

Study of Carbonization for Cashew Nut Shell

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Abstract

Cashew nut shell (CNS) was utilized for carbonization in developed prototype kiln. Prototype kiln was evaluated with direct and indirect methods and characteristics of CNS and CNS char were determined by proximate and ultimate analysis. The maximum CNS temperatures obtained inside the kiln during direct and indirect method were recorded as $452.2^{\circ}C$ and $458.8^{\circ}C$ respectively. Maximum oil percentage, charcoal percentage and ash percentage in direct method were observed as 21.1 per cent, 21.04 per cent and 3.34 per cent respectively whereas 23.8 per cent, 18.3 per cent and 1.27 per cent in indirect method respectively. Hydrogen content in CNS was found about 6 to 7 per cent and nitrogen content in CNS was found about 0.70 to 0.75 per cent. Oxygen content in CNS was observed about 29 to 31 percent. Carbon, hydrogen and nitrogen content of the CNS char were observed in the range of 73 to 76 per cent, 4 to 5 per cent and 1 to 2 per cent respectively. It was found that nitrogen content has increased in CNS char after the carbonization of CNS. Oxygen content in the CNS char gets reduced to 13 to 14 percent, which was comparatively very less than CNS. It was observed that indirect method is more suitable for carbonization than direct method for obtaining higher calorific value char and maximum fixed carbon percentage as found in cashew nut shell char as 60 per cent.

Introduction

Konkan region the cashew (Anacardium In occidentale L) is one of the major horticultural crops. Cashew is an important evergreen tropical crop. India is the largest producer, processor, exporter and second largest consumer of cashew in the world¹. Total area in India under cashew cultivation is about 8,54,000 hectare with annual production of 6,20,000 tones giving average productivity 820 kg/ha with highest productivity reported in Maharashtra (1500 kg/ha) from 1,73,601ha (Fig.1) under cultivation² and produced 1,97,000 tones of raw cashew nut seeds through 2200-3650 cashew processing units³. Production of Cashew nut shell in Koknan region is 20,000 metric tons⁴ as waste product obtained during deshelling of cashew kernels. When CNSL removed, deoiled shells are abundantly available as a biomass waste⁵. The shell comprises some 50% of the weight of the raw nut, the kernel represents 25% and the remaining 25% consists of the natural CNSL⁶⁻⁸ and shell production of cashew nut shells may be

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estimated to 3,10,000 tones from available stats. The cashew nut shell has calorific value of 4252 kcal/kg⁹ and calorific value of CNSL is 40MJ/kg¹⁰. The waste biomass generated in cashew processing is utilized as a substitute to wood fuel by making charcoal with carbonization process¹¹. Biocarbons have been manufactured by man for more than 3800 years¹² and are among the most important renewable fuels in use today.

Carbonization process¹³ has added advantage over direct combustion of cashew nut shell. In direct combustion, vapors of an anacardic acid are released which may cause harm to eyes. Carbonization process of cashew nut shell produced char as well 25-30 per cent^{7,10} cashew nut shell liquid (CNSL) by weight. Industrial applications of the CNSL-based products¹⁴ are numerous and include fungicide, pesticide, insecticide¹⁵, brake linings¹⁶, paints and primers, foundry chemicals, lacquers, cements, and specialty coatings, resin¹⁷. Lately, the biological activities¹⁸ of the CNSL components have attracted

considerable attention in the areas of macrolide, plant growth, acid activity⁸, wood preservative and pressure treatment activity. Much of the biological activity is attributed to the anacardic acids, which are the major constituents of the cashew nutshells, along with cardols. However, the major constituents of the technical CNSL, as it is obtained in the current industrial practice of roasting or hot oil bath methods¹⁹, are the cardols and cardanols. In the carbonization process, solid residues with increasing content of carbon element of higher activation energy²⁰ are formed from organic material usually by pyrolysis in an inert atmosphere. Char preparation by this method will help in self-reliance of cashew processing unit for fuel supply with higher combustion efficiency. Keeping this view, the present study was undertaken.

Material and Methods

The cashew nut shell available in the cashew processing industry was selected as a major raw material⁴ for the carbonization process. The proximate^{21,7} and ultimate analysis³ of CNS was carried out to find out the fuel properties. In addition to CNS properties, carbonization processes were studied using metal kiln and tin boxes under direct and indirect process.

Experimental set up for carbonization of cashew **nut shell:** The carbonization of CNS was carried²² out in developed small capacity single drum kiln²³, which accommodate about 5 kg cashew nut shells. The kiln (plate 1.a) was designed with 8 mm diameter holes for the perforations with outlet for the oil at the bottom and vent for the exhaust at the top (plate 1c). The size selected was suitable for small amount of burning, low cost and fabrication could be developed locally. Design detail specification of kiln is depicted in table 1. At the beginning, the small vent at the top and the oil collecting tube at bottom allowed the burning of the cashew nut shells, and then operated as the pyrolysis mode in a closed kiln without air. Kiln was evaluated with and without perforated hole. The selected small capacity kiln was used for direct carbonization process (plate 1.a). The eight of raw CNS was measured and filled the kiln

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with full capacity and burn directly. Various temperatures at different location under kiln, exhaust temperature of vent and oil collected from the bottom sump were observed periodically. Time require to complete carbonization process and amount of char remain in kiln was observed at the end of process. The detailed flow chart of carbonization processed used is shown in fig.2.

Direct heating method of carbonization: Sample of the cashew nut shell was weighed and recorded. Developed kiln was checked for any leakage and which could not generate heat loss. The wire mesh grate was kept for support at the bottom of the kiln. The height of the great support was 6 cm above the bottom and would act as a convective heat media for the partial oxidation process, which would make heat, flow inside the kiln become more effective. Kiln was closed after placing the CNS for the carbonization; initial start up firing²⁴ was done using loose grass²⁵ that would transfer the heat to the CNS. Continuous observations were done to know the transfer of heat; the kiln air inlet size was adjusted based on the changes observed at the exhaust. Inside temperature of the CNS, outside temperature of the kiln and temperature of the exhaust fumes were recorded for the every 60 minutes. The time was recorded and the carbonization stage changes were noticed.

The kiln was continuously observed to see the smoke colour change from blue to light blue, it found that all the CNS had turned to charcoal; during that stage the light blue smoke would become clearer. The kiln was allowed to cool down for 8 hours. After that, ash and char were separated, weighed and recorded.

Indirect heating method of carbonization: Two small tin boxes having 0.3 kg capacity were selected for the indirect heating method of the carbonization (plate 1.b). The hole was made at the center of the tin box lid in order to remove the volatile matter and moisture associated with it. These tin boxes were placed inside the kiln and were surrounded by the cashew nut shells. Sample of the cashew nut shell were weighed and recorded. Prepared kiln was

checked for any leakage and which could generate heat loss. The wire mesh grate was kept for support at the bottom of the kiln; the height of the great support was 6 cm above the bottom and would act as a convective heat media for the partial oxidation process, which would make heat, flow inside the kiln become more effective. Kiln was closed after placing the CNS for the carbonization; initial start up firing was done using wood chips that will transfer the heat to the CNS. Continuous observations were done to know the transfer of heat; the kiln air inlet size was adjusted based on the changes observed at the exhaust. Inside temperature of the CNS, outside temperature of the kiln and temperature of the exhaust fumes was recorded for the every 60 minutes. Recorded the time and the carbonization stage changes were observed.

The kiln was continuously observed for colour change of the smoke from blue to light blue as it direct heating method.

Proximate analysis of CNS and its char: Determination of moisture content: About 1g of finely powdered air-dried sample was weighed in a crucible. The crucible was placed inside an electric hot air-oven, maintained at 105° C. The crucible was allowed to remain in oven for 1 hour and then taken out (with the help of a pair of tongs), cooled in desiccators and weighed. Loss in weight (ASTMD-3173) was reported as moisture (on percentagebasis). (26)

Moisture content, (% wb) = $\frac{w_2 - w_3}{w_2 - w_1} \times 100$

Where, w₁ = weight of crucible, g w₂ = weight of crucible + sample, g w₃ = weight of crucible + sample, after heating, g

Determination of volatile matter volatile matter: Volatile matter was determined by keeping the dried sample in a closed crucible at 600° C for six minutes and then at 900° C for another six minutes (ASTMD-3275). The difference in the weight duo to loss of volatiles was taken as the total volatile matter

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present in the biomass. Loss in weight was reported as volatile matter on percentage basis.

Volatile matter (%) =
$$\frac{w_5 - w_6}{w_5 - w_1} \times 100$$

Where,

 w_4 = weight of crucible + weight of sample before oven drying, g

 w_5 = weight of crucible + weight of sample before keeping in muffle furnace, g

 w_6 = weight of crucible + weight of sample after keeping in muffle furnace, g

Determination of ash content: The residual coal in the crucible in² was then heated without lid in a muffle furnace at 750 0 C for half hour for (ASTMD-3174). The crucible was then taken out, cooled first in air, then in desiccators and weighed. Heating, cooling and weighing was repeated, till a constant weight was obtained. The residue was reported as ash on percentage-basis.

Ash content, (%) =
$$\frac{w_8 - w_9}{w_7 - w_1} \times 100$$

Where,

 w_7 = weight of crucible + weight of sample before oven drying, g

 w_8 = weight of crucible + weight of sample before keeping in muffle furnace, g

 w_9 = weight of crucible + weight of sample after keeping in muffle furnace, g

Determination of fixed carbon: The fixed carbon in percentage was calculated by difference. Fixed carbon (%) = 100 - % of (moisture content + volatile matter +ash)

Procedure for determination of calorific value of the fuel by using the Oxygen Bomb Calorimeter: A known mass of the given sample was taken in clean crucible. The crucible was then supported over the ring. A fine magnesium wire, touching the fuel sample, was then stretched across the electrodes. The bomb lid was tightly screwed and bomb filled with oxygen 25 atmospheric 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

are then connected to 6-volt battery and circuit completed. The sample burns and heat was liberated. Uniform stirring of water was continued and the maximum temperature attained was recorded, the experimental setup for determination of calorific value using Bomb calorimeter.

The calorific value of the CNS and its char was determined by using Bomb Calorimeter. The calorific value of the CNS and its char was determined by using the following formula²⁶.

Calorific value (kcal/kg) =
$$\frac{(W + w) \times (T_1 - T_2)}{X}$$

Where,

W = weight of water in calorimeter (kg), w = water equivalent of apparatus, T₁ = initial temperature of water (0 C), T₂ = final temperature of water (0 C), X = weight of fuel sample taken (kg)

Ultimate analysis of CNS and char: Carbon, hydrogen, oxygen, nitrogen, and sulphur content of CNS and its char were found out under the ultimate analysis. The ultimate analysis is helpful in calculating heat balances in any process in which coal is used as fuel. Using the values of proximate analysis, ultimate analysis of CNS char could be done theoretically by using the various formulas²⁷.

Calculation of C, H, N and O from the proximate analysis: These values were carried out through the following steps²⁷.

Determination of carbon content: Carbon content of the sample was calculated theoretically on the basis of following formula, C = 0.97 FC + 0.7 (VM - 0.1 A) - M (0.6 - 0.01 M), %

Determination of hydrogen content: Hydrogen content of the sample was calculated theoretically which was given by,

H = 0.036 FC + 0.086 (VM – 0.1 A) – 0.0035 M^2 (1 – 0.02 M), %

Determination of nitrogen content: Nitrogen content of the sample was calculated theoretically which was given by,

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 $N_2 = 2.10 - 0.020$ VM, %

Determination of oxygen content: Oxygen content of the sample was calculated theoretically by difference on the basis of the following formula,

 $O_2 = 100 - \%$ of (C + H + N + Ash), %

Where, FC = fixed carbon, % A = ash, % VM = volatile matter, % M = moisture, %

Results and Discussion

CNS was selected as a biomass for carbonization because CNS was treated as waste in Konkan region and it is abundantly available in this region. Bulk density of CNS was 481.83 kg/m³, calorific value was nearly about 5000 kcal/kg and oil content was about 20 to 25 percent. The calorific values and oil content values were observed similar to values observed by Ramanan in 2008.

Carbonization of CNS: In the carbonization process, solid residues with increasing content of the element carbon were formed from the organic material usually by pyrolysis in an inert atmosphere. Char preparation by this method would help in self reliance of cashew processing unit for fuel supply combustion efficiency. higher with The carbonization process of CNS was carried out in direct and indirect ways, which results into the production of charcoal (Plate 1 d) as the main product plus gaseous product along with the CNSL (Plate 1 e) and ash. For thorough study of the carbonization process, shell temperature inside the kiln, exhaust temperature at the top vent and the outside temperature of the cylinder were recorded. The temperatures recorded in the direct and indirect method are shown below in the graphical format in fig. 3 and fig. 4 respectively.

It was observed from the fig. 3 and fig. 4 that time required to reach maximum temperature inside the kiln using indirect method was comparatively less than direct method for obtaining CNS char. maximum temperature was achieved in indirect

method in less time while direct method took more time for the carbonization. This may happen due as temperature of dried fuel was evaluated to about 225-325^oC, pyrolysis of hemicelluloses begins, cellulose gets pyrolysed at a temperature range of $325^{\circ}C$ $-375^{\circ}C$ while legnin starts pyrolysing at a temperature range of 350-500°C²⁸. Pyrolysis gases escape and char layer is form on fuel particle. It could be observed, in both methods, inside temperature varies more drastically than outside exhaust temperatures. Average temperature of shell at core part of kiln varies from 86 °C to 445°C in direct method whereas it varies from 80^oC to 448^oC in indirect method. Average exhaust temperature at the top vent varies from 172°C to 218°C in direct method while it varies from 175°C to 230°C in indirect method. Average outside temperature of the kiln was recorded in the range of 44° C to 60° C for direct method and 45° to 61° to 61° for indirect method. It was also observed that smoke colour gradually changes from blackish to white and then from white to colourless when all CNS turned to charcoal at the temperature 350° C onwards in both the methods.

Similarly, for comparing between the direct and indirect method, char percentage, oil percentage and ash percentage were observed and recorded which is shown graphically in fig. 5, fig. 6 and fig. 7 respectively.

From the fig. 5, fig. 6 and fig. 7, it was observed that char and ash percentage obtained in direct method was more than indirect method and oil percentage obtained in direct plus indirect method was more compared to direct method. Maximum oil percentages obtained in direct and direct plus indirect method were recorded as 21.1 per cent and 23.8 per cent respectively. Properties of CNSL like flash and fire point; viscosity, pH and calorific value were determined (table 2) for safe handling, storage and use of CNSL on commercial scale.

In direct method, maximum char and ash percentages were recorded as 21.04 per cent and 3.34 per cent respectively while in case of indirect method these values were recorded as 18.45 per cent and 1.27 per cent respectively. Charcoal obtained in

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indirect method was comparatively low than direct method but had more calorific value reason being higher temperature while heating of partial at lower rate to lower ultimate temperature favors char formation²⁹. Ash obtained in indirect method was observed less than that of direct method. This happened due to the reason that flame did not come in direct contact with CNS in indirect method. Since, ash obtained was less in indirect method; it is therefore indirect method considered as more suitable for carbonization of CNS.

Char obtained from prototype kiln was tested in improved chulhas for water boiling test. Most things are found, while burning the char (Plate 1.f) of cashew nut shell smoke was not produced as produced by burning the raw cashew nut shell in same chulhas.

Proximate analysis of CNS and its char: Proximate analysis³⁰ of CNS and its char for determination of moisture content, volatile matter, ash content and fixed carbon was carried out. Calorific value of the raw material was determined using standard procedure. The results of proximate analysis and calorific value are shown in figure 8 and figure 9 respectively.

From the figure 8, it was observed that moisture content of the CNS varies from 10 to 11% while moisture content in char varies from 5 to 6 %. For CNS the volatile matter observed in the range from 65 to 70% while in char varies from 25 to 30%. It could also be observed that ash content in the CNS sample was less than that of the CNS char. After carbonization fixed carbon percentage was found considerably increased in CNS char.

From the figure 9, it was observed that maximum calorific value of char obtained in direct method was calculated as 6474.6 kcal/kg and char obtained in indirect method has maximum calorific value 6714.8 kcal/kg. Char obtained in indirect method was more superior to the char obtained in direct method due to its high calorific value³¹.

Ultimate analysis of CNS and its char: The ultimate analysis of CNS and its char was carried out in order to determine its carbon, hydrogen and oxygen and nitrogen percentage. Ultimate analysis of the given sample was carried out theoretically from the results obtained in proximate analysis. Ultimate analysis of the given sample could be carried out theoretically on the basis of formulae. The results of ultimate analysis of CNS and CNS char are shown graphically in figure10.

From the figure 10 (a), it was found that carbon percentage in the CNS was in the range of 60 to 62 percent. Hydrogen content in CNS was found about 6 to 7 per cent and nitrogen content in CNS was found about 0.70 to 0.75 per cent. Oxygen content in CNS was observed about 29 to 31 percent.

Similarly, from the figure 10 (b), carbon, hydrogen and nitrogen content of the CNS char were observed in the range of 73 to 76 per cent, 4 to 5 per cent and 1 to 2 per cent respectively. It was found that nitrogen content has increased in CNS char after the carbonization of CNS. Oxygen content in the CNS char gets reduced to 13 to 14 percent, which was comparatively very less than CNS.

Mass and Energy balance: Actual amount of CNS char obtain in direct combustion after thermal decomposition in kiln comparing to raw CNS material was low but while analyzing carbon balancing depicted in figure 10 shows actual utilization of carbon was 28 % and it get lost 28.4 % carbon in exhaust gases, 17 % kg carbon in condensate, 0.6 kg in ash and remaining 26 % is un burn. That many losses occurred in condensate and exhaust gases due to evaporation of moisture and formation of CNSL oil, which required 2.8 MJ of energy to drive out one kilogram of moisture in fuel³².

There is large unaccounted heat loses due to several factor as heat energy loss itself due to the kiln heat losses in terms of startup energy as well as heat losses¹³ in direct combustion. The energy balance predicted the share of energy was 31 % in CNS char,

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rest of 23 % lost in exhaust, 14 % in condensate, 17 % in un burnt char and 14 % energy losses found as unaccounted.

Conclusions

It was observed that indirect method is more suitable for carbonization than direct method for higher calorific value char. It was observed that time required for the carbonization using indirect method was comparatively less than direct method.

It was observed that maximum fixed carbon percentage found in cashew nut shell char as 60 per cent.

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Table-1:	Overall	dimensions	of kiln
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Particular	Dimensions	
A) Kiln cylinder		
1. Total height	51cm	
2. Diameter	30cm	

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3. Thickness	1cm
4. Diameter of bottom	0.5cm
5. Material	Mild steel
B) Kiln lid	
1. Total height	2.5cm
2. Diameter	31cm
3. Thickness	1cm
4.Diameter of top vent	0.8 cm
5.Air required for 5 kg	25m ³
6. No. of vents provided	16
7.Time required	13 hours
8. Material	Mild steel
C) Overall height of kiln	52 cm

Table- 2: Properties of cashew nut shell oil

Properties	Value of the CNSL
Flash point	114 ⁰ C
Fire point	118 ⁰ C
pН	5.7
Calorific Value	1053 cal/gm
Viscosity at 33 ^o C	693 Redwood
Viscosity at 43 ^o C	480 Redwood
Bulk density	0.957 gm/cc

Distribution of (173601ha) area under cashew in Konkan

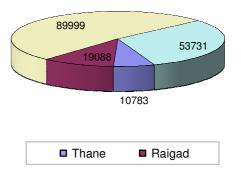


Figure-1: Area under cashew cultivation in Konkan region of Maharashtra

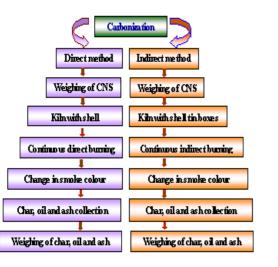


Figure-2: Process flow chart of carbonization methods

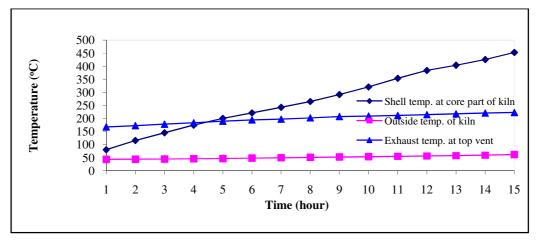


Figure-3: Variation of carbonization temperature with time during direct method

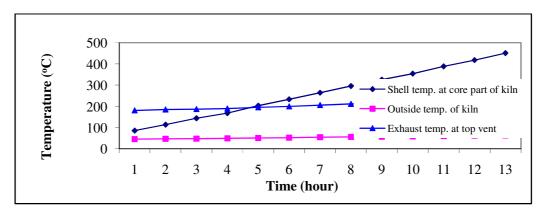


Figure-4: Variation of carbonization temperature with time during indirect method

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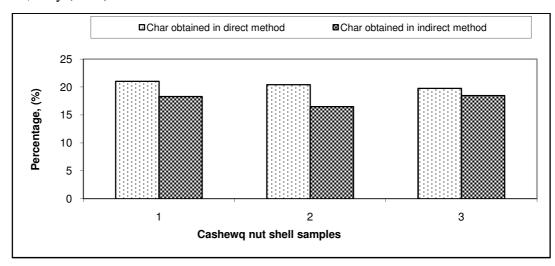
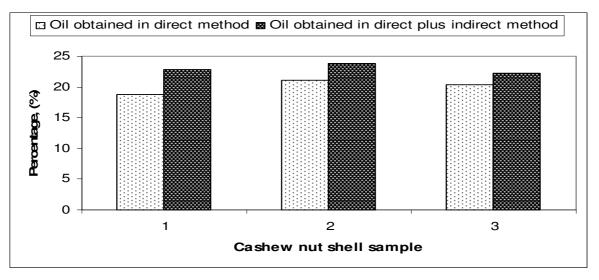
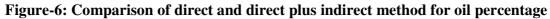
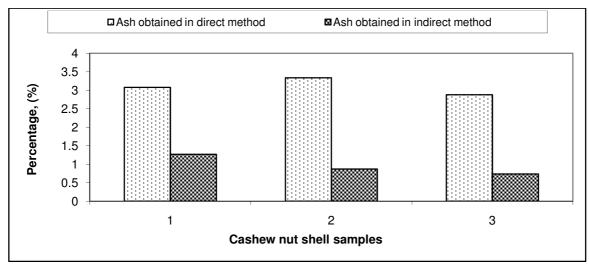


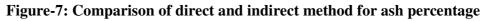
Figure-5: Comparison of direct and indirect method for char percentage

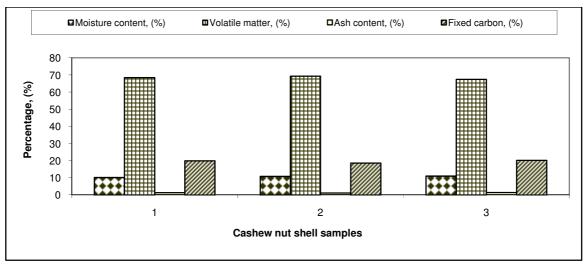




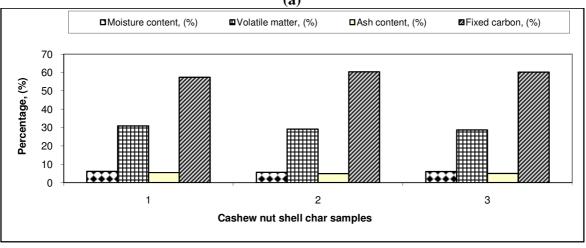


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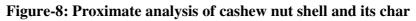


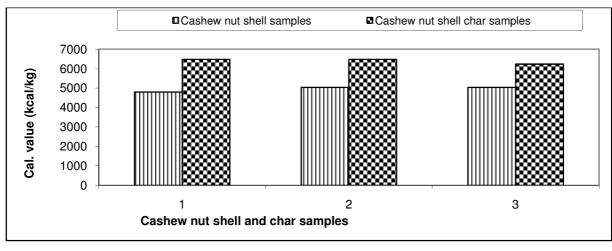






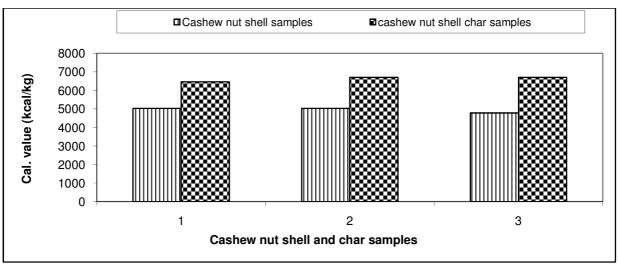




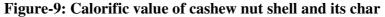


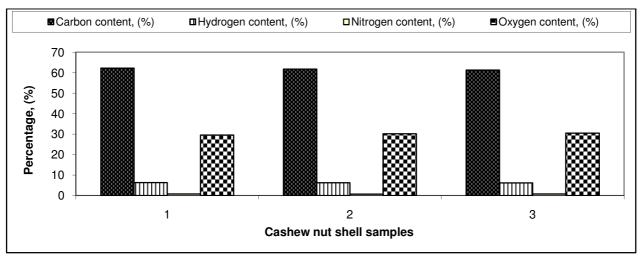
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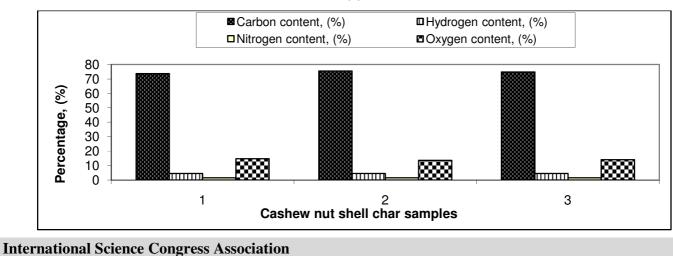












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(b) Figure-10: Ultimate analysis of CNS and its char



Plate-1: Prototype kiln for carbonization