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Cashew Nut Shell a Green Energy Option for Gasification

H. Y. Shrirame[1], A. G. Mohod[2], Y. P. Khandetod[3], K. G. Dhande[4], J. S. Dhekale[5]

Senior Research Assistant, Department of Electrical and Other Energy Sources, College of Agricultural Engineering and Technology, DBSKKV, Dapoli, Ratnagiri, Maharashtra, India[1]

Head, Department of Agricultural Engineering, DBSKKV, Dapoli, Ratnagiri, Maharashtra, India[2]

Professor and Head, College of Agricultural Engineering and Technology, DBSKKV, Dapoli, Ratnagiri, Maharashtra, India[3]

Associate Professor, Department of Farm Machinery and Power, College of Agricultural Engineering and Technology, DBSKKV, Dapoli, Ratnagiri, Maharashtra, India[4]

Assistant Professor (Statistic), D. Y. Patil Agricultural and Technical University, Talsande, Kolhapur, Maharashtra, India[5]

Abstract: Cashew nut shell waste from processing industries after removal of cashew kernel was characterized and deoiled in a simple batch type kiln by radiant heating (indirect heating) method. This paper present the results of fuel properties of cashew nut shell (CNS), deoiled cashew nut shell (DCNS) and its feasibility for gasification. The physiochemical characteristics of CNS and DCNS were determined at moisture content of 9.16 % (wb) and 4.91 % (wb), respectively. The physicochemical characterization revealed that CNS contain higher volatile matter (66.84 wt.%), ash and moisture content, whereas DCNS contain lower volatile matter (35.64 wt.%), ash and moisture content also DCNS contain higher fixed carbon (53.85 %) than CNS (16.89%) are the main advantages of DCNS gasification. Hydrogen, Nitrogen, Carbon and Oxygen content in CNS were observed as 4.12 %, 0.23 %, 45.90 % and 38.14 % respectively. Carbon, hydrogen and nitrogen content of the DCNS were observed as 70.80 %, 2.40 % and 1.4 % respectively. Oxygen content in the DCNS gets reduced to 13.7 %, which was comparatively very less than CNS. The thermo gravimetric analysis of CNS and DCNS revealed that, the DCNS were more suitable for gasification than CNS as the average calorific value were observed 6484.41 kcal kg^{-1} and 4880.19 kcal kg^{-1}, respectively. The availability and characterization of the DCNS as a fuel revealed its feasibility for thermal application through gasification. The availability and characterization of the DCNS as a fuel revealed its feasibility for producer gas generation through gasification for thermal application. Also a solution to reduce the disposal problem of cashew nut shells generated from cashew processing industries.

Keywords: Cashew nut shell, Deoiled cashew nut shell, Proximate analysis, Gasification, Thermo-gravimetric analysis

I. INTRODUCTION

Cashew (Anacardium occidentale) was introduced to India from Brazil about 500 years ago as a crop of afforestation and soil conservation [1]. The cashew trees were cultivated in warm and humid climatic regions [2]. It is grown in India, Brazil, Mozambique, Tanzania, Kenya, Vietnam, Indonesia and some other African and Asian countries. The global cashew nut production during 2019-2020 was nearly 3.96 million tons. Among the cashew producing countries, with the highest volumes of cashew nut production (with shell) were Cote d'Ivoire (792.68 K tonnes), India (743 K tonnes) and Viet Nam (283 K tonnes), together comprising 45.92 % of global production. It can be seen from the Figure 1 that Cote d'Ivoire ranks first in global production (20 %) followed by India (19 %), Vietnam (7 %). Burundi, Philippines, Tanzania, Benin and other minor countries contribute rest of the production [3].

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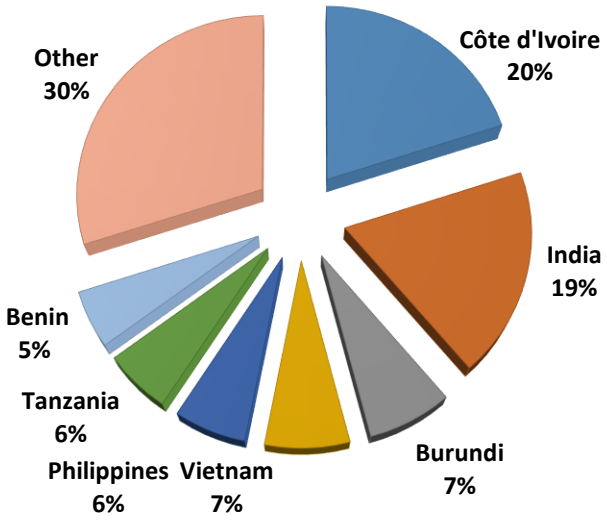

Figure 1. Percent contribution of different countries to world cashew production

India is the largest producer, processor and exporter of cashews (*Anacardium occidentale L.*) in the world [4], [5] and [6]. The total area under cashew in India is about 11.74 lakh hectares with production of 6.75 lakh MT during 2021-22 (AGRICOOP). Cashew nut shells are a residue obtained from cashew shelling, an abundant and cheap biomass residue, and could generate high energy. Currently, cashew nuts shells are rejected by artisanal traders without being valued. They were often burned in open air and cause several socio-environmental problems [2].

Cashew nut shells are one of the most abundant forms of tropical biomass waste generated in cashew processing industries during deshelling of cashew kernels, was found to be 676 kg per 1000 kg of raw cashew seed, which can be utilized as fuel for thermal energy supply [8]. The cashew nut shell comprises around 50-70 % weight of raw nut, 20-25 % kernel, 2-5 % testa and remaning 20-30 % cashew nut shell liquid that obtained during the cooking of the raw nuts and the separation of kernel by roasting [9], [10] and [6]. The waste biomass generated in cashew processing is utilized as a substitute to wood fuel during cashew processing or thrown as a waste. The average higher heating value of the cashew nut shell was reported to be 4890 kcal kg^{-1} which makes it suitable fuel for cashew processing industry [8].

Cashew nut shell is the by-product of the cashew processing industry, which have kidney shaped with 3.5 mm thick soft leathery outer skin (epicarp) and thin hard inner skin (endocarp). In-between these two walls of the cashew nut shell is a honeycomb structure, which contains about 25 % phenolic (tannin) material, known as cashew nut shell liquid (CNSL). When the cashew nut shell was used for gasification, the shell oozed natural phenol oil upon gasification, which clogging the gasifier throat, downstream equipment and associated utilities with oil and resulted in ineffective gasification and premature failure of utilities due to its corrosive characteristics [11]. This can be minimized through thermal extraction of cashew nut shell liquid (CNSL) from cashew nut shell (CNS) before gasification. Keeping this views, a feasibility study of cashew nut shell (CNS) was carried to use as feedstock for gasification.

II. Material and Method

The available cashew nut shell (CNS) of variety 'Vengurla-4' from the cashew processing industries was used as a raw material for the deoiling process. The deoiling processes was carried out using metal kiln using radiant heating (indirect heating) method [12].

A. Experimental set up for deoiling of cashew nut shell

The deoiling of cashew nut shell (CNS) was carried out in a metal kiln of 18 SG MS sheet, with 5 kg shell-holding capacity. The kiln has 8 mm diameter holes at bottom side for oil outlet and vent for the exhaust hot gases at the top with manual stirring mechanism to distribute the heat uniformly to the cashew nut shell. The 5 kg cashew nut shell (CNS) was measured and filled in the kiln and heated externally i.e. at outer periphery. The radiant heat (indirect heat)

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was provided to kiln by burning the coconut shell surrounded the kiln. The temperatures at different location of kiln and cashew nut shell liquid (CNSL) collected from the bottom were observed periodically. The time required, amount of deoiled cashew nut shell (DCNS) and cashew nut shell liquid (CNSL) were observed at the end of process. The technical specification of kiln is depicted in Table 1 and deoiling processed setup used is shown in Figure 2. The products of deoiling process of cashew nut shell (CNS) ware depicted in Plate 1.

The physical properties like size, surface area, bulk density, angle of repose of cashew nut shell (CNS) and deoiled cashew nut shell (DCNS) were studied using both the standard procedure and derived formulae [13], [14] and [15]. The proximate, ultimate and thermogravimetric analysis of cashew nut shell (CNS) and deoiled cashew nut shell (DCNS) was carried out to determine the fuel properties. The calorific value of CNS and DCNS were measure by using bomb calorimeter as per Bureau of Indian Standards (IS: 1359-1959) and the Institute of Petroleum (IP 12/63 T) [16].

TABLE 1 TECHNICAL SPECIFICATION OF THE KILN

A. Kiln		
Type	:	Vertical cylinder
Capacity	:	5 kg
Total height	:	510 mm
Diameter	:	300 mm
Thickness	:	10 mm
Bottom vent diameter	:	5 mm
B. Kiln lid		
Diameter of lid	:	310 mm
Height of lid	:	25 mm
Overall height of kiln	:	5520 mm
Material used	:	Mild steel
Biomass for radiant heat	:	Coconut shell

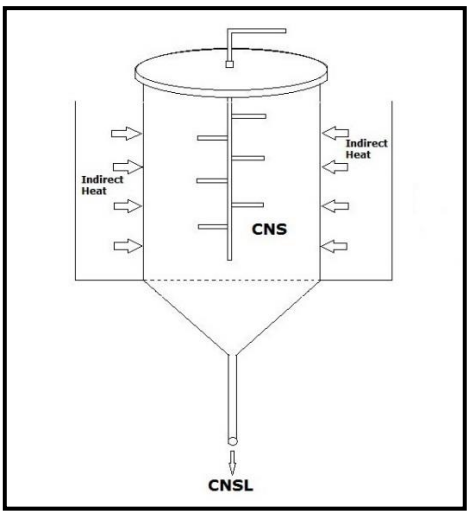

Figure 2. Schematic view of deoiling the cashew nut shell (CNS) using radiant heating (indirect heating) method

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(A) Deoiled cashew nut shell (DCNS)

(B) Cashew nut shell liquid (CNSL)

Plate 1. Results of deoiling process of cashew nut shell (CNS)

B. Proximate analysis of CNS and DCNS

The proximate analysis were carried out using the analytical method ASTMD-3173, 3174 and 3175 for determination of moisture content, volatile matter, fixed carbon content and ash content in the CNS and DCNS. The proximate analysis and calorific value were determined using both the standard procedure and derived formulae [17]. 2011).

Moisture content

The moisture content of a solid material was defined as the quantity of water per unit mass of the wet solid material. About 1 g of finely powdered air-dried sample of biomass with three (03) replication was weighed in crucible. The crucible was placed in an electric hot air-oven maintained at 105 ± 5 °C as per ASTM D-3173. 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 was reported as moisture content (on percentage-basis) [18].

$$\text{M.C}(\%) = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Where,

MC = Moisture content, %
W_1 = Weight of crucible, g
W_2 = Weight of crucible + sample, g
W_3 = Weight of crucible + sample, after heating, g

Volatile matter

The volatile matter was determined by keeping the dried sample of biomass sample obtained after moisture content determination in a crucible with lid at 925 ± 20 °C for seven minutes in a muffle furnace as per ASTM D-3175. The difference in the weight due to loss of volatiles was taken as the volatile matter present in the biomass sample on percentage basis.

$$\text{V.M}(\%) = \frac{W_3 - W_4}{W_2 - W_1} \times 100$$

Where,

V.M = Volatile matter, %
W_1 = Weight of crucible, g
W_2 = Weight of crucible + sample, g
W_3 = Weight of crucible +weight of sample before keeping in muffle furnace, g
W_4 = Weight of crucible + weight of sample after keeping in muffle furnace, g

Ash content

The residual samples of biomass obtained after volatile matter determination in crucible without lid were heated gradually in a muffle furnace to 700 ± 50 °C for half an hour as per ASTM D-3174. The crucible was taken out, cooled

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first in air, then in desiccator and weighed. Heating, cooling and weighing was repeated till constant weight was obtained. The weight of residue was reported as the ash content of the biomass sample on percentage basis.

$$\text{Ash content}\ (\%) = \frac{W_5 - W_1}{W_2 - W_1} \times 100$$

Where,

W_1 = Weight of crucible, g
W_2 = Weight of crucible + sample, g and
W_5 = Weight of crucible + Constant weight of sample after keeping in muffle furnace, g

Fixed carbon

The fixed carbon content was the value obtained after subtracting the value of moisture content (MC), volatile matter (VM) and ash content (AC) of CNS sample from the hundred percent, gives the percentage of fixed carbon.

$$\%\ \text{of Fixed carbon} = 100 - \%\ \text{of}\ (MC + VM + AC)$$

Where,

MC = Moisture content, %
VM = Volatile matter, %
AC = Ash content, %

C. Ultimate analysis of CNS and DCNS

The 2400 CHNS Organic Elemental Analyzer 100V, Perkin Elmer was used to determine the contents of Carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) available in selected biomass i.e. CNS and DCNS.

D. Calorific value of CNS and DCNS

The calorific value of feedstock (CNS and DCNS) was measure by using bomb calorimeter as per Bureau of Indian Standards (IS: 1359-1959) and the Institute of Petroleum (IP 12/63 T). The bomb calorimeter consisted of a strong cylindrical stainless steel bomb in which the combustion of biomass sample (fuel) took place. The bomb was placed in a copper calorimeter, which was surrounded by an air jacket and water jacket to prevent heat losses due to radiation. The known mass of fuel (≳ one gram) was placed in clean crucible supported by a ring, a fine fuse wire tightly screwed and the bomb was filled with oxygen gas at 25-30 atmospheric pressure. After that bomb was lowered down into the copper calorimeter containing a known quantity of water, the stirring was performed and the initial temperature was noted. The electrodes on the bomb were connected to electric supply for firing out the fuse wire so as to start the ignition in the bomb. Due to the combustion of the fuel, heat was liberated and the temperature of the water surrounding the bomb increased. The rise in temperature of the water in the calorimeter was noted till the stagnation temperature was obtained. The rise in temperature was due to combustion of the biomass sample (fuel) and it was used for determination of the calorific value of biomass sample (fuel). The calorific value is mainly used to determine the fuel quality of the biomass (fuels). Greater the calorific value, greater is the fuel quality of the biomass (fuel) and better the use as fuel [16].

Heat liberated by burning of fuel = $X\,L + E_1$
Heat absorbed by water and apparatus, etc. = $(W + w)(t_2 - t_1)$
But heat liberated by the fuel = Heat absorbed by water, apparatus etc.

$$X\,L + E_1 = (W + w)(t_2 - t_1)$$

$$\text{Higher calorific value of fuel (L)} = \frac{[(W + w)(t_2 - t_1)] - E_1}{X}\ \text{cal g}^{-1}\ (\text{or kcal kg}^{-1})$$

Where,

X = Mass of CNS sample (fuel) placed in the crucible, g
W = Mass of water placed in the calorimeter, g
w = Water equivalent of the bomb, stirrer, thermometer, g
t_1 = Initial temperature of water in calorimeter, °C
t_2 = Final temperature of water in calorimeter, °C
L = Higher calorific value of the CNS sample (fuel), cal g^{-1}
E_1 = Correction for heat of combustion of firing wire and cotton thread, cal

Water equivalent (w), g

$$L = \frac{(W + w) \times (t_2 - t_1)}{X}$$

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Where,

X = Weight of benzoic acid, g
W = Weight of water in calorimeter, g
t_1 = Initial temperature, °C
t_2 = Final temperature, °C
L = Calorific value of benzoic acid, 6324 cal g^{-1}

Correction factor (E1), cal

E_1= Correction for heat of combustion of firing wire and cotton thread, cal
= (Length of wire, cm × Calorific value of nichrome wire, 0.82 cal cm^{-1}) + (Weight of cotton thread, mg × Calorific value of cotton thread, 4.180 cal mg^{-1})

E. Thermo-gravimetric analysis of CNS and DCNS

The thermo-gravimetric analysis of CNS and DCNS was carried out using the analytical method ASTM E-1131-08. The rate of devolatilisation of biomass sample was determined by a thermo-gravimetric analysis (TGA). Thermo-gravimetric analysis (TGA) for the feasibility study of CNS and DCNS was conducted in a high purity nitrogen (99.95%) environment with flow rate of 20 ml min^{-1} to investigate the mass loss characteristics as a function of temperature and time. The thermo-gravimetric analysis (TGA) was performed with a thermo-gravimetric analyzer (TGA) STA 7300 Hitachi, Germany to measure the finely powdered samples of CNS and DCNS weights 5.0 mg and 14 mg respectively, by keeping the heating rate 20°C/min form 30°C to 900°C [19].

III. Result and Discussion

The various physic-chemical properties like physical, proximate and ultimate analysis was carried out to analyze the feed stock (CNS and DCNS) shown in Table 2. The moisture content of the CNS and DCNS used for the present investigation were found to be 9.16 % (wb) and 4.91 % (wb) respectively. The physical properties of CNS and DCNS were determined and revealed that, the average values of surface area (cm^2), bulk density (kg m^{-3}) and angle of repose (°) of CNS were found to be 5.86, 350 and 20.96 for, respectively. The values for DCNS were found to be 5.28, 207 and 22.25 [20].

TABLE 2. PHYSICOCHEMICAL PROPERTIES OF CNS AND DCNS

Parameters	Cashew nut shell (CNS)	Deoiled cashew nut shell (DCNS)
Physical properties		
(a) Size (mm)		
i. Length (mm)	31.76	31.42
ii. Width (mm)	20.82	20.55
iii. Thickness (mm)	4.33	4.20
(b) Surface area (m^2)	5.86	5.28
(c) Bulk density (kg m^{-3})	350.00	207.00
(d) Angle of repose (º)	20.96	22.25
Thermal properties		
Moisture content (% wb)	9.16	4.91
Volatile matter (% db)	66.84	35.64
Ash content (% db)	7.11	5.60
Fixed carbon (% db)	16.89	53.85
Carbon (wt. %)	45.90	70.80
Nitrogen (wt. %)	0.23	1.40
Hydrogen (wt. %)	4.12	2.40
Oxygen (wt. %)	38.14	13.70
Calorific value (kcal kg^{-1})	4880.19	6484.41

From the Figure 3, it was observed that the average deoiled cashew nut shell (DCNS) and CNSL (cashew nut shell liquid) percentage obtained during the deoiling process were found to be 56 % and 26 % respectively, by radiant heating (indirect heating) method. The properties of CNSL like density, kinematic viscosity, pH, flash point, fire point and calorific value were determined (Table 3).

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TABLE 3. PROPERTIES OF CASHEW NUT SHELL LIQUID (CNSL)

Properties	Value of the CNSL
Density (g ml^{-1})	0.982
Kinematic viscosity at 38 ºC (cS)	64.21
pH	3.63.6
Flash point (ºC)	118118
Fire point (ºC)	121.66
calorific value (kcal kg^{-1})	8663.12

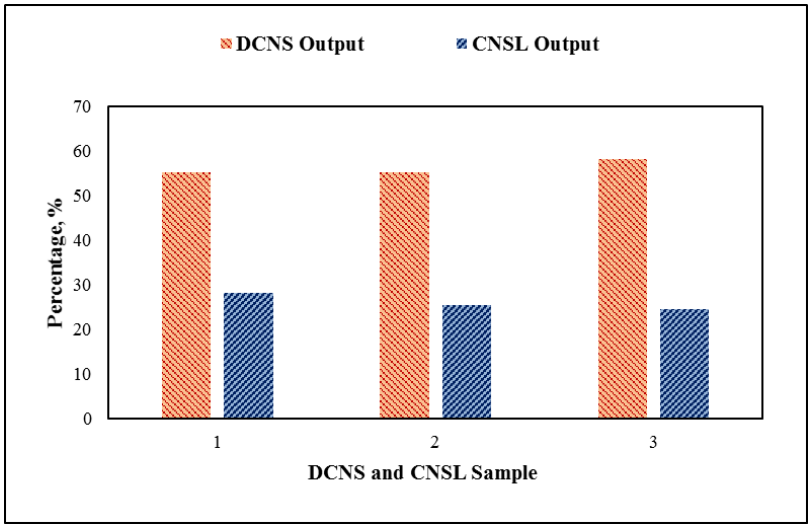

Figure 3. Percentage output of DCNS and CNSL

A. Proximate analysis of CNS and DCNS

Proximate analysis of CNS and DCNS for determination of moisture content, volatile matter, ash content and fixed carbon was carried out. The calorific values of the CNS and DCNS were determined using standard procedure as per Bureau of Indian Standards (IS: 1359-1959) and the Institute of Petroleum (IP 12/63 T).

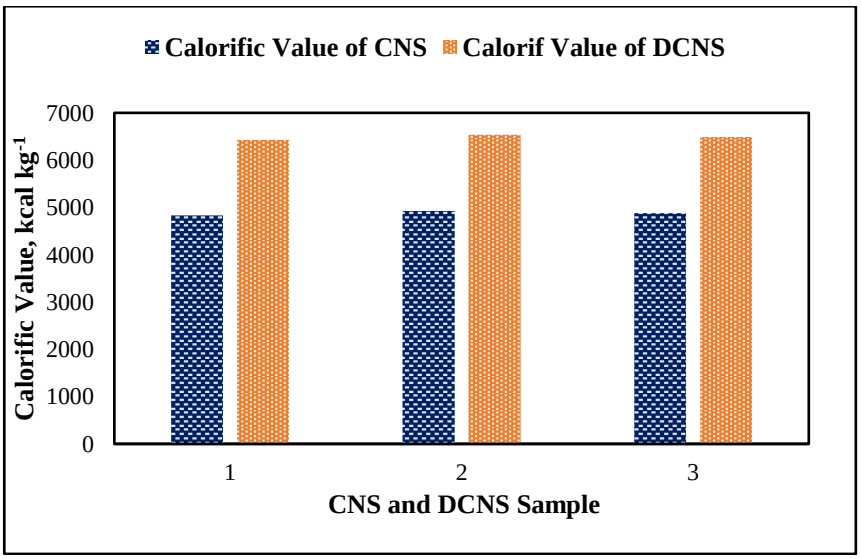

Figure 4. Calorific value of CNS and DCNS

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The result obtained are summarised in Table 2. From proximate analysis it was observed that the moisture content was 9.16 wt% and the CNS contained 66.84 dry% of volatile matter and 16.89 dry% of fixed carbon whereas 4.91 wt%, 35.64 dry% and 53.85 dry% in DCNS. These values of proximate analysis are similar to those already described for CNS from different topographical origins. Only the ash content of CNS and DCNS (7.11 dry% and 5.60 dry% respectively) was greater than in previous studies, which were in the range of 0.9–2.0 dry% [4], [21] and [22]. From the Figure 4, the average calorific value of CNS was observed to be 4880.19 kcal kg^{-1} whereas DCNS has 6484.41kcal kg^{-1} that is among the highest found for different types of biomass [17] and [23].

B. Ultimate analysis of Cashew Nut Shell and Deoiled Cashew Nut Shell

The ultimate analysis of CNS and DCNS were carried out in order to determine its C, H, N, O and S percentage. The results obtained are shown in Figure 5. It was observed that, carbon, hydrogen, nitrogen and oxygen content of CNS were observed as 45.90 %, 4.12 %, 0.23 % and 38.14 %, respectively. Similarly, the values of ultimate analysis of DCNS were observed as 70.8 %, 2.40 %, and 1.4 %, respectively. Oxygen content in the DCNS gets reduced to 13.7 %, which was comparatively very less than CNS. The resultant values of C, H, N, O and S contents of CNS and DCNS were similar to the ones described in the literature [4], [17] and [24].

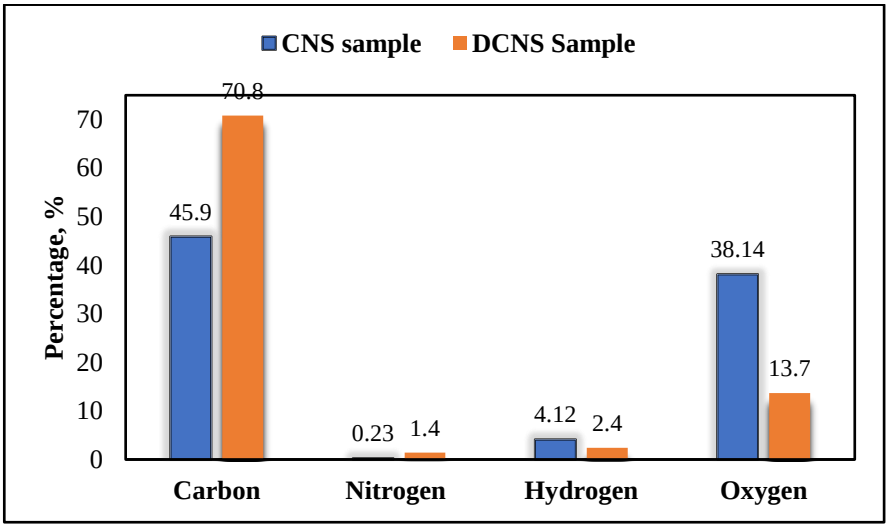

Figure 5. Ultimate analysis of CNS and DCNS

C. Thermal-gravimetric Analysis of Cashew Nut Shell

The TGA and derivatives thermal-gravimetric curves of CNS done with thermo-gravimetric analyser (TGA) STA 7300 Hitachi, Germany, operated under highly purity nitrogen (99.95%) environment (20 ml min^{-1}) at a heating rate of 20°C min^{-1} is shown in Figure 6. It was observed that the mass loss of CNS was distributed in three different stages: stage-I, stage-II and stage-3 which is drying, devolatilisation, and finally residues (char and ash), respectively. In stage-I, mass loss with respect to pyrolysis temperature around 150°C, which was attribute to removal of initial unbound moisture content and simultaneously degradation of volatile matter of CNS. The stage-II, was the active pyrolysis stage, at temperature ranged from 150 to 450°C, on which degradation of organic hemicellulose and cellulose material was occurred. In this stage-II, there are two distinct peaks from temperature of 150 to 450°C. Among the two peaks, the first peak was attributed to thermal decomposition of hemicellulose at temperature 150 to 250°C and the second peak, thermal decomposition of cellulose at temperature 250 to 450°C [21]. The stage-III start from 450°C onwards indicate the degradation of lignin, due to exothermic and endothermic reactions at temperature range 450 to 600°C [21] and [25]. In char formation zone, all the volatiles were evolved at temperature range 600 to 900°C and only the char remained [22].

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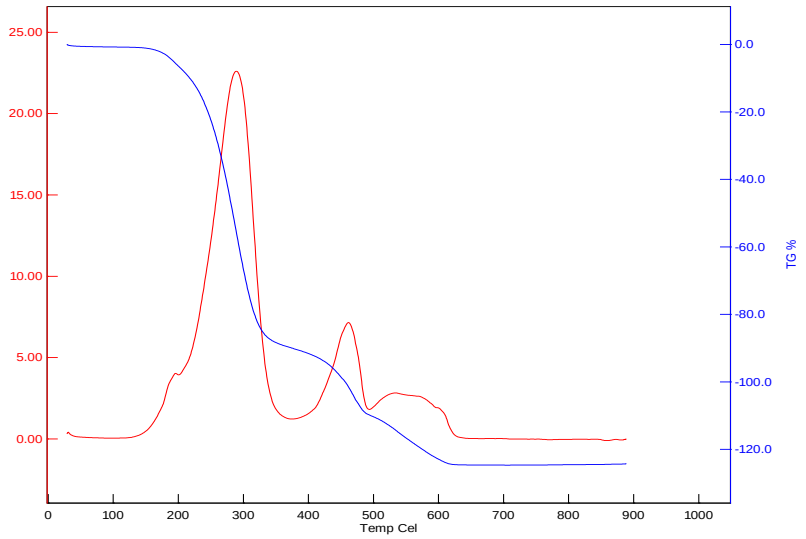

Figure 6. TG and DTG thermo-gravimetric analysis of CNS at 20 °C min-1 heating rate

D. Thermal-gravimetric Analysis of Deoiled Cashew Nut Shell

The TG-DTG curves of DCNS using similar instrument is shown in Figure 7. The TGA analysis of DCNS basically carried out to analyze the thermal resistance and its pyrolytic performance [26]. It was observed that the moisture content and some extractives from DCNS has been removed upto temperature 300°C, this is the stage-I of thermal degradation. In stage-II, some parts of hemicellulose and cellulose were degraded in the temperature range of 300 to 550°C. This stage mainly known as active pyrolysis stage. Stage-III, is started from temperature range 550 to 800°C in which degradation of lignin was occurred, which may be happened due to the exothermic and endothermic reactions takes place between the organic compounds [27]. And from temperature range 800°C to onwards, char formation stage where percentage of mass loss in DCNS was observed almost stable, which indicate the complete conversion of DCNS into char i.e. char formation stage.

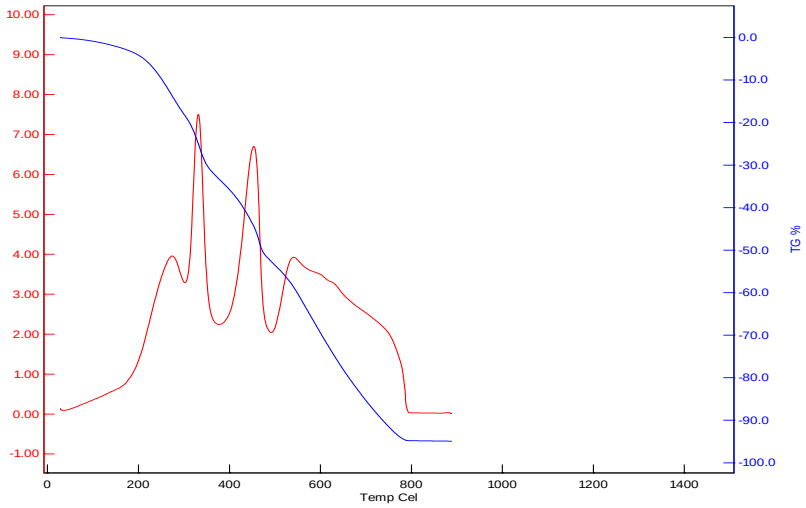

Figure 7. TG and DTG thermo-gravimetric analysis of DCNS at 20 °C min-1 heating rate

IV. Conclusion

The study on cashew nut shell (CNS) waste was carried out as a green energy option through pyrolysis and gasification processes. The pyrolysis process of CNS and DCNS were achieved in three different mass loss regions. A low heating rate (20 °C min^{-1}) was suitable for thermal degradation of the CNS and DCNS, resulting in less amount of residue (char). The above study observed that DCNS were an excellent feedstock for gasification, due to their fuel characteristics, which was comparable to CNS. It was observed that maximum fixed carbon percentage found in DCNS

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as 70.80 per cent. The higher heating value is the factor determining the suitability of fuel for gasification. The observed result showed that the DCNS has higher gross calorific value 6484.41 kcal kg^{-1} than CNS 4880.19 kcal kg^{-1} presenting suitable properties for use as energy source. The proper utilization of the DCNS waste through gasification route will conserve the biomass fuel and make its use self-sustainable for thermal application.

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