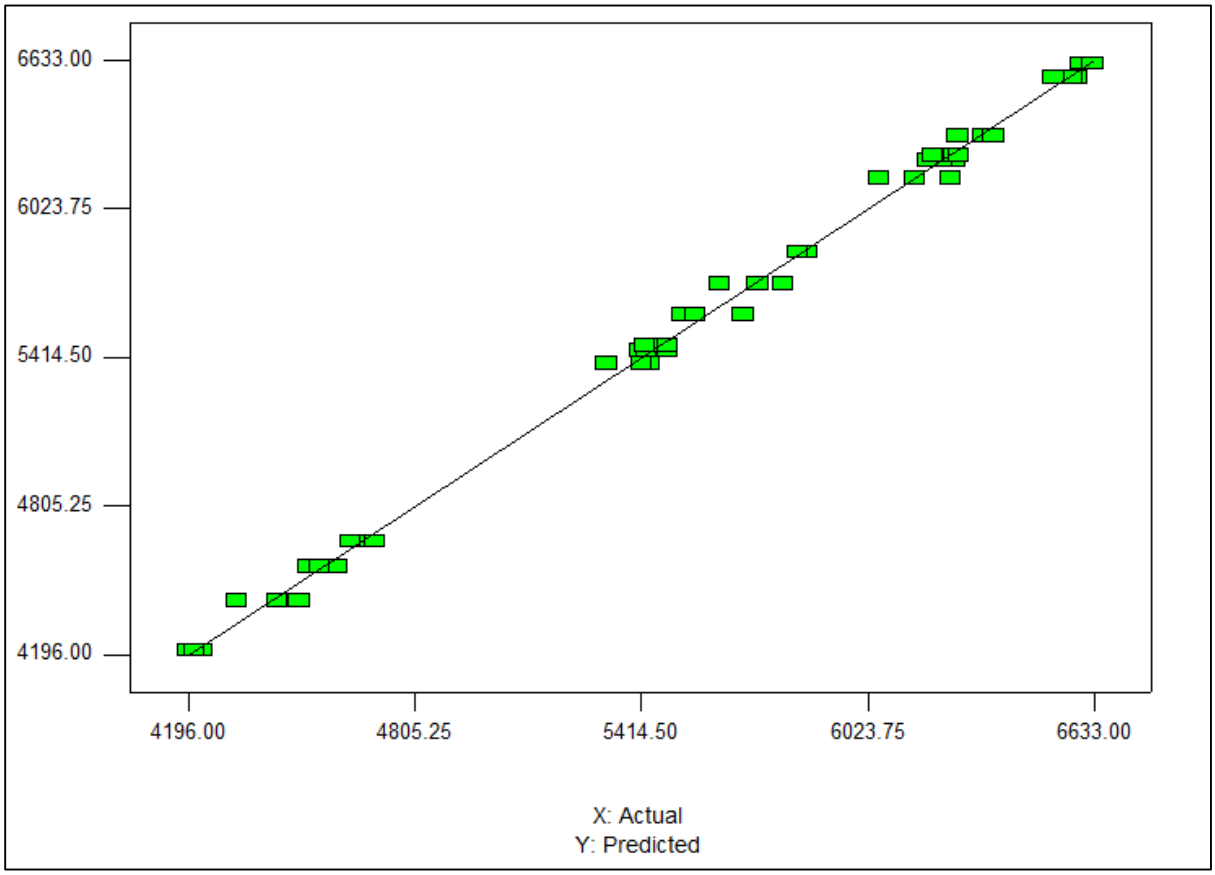

Figure 4.11: Calorific value (Actual and Predicted)

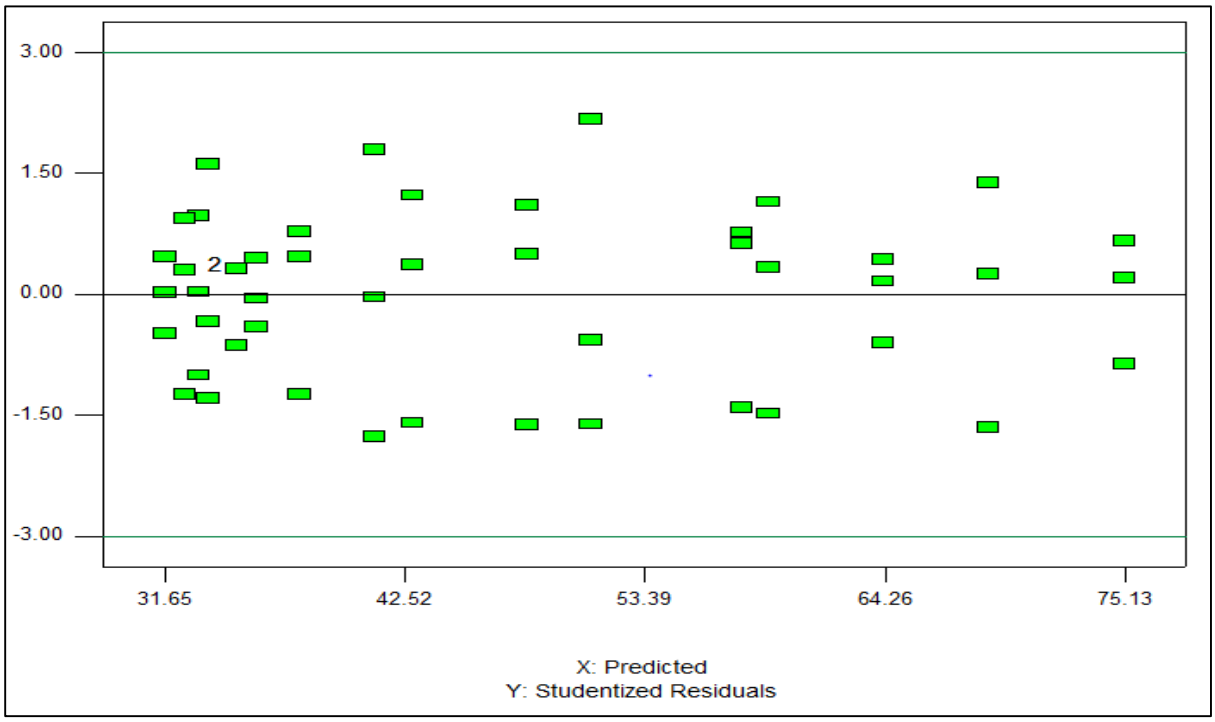

Figure 4.12: Residuals vs. Predicted Values for Charcoal yield

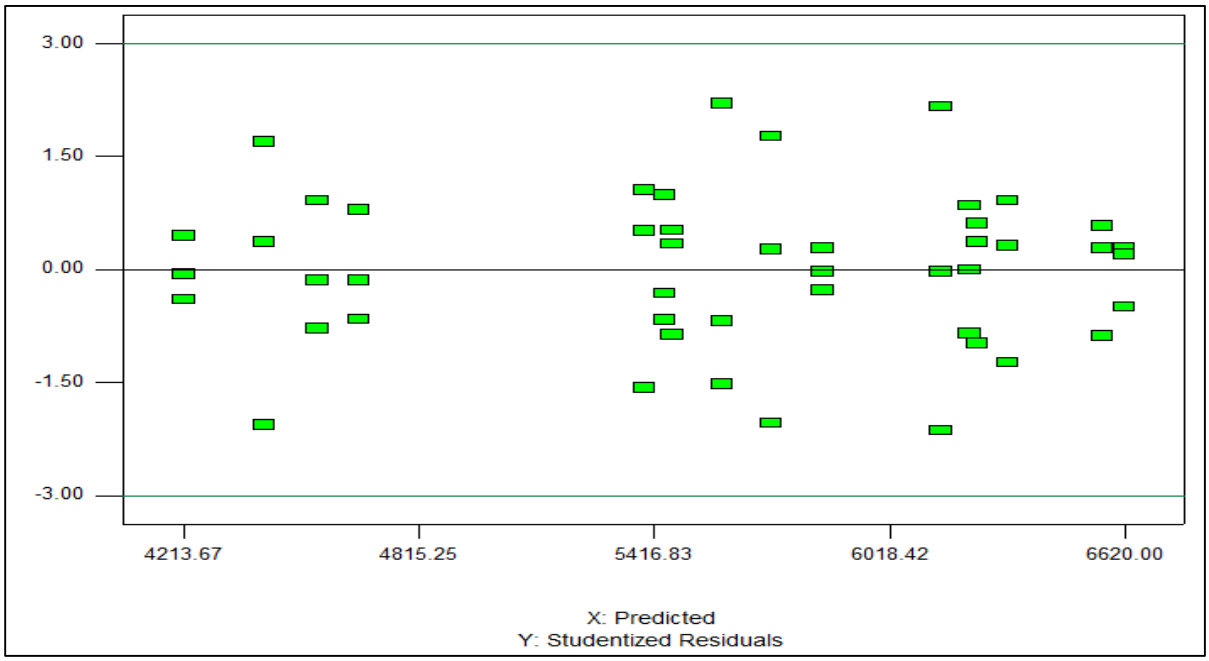

Figure 4.13: Residuals vs. Predicted Values for Calorific value

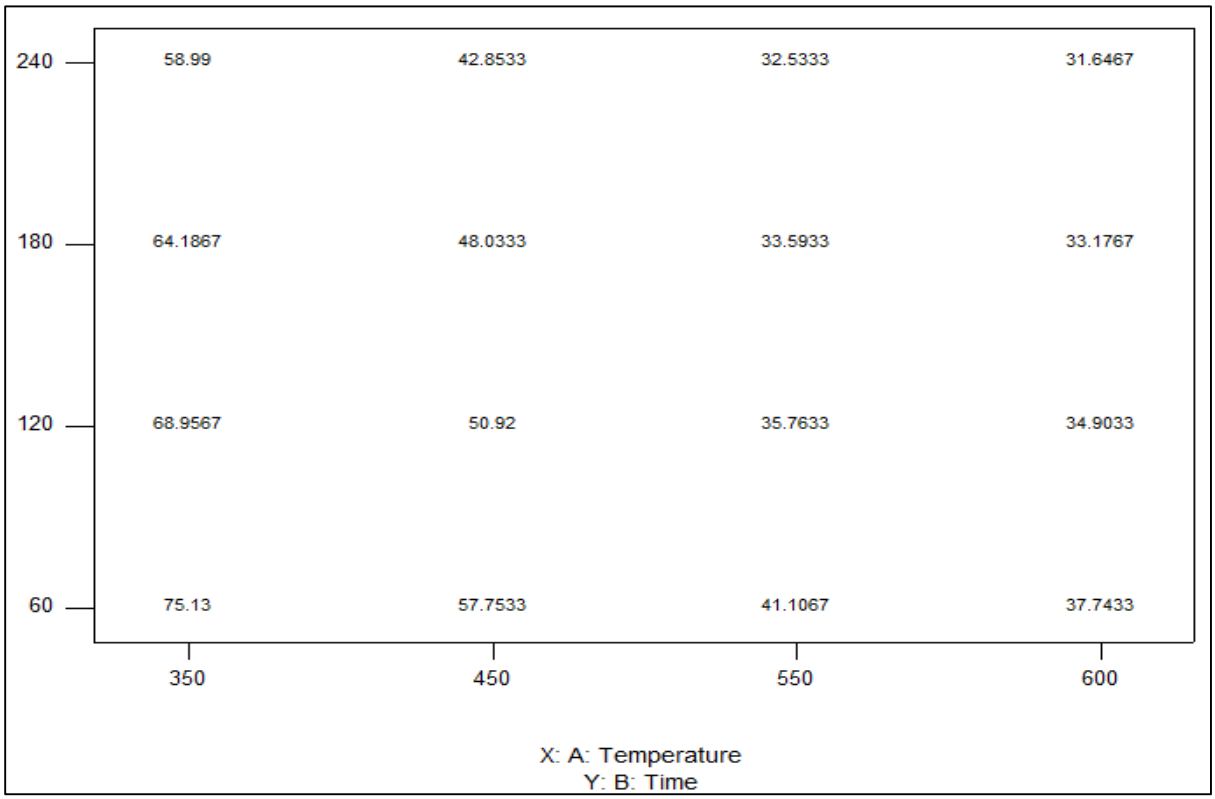

Figure 4.14: Contour plots for Charcoal yield

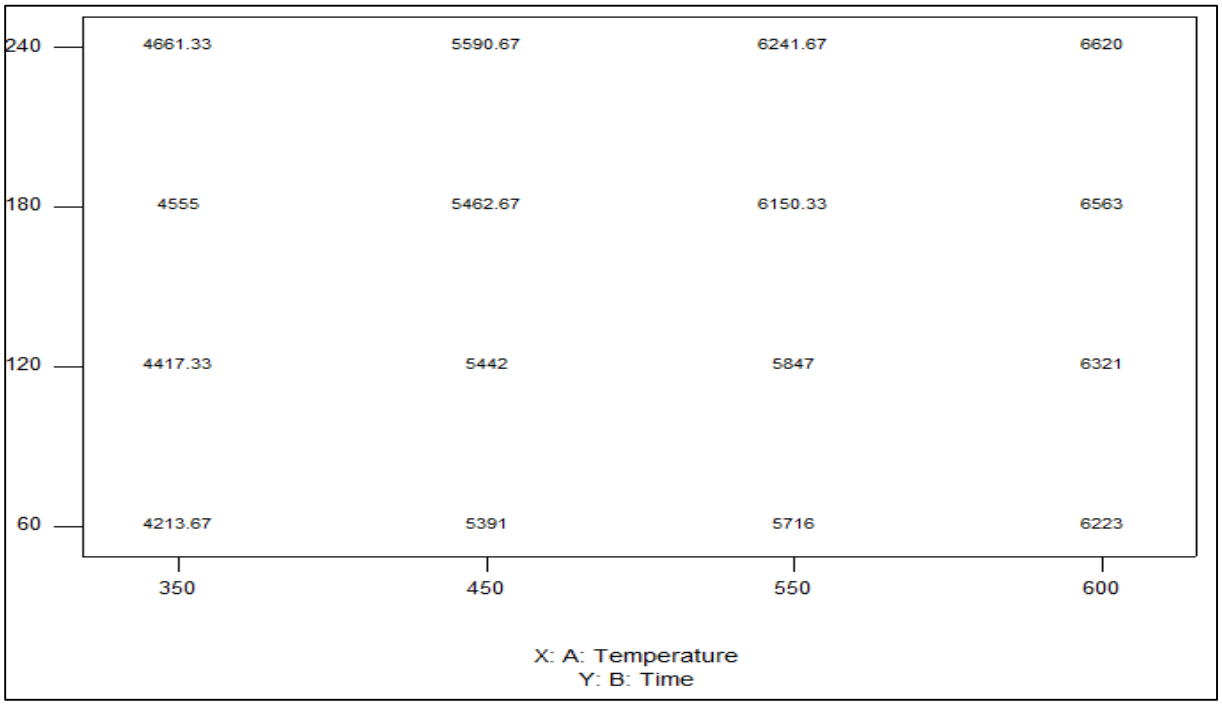

Figure 4.15: Contour plots for Calorific value

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The finding of this work suggests that high amount of calorific value can be produced from carbonization of Prosopis juliflora at controlled variables of time and temperature. The study shows that fixed carbon content and calorific value of laboratory scale carbonized Prosopis juliflora is higher than traditionally produced Prosopis juliflora charcoal whereas ash content of traditionally produced Prosopis juliflora charcoal was greater than laboratory scale carbonized Prosopis juliflora. This can be justified that traditional kilns with no proper insulation, large heat loss occurs during long period of operation and poor process control.

The proximate analysis results indicate that increasing carbonization temperature and holding time results in reduced volatile matter content and increased fixed carbon and ash content. Prosopis juliflora charcoal possesses a very low ash, low moisture content, appreciable calorific value and high fixed carbon content. Carbonization temperature has a significant effect on the percentage of charcoal yield when temperature increases from 350^0C to 600^0C, the charcoal yield decreases from 75.83% to 31.13%. On the other hand, as time increases charcoal yield decreases due to higher rate of the removal of volatile matter.

Calorific value for Prosopis charcoal increases from 4213 kcal/kg - 6620 kcal/kg with a carbonization temperature of 350 ^{O}C - 600 ^{O}C whereas Prosopis wood yields a calorific value of 4068 kcal/kg. The maximum amount of energy was found to be 255.08 kcal at carbonization time and temperature of 180 minutes and 350^0C respectively. The calorific value obtained for Prosopis charcoal is within the range of ordinary coal imported from South Africa. It can be concluded that cement industries can carbonize Prosopis juliflora wood at 350^{o}C and 180 minutes and use it blending with a significant proportion of ordinary coal imported from abroad.

5.2. Recommendation

The present study was concentrated on Prosopis juliflora charcoal production for the purpose of energy utilization in cement industries. Other related research works in this area are suggested to be carried out in future.

- Since the benefit of Prosopis juliflora assured as energy source, its management and utilization mechanism should be established between different concerned institutions and community members within the country.
- To reduce the negative impacts and to control the wide spread of invasive species of Prosopis juliflora, the cement industries should use the species as alternative energy. It can be achieved through the production of its charcoal by regulating all affecting parameters, hence job opportunities can be created in supplying of well-produced charcoal to cement factories.
- Prosopis juliflora is found in many parts of the country. Therefore, further studies are suggested to know the overall social and environmental impact of the plant and its rates of expansion.
- Similar type of study need to be extended for another woody biomass species available in the local area.

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APPENDIX

Appendix A

Table A1: Proximate Analysis of charcoal obtained from Prosopis wood for different time periods and a temperature of 350°C

Carbonization Temperature	Holding Time (hours)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)
350	1	0.19	70.9	28.91
350	2	0.23	70.52	29.25
350	3	0.46	69.2	30.34
350	4	0.39	69.25	30.36

Table A2: Proximate Analysis of charcoal obtained from Prosopis wood for different time periods and a temperature of 450°C

Carbonization Temperature	Holding Time (hours)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)
450	1	0.24	65.59	34.17
450	2	0.56	64.44	35
450	3	0.14	63.43	36.43
450	4	0.18	61.37	38.45

Table A3: Proximate Analysis of charcoal obtained from Prosopis wood for different time periods and a temperature of 550°C

Carbonization Temperature	Holding Time (hours)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)
550	1	0.75	56.55	42.7
550	2	0.54	56.26	43.2
550	3	1.21	54.7	44.09
550	4	1.27	54.27	44.46

Table A4: Proximate Analysis of charcoal obtained from Prosopis wood for different time periods and a temperature of 600°C

Carbonization Temperature	Holding Time (hours)	Ash Content (%)	Volatile Matter (%)	Fixed carbon (%)
600	1	1.23	50.59	48.18
600	2	1.29	48.7	50.01
600	3	1.46	47.81	50.73
600	4	1.59	45.88	52.53

APENDIX B

APENDIX B1. Determination of Calorific value of Prosopis juliflora wood

$$Q = \frac{E \times \Delta T - 40}{m1 * 4.185}$$

$$E = \frac{26463 \times 4.185 \times m2 + 40}{\Delta T} \quad E = 14474$$

Where

m_1=mass of the sample (0.5001gm)

m_2=mass of the Benzoic acid tablet

initial temperature = 24.477, final temperature = 25.068

Q= 4068 Kcal/Kg

APENDIX B.2. Determination of oxides of Prosopis juliflora wood

Determination of SiO_2 in the solution

$$\% \ SiO_2 = \frac{vNaOH * T\ SiO2 * 0.5}{M}$$

T SiO_2= C(NaOH) actual concentration of NaOH * 15.02

$TSiO_2$ = 2.1795

$$\% \ SiO_2 = \frac{1.9 * 2.1795 * 0.5}{0.5006}$$

$\% \ SiO_2$=4.14

Determination of Fe_2O_3 in the solution

$$\% Fe_2O_3 = \frac{TFe2O3 * VEDTA}{M}$$

TFe_2O_3= C(EDTA) Actual concentration of EDTA * 79.84

T Value of Fe_2O_3 = 1.2103

$$\% Fe_2O_3 = \frac{1.2103 * 0.5}{0.5006}$$

$\% Fe_2O_3$ = 1.21

Determination of Al_2O_3 in the solution

$$\% Al_2O_3 = \frac{15 - (KVCuSO4) * TAl2O3}{M}$$

K= excess EDTA + consumption of CuSO4

T Al_2SO_3= C(EDTA) Actual concentration of EDTA * 50.98

T value Al_2SO_3= 0.7728

$$\% Al_2O_3 = \frac{1.0204 * 0.015 * 0.7728}{0.5006}$$

$\% Al_2O_3$=0.79

Determination of CaO in the solution

$$\% CaO = \frac{vEDTA * TCaO}{M}$$

T CaO= C(EDTA) Actual concentration of EDTA * 56.08

T value = 0.8501s

$$\% CaO = \frac{25.7 * 0.8501}{0.5006}$$

% CaO=43.64

Determination of MgO in the solution

$$\% MgO = \frac{(vMgO - CaO) * TMgO}{M}$$

T MgO= C(EDTA) Actual concentration of EDTA * 40.31, T value = 0.611

$$\% MgO = \frac{(30.8 - 25.7) * 0.611}{0.5006}$$

% MgO =6.22

APENDIX B.3. Determination of oxides of Prosopis juliflora Charcoal

Determination of SiO_2 in the solution

$$\% \ SiO_2 = \frac{vNaOH * T\ SiO2 * 0.5}{M}$$

T SiO_2= C(NaOH) actual concentration of NaOH * 15.02

$TSiO_2$ = 2.1122

$$\% \ SiO_2 = \frac{2.1 * 2.1122 * 0.5}{0.5003}$$

$\% \ SiO_2$=4.43

Determination of Fe_2O_3 in the solution

$$\% \ Fe_2O_3 = \frac{TFe2O3 * VEDTA}{M}$$

TFe_2O_3= C(EDTA) Actual concentration of EDTA * 79.84

T Value of Fe_2O_3 = 1.21073

$$\% \ Fe_2O_3 = \frac{1.2073 * 1}{0.5003}$$

$\% \ Fe_2O_3$ = 2.41

Determination of Al_2O_3 in the solution

$$\% \ Al_2O_3 = \frac{15 - (KVCuSO4) * TAl2O3}{M}$$

K= excess EDTA + consumption of CuSO4

T Al_2SO_3= C(EDTA) Actual concentration of EDTA * 50.98

T value Al_2SO_3= 0.7709

$$\% \ Al_2O_3 = \frac{15 - (1.0135 * 14.2) * 0.7709}{0.5003}$$

$\% \ Al_2O_3$=0.9373

Determination of CaO in the solution

$$\% \text{ CaO} = \frac{vEDTA * TCaO}{M}$$

T CaO= C(EDTA) Actual concentration of EDTA * 56.08

T value = 0.8484

$$\% \text{ CaO} = \frac{25.6 * 0.848}{0.5003}$$

% CaO=43.39

Determination of MgO in the solution

$$\% \text{ MgO} = \frac{(vMgO - VCaO) * TMgO}{M}$$

T MgO= C(EDTA) Actual concentration of EDTA * 40.31

T value = 0.6095

$$\% \text{ MgO} = \frac{(31.6 - 25.6) * 0.6095}{0.5003}$$

% MgO =7.31

Determination of Sulphur

$$\% \text{ Sulfur} = \frac{(M2 - M1) \times 0.1373}{M}$$

Where; M_1= mass of the crucible before burning

M_2= mass of the crucible after burning

M=mass of the Prosopis sample

$$\% \text{ Sulfur} = \frac{(16.5774 - 15.7831) \times 0.1373}{1.009}$$

% Sulfur= 0.11%

Appendix C: Laboratory work pictures

Prosopis juliflora

Grinded Prosopis juliflora

Centrifugal mill

SDT Q600 Thermogravimetric analysis

Bomb calorimeter

Milling machine

Prosopis juliflora charcoal

Grinded Prosopis juliflora charcoal

Chemicals used for determination of oxides

Preparation of solution


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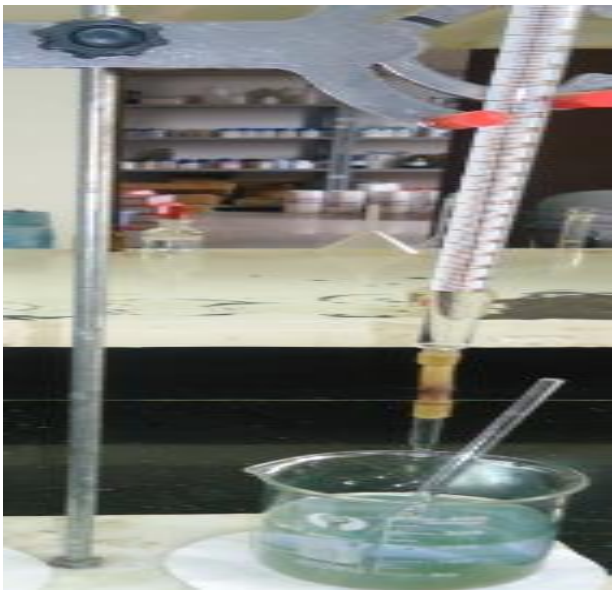
Preparation of solution to determine oxides

Determination of MgO in the solution



Determination of SiO_2 in the solution