North American Academic Research

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Research

Synthesis of Charcoal from *Prosopis juliflora* for Energy Use in Cement Industries

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***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, ultimate analysis and calorific value of Prosopis juliflora wood and its laboratory and traditionally produced charcoal were analyzed. Thermo-chemical decomposition behavior of Prosopis juliflora was carried out in the temperature range of 25 -700°C at the heating rates 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 was obtained 6620 kcal/kg at 600°C and 240 minutes of holding time and the minimum calorific value was 4196 kcal/kg at 350°C and 60 minutes.*

***Keywords**: Prosopis Juliflora, charcoal, cement industry*

1. INTRODUCTION

Cement has played a key role as a construction material throughout the history of civilizationCement production is an energy-intensive process (Cembureau, 1997). coal is the predominant fuel burned in cement kilns (Chinyama, 2011). Since coal is carbon-enriched materials, (CO_2) is released during burning process. Carbon dioxide is primary greenhouse gas that drives global climate change in a significant amount (Ali et al., 2011).

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 & Uliasz-bochen, 2003). Cement factories can potentially use alternative fuels, including biomass and biomass residues, to heat their kilns(Chinyama, 2011).

Biomass is one of the most promising renewable energy sourcesand 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).

Among the wide range of biomass species Prosopis juliflora (mesquite) has been proposed as energy source by different researchers. It is a tropical and subtropical tree and shrub, mainly found in the arid and semi-arid regions 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).

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 mesquite while the other one supports eradication and control (Magid et al., 2014).

In the case of Ethiopia, Prosopis juliflorais largely employed for: charcoal production, fuelwood, construction wood, providing timber, livestock feed, shade and shelter (Kathirvel & Kumudha , 2011). Conversely, it takes over pasture lands and irrigable areas; mechanical injuries by sharp and poisonous thorns; livestock lost in thicket missing their way out; destruction of indigenous trees and pasture species; blocking access roads; increasing challenges from predators; unrestricted livestock feeding on pods poses health problems; agro pastoralists spend huge amounts of money, time and energy to clear P. juliflora; affecting traditional way of life; puncturing vehicle tire; increasing malaria cases have identified bad (Argaw, 2015)

As it can be seen from (Argaw, 2015) statements, Prosopis juliflora socio- economic disadvantages has become critical and needs a control mechanism. Since it has high quality of calorific value(Mwangi & Swallow, 2005), it can replace coal partially for cement industries.

In Ethiopia the use of energy in the cement manufacturing process produces large amounts of CO_2, SO_2 and particulate matter (PM) emissions. The 2010 CO_2 emissions from fuel, electricity use and process emissions (calcination of limestone) are estimated at 513 kt CO2, 1.1 kt CO2, 853 kt CO2, resulting in an annual emission of 1.4Mt CO2 (Tesema & Worrell, 2015).

Generally, in view of energy & environmental problems associated with the use of fossil fuels, attempts have been made to develop biomass energy source for cement industries such as application of seismic husk as fuel in Messebo cement factories.

The aim of this study was to prepare charcoal as fuel source from Prosopis julifloraand use it as energy mix in cement industries.

2. MATERIALS AND METHODS

2.1. Source of Prosopis juliflora sample

The main raw material, Prosopis juliflora was collected from Gewane, Afar regional state of Ethiopia. GewaneWeredais 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 minimaof 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 %.

2.2. Experimental equipment and chemicals

The equipmentused during the experimentations were cutter, crusher mill, sieves, electronic balance, ceramic crucibles, oven, muffle furnace, desiccators, tubular furnace with a stainless steel tubular reactor, thermogravimetric analyzer,bomb calorimeter.Equipment were obtained from different research institutes and organization at where laboratory analysis was performed.

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 used were analytical reagent grades and bought from different chemical stores in Addis Ababa.

2.3. Experimental procedure

Sample preparation

Raw Prosopis juliflorawas 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 (3× 3× 3) cm 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.

2.4. 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 the 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 expressed as moisture content in the sample. The moisture content of sample was calculated by following formula (ASTM, 93).

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

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 cruciblewascovered 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, 93).

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

Where; W_1 =Weight of crucible

W_2=Weight of crucible and sample

W_3=Weight of crucible &residual content

III. Ash content

It was determined by weighing one grams of finely ground, dried samples into a pre-ignited and previously weighed ceramic crucible, 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 to be determined by using the following formula (ASTM, 93).

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

Where; W_1=Weight of crucible

W_2 = Weight of crucible + Weight of sample before ashing

W_3= Weight of crucible + ash

Fixed carbon

The residue remaining after volatile matter release has been expelled, contains the mineral matter originally present and nonvolatile or fixed carbon. The fixed carbon was thus calculated as follows (ASTM, 93).

$$\%FC = 100 - (\text{Ash} + \text{volatile content} + MC)$$

Where; FC=fixed carbon

MC =moisture content

2.5. 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.

Determination of oxides

Oxides determination were done by measuring0.5gm 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 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

$$\% \ SiO_2 = \frac{vNaOH \ *T \ SiO\,2*0.5}{M}$$

Where

M=mass of the ash

V=volume of the solution

- ✓ **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

$$\% \ Fe_2O_3 = \frac{TFe\,2O3*VEDTA}{M}$$

- ✓ **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

$$\% \ Al_2O_3 = \frac{\frac{20}{15} - (KVCuSO\ \ 4)*TAl\,2O3}{M}$$

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;

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

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;

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

- ✓ **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 D3177).

$$\text{Sulfur(S)} = \frac{(\text{M}2 - \text{M}1) \times 0.1373}{\text{M}} \times 100$$

Where; M_1= mass of the crucible before burning

M_2= mass of the crucible after burning

M=mass of the Prosopis sample

2.6. 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.

2.7. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a SDT Q600. 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.

2.8. Carbonization of Prosopis juliflora wood

Prosopis juliflora wood pieces of (3× 3 × 3) cm 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 such as at 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:

$$\text{Charcoal yield} = (A / B) \times 100$$

Where, A = weight of charcoal after pyrolysis

B = fresh biomass before pyrolysis

2.9. 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).

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

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

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

3. RESULT AND DISCUSSION

3.1. Characterization of Prosopis juliflora

A proximate analysis and ash chemistry of Prosopis wood and charcoal were shown in Table 4.1 and 4.3. The proximate analysis determines only the volatile matter, ash content, moisture content, fixed carbon and ash chemistry determines the elemental composition of the sample.

Table 1. Proximate analysis

Sample	Prosopis juliflora wood	Prosopis juliflora charcoal
Moisture content (%)	7	2.16 - 4.65
Ash content(%)	2.37	0.14 - 1.59
Volatile matter(%)	75.81	41.23 - 68.36
Fixed carbon(%)	14.82	28.91 - 52.53
Calorofic value(kcal/kg)	4068	4213 – 6620

As it can be shown from table 1 moisture content of both Prosopis wood and charcoal was 7% and 2.16% - 4.65% respectively. The values obtained were very small which can be confirmed with the fact that high moisture content lowers the calorific value of charcoal (Patel & Gami, 2012). The lowest amount of Prosopis juliflora wood's moisture content gave a well reduced moisture content of its charcol.This attributed to the reason that high moisture levels lead to reduced charcoal yields so as a greater quantity of biomass must be burnt to dry and heat the feed. (Antal , 2003).

Volatile content of Prosopis wood was found to be 75.81% and that of Prosopis charcoal was 41.23%-68.36%. 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, 2014) 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. Ash, component 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 analysis was obtained which gives a rough estimation of the heating value of a fuel and acts as the main heat generator 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. This implies that fixed carbon content of charcoal was found to be increased from initial biomass. 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, 1996)verified that to enhance the energy in the biomass; the biomass can be converted into charcoal.

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

The calorific value of carbonized Prosopis juliflora was compared with uncarbanized sesamestalk's energy content, which is currently utilized as energy source in Messebo cement. The calorificvalues were in the range of 4213-6620 kcal/kg and 3511 kcal/kg for Prosopis juliflora and sesamestalk respectively. The proximate results obtained were compared with other previous works in table 2.

Table 2.Comparison of proximate analysis and calorific value results of the previous work and the present study

Parameters	(Patel & Gami, 2012)	Present work	
	Biomass	Biomass	Charcoal
Moisture content (%)	7.7	7	2.16 - 4.65
Ash content (%)	0.5	2.37	0.14 - 1.59
Volatile matter (%)	78.9	75.81	41.23 - 68.36
Fixed carbon (%)	12.9	14.82	28.91 - 52.53
Calorific value(kcal/kg)	4237	4068	4213 - 6620

3.2. Proximate analysis of Prosopis charcoal at different parameters

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^{0}C. The experimental results at fixed temperature of 350^{o}C indicated that fixed carbon was in the range of 28.91% -30.36 %, moisture content was from 2.16%-3.25%, ash content was in the range of 0.19- 0.46% and volatile matter was from 66.58 - 68.36%. On the other hand, charring process was observed to be completed in about 4 hours.

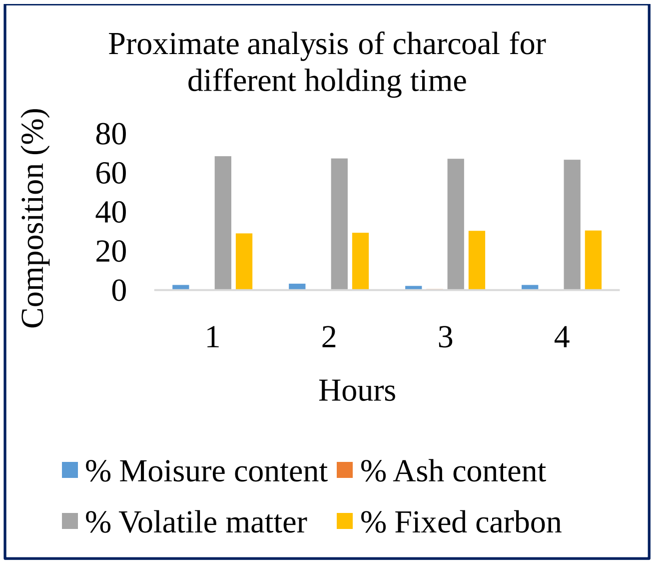

Figure 1. Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 350^{o}C

Proximate analysis of Prosopis charcoal at 450°C was analyzed for fixed carbon, moisture content, ash content and volatile and the values were found to be in the range of 34.17% -38.45%, 2.23%-4.21%, 0.18%- 0.56% and 59.14%–62.23% respectively.

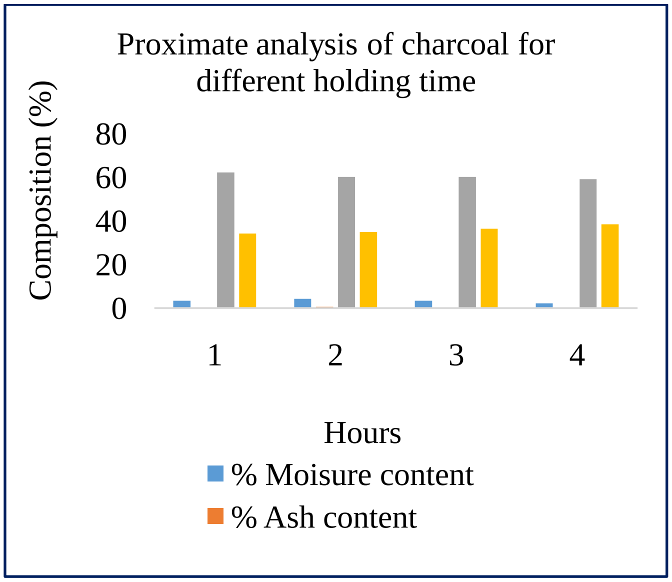

Figure 2. Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 450°C

The experimental results from figure 3 show that fixed carbon of Prosopis were in the range of 42.7% - 44.46%, moisture content from 2.32%-4.23%, ash content were in the range of 0.75% -1.27% and increased with increasing carbonization temperature whereas volatile matter decrease from 54.23% - 50.12%.and also Charring process were observed to complete in about 4 hours.

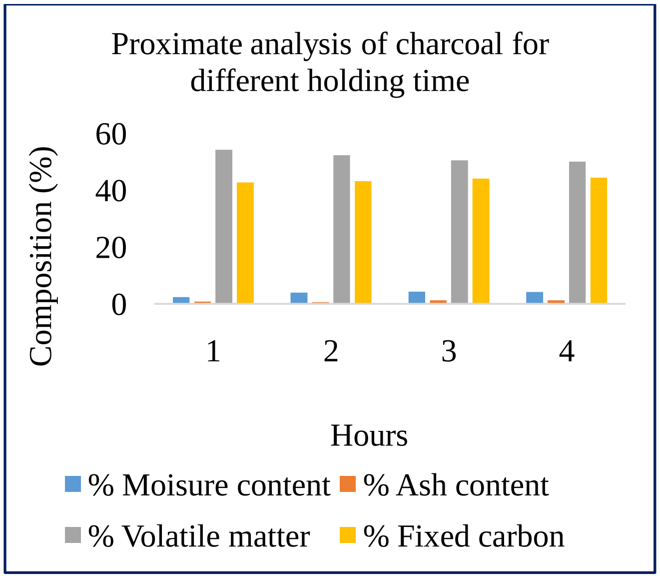

Figure 3. Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 550^{o}C

At 600^{o}C, proximate analysis results were showedover a charring process of about 4 hours. The of resultvalues of fixed carbon, ash content, moisture content, and carbonization temperature were within the range of 48.18% -52.53 %, 2.36%-4.65%, 1.23%- 1.59% and 48.23%–52.53% respectively.

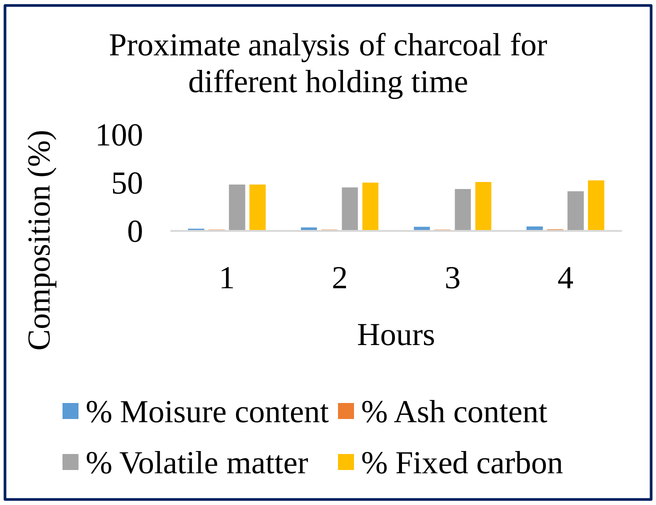

Figure 4. Variation of proximate analysis of charcoal obtained from Prosopis wood for different holding time and at a temperature of 600^{o}C

3.3. 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 was determined to be fixed carbon content, volatile content, ash content and energy content of 28.91-52.53%, 41.23-68.36 %, 0.14-1.59 % and 4213-6620 kcal/kg respectively whereas, traditional charcoal was found to have 25.04%, 62%, 7.96% and 4120 kcal/kg of fixed carbon content, volatile content, ash content and energy content respectively. The fixed carbon content and calorific value of laboratory scale carbonized Prosopis juliflora was 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 may be attributed to the fact that traditional kilns 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 3.Comparison of traditional Prosopis juliflora charcoal with laboratory scale carbonized Prosopis

	Traditional system	Laboratory work
Moisture content (%)	5	2.16 - 4.65
Volatile matter (%)	62	41.23 - 68.36
Ash content (%)	7.96	0.14 - 1.59
Fixed carbon (%)	25.04	28.91 - 52.53
Calorific value(kcal/kg)	4120	4213 – 6620

3.4. Ultimate analysis of Prosopis wood and charcoal

From the result of table 4ultimate 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. To optimize the burning condition and clinker quality, the raw mix design (limestone and clay) feeding rate was depending on the oxide analysis result. On the other hand, the chemical composition of the ash was a determinant parameter to consider for the operation of a thermal conversion unit. This may be due to the problems of slagging, fouling, and corrosion(Mckendry, 2002)

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 et al., 2009) 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. For 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. Ultimate analysis

Sample	Prosopis juliflora 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

3.5. Thermo-Gravimetric Analysis

Thermogravimetric Analyzer (TGA) was used to measure weight changes in a material as a function of temperature under a controlled atmosphere. Figure 5 showed the mass loss curve (TG) of Prosopis juliflora in nitrogen atmospheres as temperature was increased. The loss of weight may be due to dehydration between the temperature range of 30-150°C, volatilization & oxidative degradation between the temperature range of 150-375°C and third one due to char combustion between the temperature range of above 375°C.

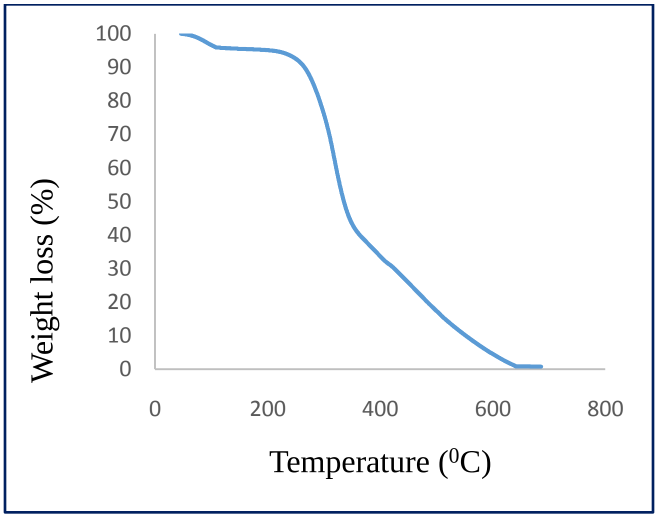

Figure 5. Thermogravimetric plot for Prosopis juliflora at heating rate of 20˚C/min

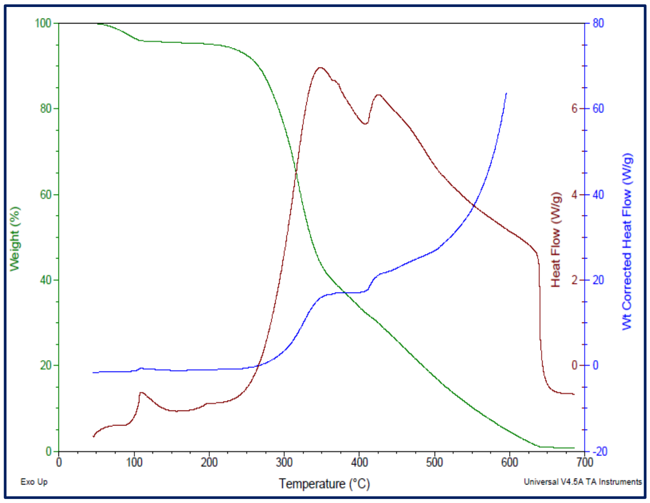

Figure 6. DSC-TGA curve

At a heating rate of 20˚C/min, thermal degradation of Prosopis juliflora was initiated at approximately 150^{o}C and thermogravimetric analysis of Prosopis juliflora wood showed that the mass loss was most dramatic in the temperature of 300-500 ^{0}C. At temperatures of 300, 350 and 500 ^{0}C mass loss was around 70%, 40% and 20% respectively. At a temperature of about at 625 ^{0}C, the devolatization process of sample was almost completed, mass loss was lower than 9%. From figure 6 it can be concluded that the operation of a pyrolysis system was at a terminal temperature of not much more than 700^{o}C.

3.6. Effect of parameters on carbonization of charcoal

Effects of carbonization temperature on charcoal yield

The effect of carbonization temperature was analyzed on the percentage of charcoal yield(Nsamba et al., 2015). As it can be shown from the figure 7, 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 600°C at which most of the volatile matter was removed. From figure 7, charcoal yield decreased from 75.83% to 31.13% as temperature was increased from 350 to 600^{0}C.

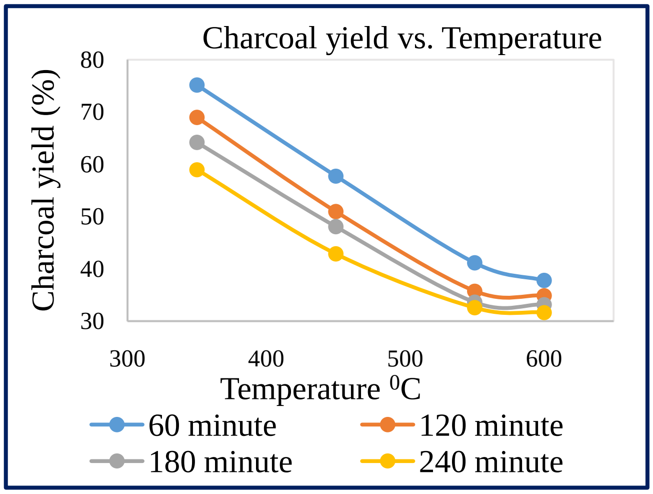

Figure 7. Effects of carbonization temperature on charcoal yield

Effects of time on Charcoal yield

Carbonization time was also investigated on the yield of charcoal with its different levels. It was presented in figure 8 that with an increase in carbonization time from 1 to 4 hour, charcoal yield was 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.

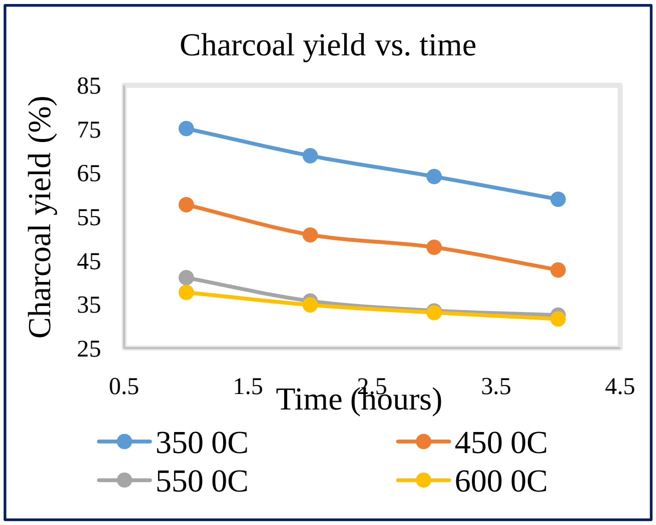

Figure 8. Effects of time on charcoal yield at different carbonization temperature

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 1-4hours 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.

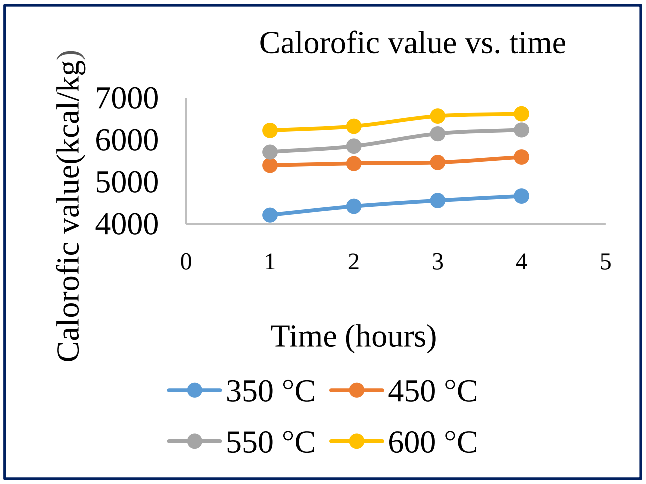

Figure 9. Effects of time on calorific value at different carbonization temperature

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).

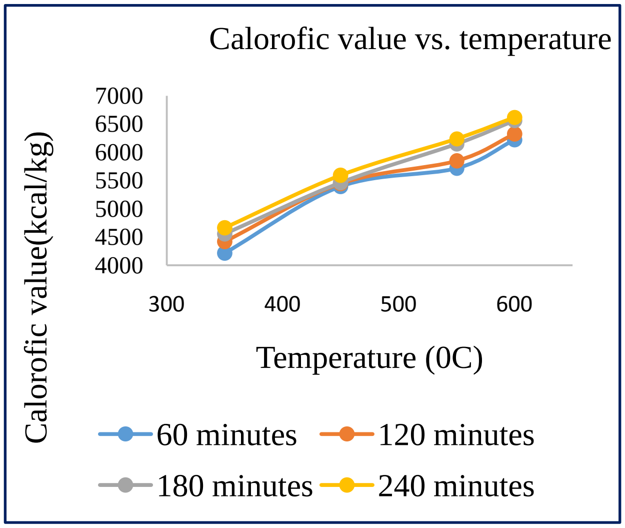

Figure 10. Effects of time on calorific value at different carbonization temperature

3.7. 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 5 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 5.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

4. 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. Prosopis juliflora charcoal possesses a very low ash, low moisture content, appreciable calorific value and high fixed carbon content. The calorific value obtained for Prosopis charcoal is within the range of ordinary coal imported from South Africa. It can be concluded that carbonized Prosopis juliflora can be utilized as fuel in cement industry with a significant proportion of ordinary coal imported from abroad.

AKNOWLEDGMENT

First and most I want to thank God. Then I want to forward my gratitude to everybody who directly or indirectly contribute for the compilation of this research work.

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