Discerning the value-addition process of de-oiled cashew nut shell

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Abstract

Cashew cultivation leads to the generation of large amounts of nut shells. In this study, the effective utilization of the nut shells for the production of value-added chemicals and fuels through pyrolysis process was investigated. The experiments were carried out in a laboratory scale fixed bed reactor with a capacity of 250 g. Cashew nuts hells (CNS) were pyrolyzed at 500 °C and 30 min residence time. The solid, liquid and gaseous fractions were quantified and characterized for its physio-chemical and thermal properties. Results indicated that, all the products obtained from pyrolysis are suitable for fuel purposes which is affirmed through their energy content. The yield of pyro-char and pyro-oil was observed as 28.36 and 41.8% respectively, with an energy value of 28.75 and 37.82 MJ/kg, respectively.

Keywords: Cashew nut shell (CNS), pyrolysis, pyro-oil, pyro-char, process temperature

Introduction

Globally, India ranks first in terms of production, processing and export of cashews. Anacardium occidentale Linn, which was brought during 1400 by Portuguese missionaries. Later, its commercial cultivation in India was started in 1960s. In India, 1.03 million ha, which cover almost the entire coastal region is under cashew cultivation, producing over 0.67 million metric tons of raw cashew nuts annually. The cashew processing industries generate large quantities of shell, which is about 50–65% (wt.) of raw nuts. The cashew fruit comprises of approximately 30% nut and 70% shell. The cashew nut shell (CNS) is about 0.125-inch thick, with a soft honeycomb structure inside, containing a dark reddish brown viscous liquid known as cashew nut shell liquid (CNSL) which finds its use in innumerable applications.

CNS is primarily consumed as such for combustion purposes as it has a net calorific value of about 20 MJ/kg. The cashew nut shell contains the residues of CNSL in the range of 10-80%, which releases acidic vapors during combustion process (Ábrego et al., 2018) [1]. This limits the direct use of CNSL residue as a fuel for supplying energy in the cashew processing stages. There is an ample number of options available for upgrading CNS into value added chemicals and higher energy valued fuels. One such technique is pyrolysis of the de-oiled CNS to produce energy intense pyro-oil and high-grade pyro-char.

Pyrolysis is the thermal treatment of biomass in the absence of oxygen, which results in the production of solid (pyro-char), liquid (pyro-oil) and gaseous fuel products. The liquid product may be stored, easily transported, upgraded to refined fuels, added to petroleum refinery feedstocks or contain chemicals in economically recoverable concentrations. Batch pyrolysis of nut shells can sequentially achieve high quality charcoal and energy rich pyro-oil liquid (at temperatures 400-600 °C). Das and Ganesh (2010) [2] reported product distributions from the pyrolysis of de-oiled CNS (CNSL removal at 150 °C in an oven prior to pyrolysis) in the temperature range of 400-600 °C and found that the maximum energy recovery was observed at 500 °C. The present study aims at utilizing de-oiled CNS for the pyrolysis process and to evolve a higher energy fuel.

Materials and Methods

Proximate analysis

Proximate analysis of CNS for the determination of moisture content (ASTM D3173), volatile matter (ASTM D3175), ash content (ASTM D3174) and fixed carbon was carried out by following standard ASTM procedures (Subramanian and Sampathrajan, 1999) [3].
Ultimate Analysis
The elemental composition of CNS was determined empirically using the following equations (Wilson et al., 2010) and presented in Table 1.

Carbon = 0.97 FC + 0.7 (VM - 0.1 Ash) - MC (0.6 - 0.01 MC), %
Hydrogen = 0.036 FC + 0.086 (VM - 0.1 Ash) - 0.0035 MC^2 (1 - 0.02 MC), %
Nitrogen = 2.10 - 0.020VM, %
Oxygen = 100 - (C + H + N + Ash), %

Where,
MC - Moisture content, VM – Volatile Matter and FC – Fixed carbon

Calorific value
Calorific value is the major thermal property in assessing the energy content of the CNS and its pyrolysis products. The calorific value of CNS, biochar and bio-oil samples was determined as per ASTM D2015-77 using Bomb calorimeter (M/S. Aditya, India).

Results and Discussion
The physiochemical properties and energy content of the raw CNS sample was analyzed and the results were reported in the Table 1. The proximate analysis showed that the raw biomass had a fixed carbon content of 25.92% and a volatile matter of 71.55% which is ideal for the energy conversion processes. The calorific value of raw CNS sample was found to be 20.51 MJ/kg. The moisture content (7.29%) in cashew nut shell was lesser and hence preferable for pyrolysis process. As high moisture in feedstock leads to loss of thermal energy from the process for the evaporation of feedstock water. Pyrolysis experiments were conducted in laboratory scale fixed bed reactor for the production of pyro-char and pyro-oil. The pyro-char from CNS was produced using the pyro-char reactor at 500 °C and 30 min residence time. The heating rate of the pyrolysis process was fixed at 30 °C/min. The produced pyro-char samples were quantified and characterized for its physiochemical properties and calorific value. The pyro-oil was produced using the reactor at the same process temperatures as pyro-char production in order to compare the energy output from both the reactors. The products of the process (bio-oil and char) were quantified and used for further analysis. Produced pyro-oil and pyro-char were shown in Fig 1.

Properties of produced biochar
The results of biochar production and its properties are given in Table 1. The pyro-char yield was found to be lower (29.50%) which may be due to the conversion of compounds such as cellulose, hemicellulose and lignin into carboneous products, water and CO₂ (Akila et al., 2018) (9). Ash content of the pyro-char was found to be increased compared to the raw biomass which was due to the increase in the relative abundance of the minerals that were stable during carbonization. It can be observed that the carbon content increased with pyrolysis temperature. The pyro-char produced at 500°C had a carbon content of 78.30% compared to the raw biomass carbon content of 51.46%. In contrast to carbon content, the volatile matters found to be lower for the pyro-char (17.35%) while the raw biomass had a volatile matter of 71.55%. The calorific value of the biochar produced was found to be 28.75 MJ/kg. The char yield obtained was about 29.50% which was found to be on par with the results of previous literatures (Nithya et al., 2019) (10). The pyro-char energy yield % (EY) can be calculated using the following equation,

\[ EY \% = \frac{\text{Char yield } \% \times (\text{HHV of char sample})}{\text{HHV of biomass sample}} \]

The char energy yield was calculated as 41.35% which indicated that almost half of the biomass energy was converted into useful product through pyrolysis process.

Table 1: Physiochemical properties of the de-oiled CNS and pyro-char

| Parameter                  | Raw CNS | Pyro-char |
|----------------------------|---------|-----------|
| Proximate Analysis (Dry basis) |         |           |
| Moisture (%)               | 7.29    | 4.06      |
| Volatile matter (%)        | 71.55   | 17.35     |
| Ash content (%)            | 2.53    | 7.44      |
| Fixed carbon (%)           | 25.92   | 75.21     |
| Ultimate Analysis         |         |           |
| Carbon (%)                 | 51.46   | 78.30     |
| Hydrogen (%)               | 7.23    | 4.08      |
| Nitrogen (%)               | 0.67    | 1.75      |
| Oxygen (%)                 | 38.90   | 14.42     |
| Calorific value (MJ/kg)    | 20.51   | 28.75     |

Properties of pyro-oil
Table 4. shows the results of yield and calorific value of pyro-oil, pyro-char and gas produced from the reactor. It is evident that, the production of pyro-oil was higher at elevated temperatures. The pyro-oil yield was found to be 41.80% while the pyro-char and gas yield was observed as 28.36 and 29.84%, respectively. This affirmed that the higher volatile biomass yielded higher pyro-oil. Similarly, previous studies showed that the biomass with higher volatile matter yielded higher quantity of pyro-oil. The calorific value of pyro-oil was found to be 37.82 MJ/kg. The combined energy yield percent of the pyrolysis products was found to be 58.42%. This indicates that the simultaneous production of pyro-oil and char was found to have higher energy yield percent compared to sole biochar production. These results revealed that the cashew nut shells (CNS) can be a potential feedstock for pyrolysis process that can yield higher energy value fuels and value-added chemicals.
Table 2: Bio-oil and char yield from the pyro-oil reactor

| Pyro-oil yield (%) | Calorific Value of Pyro-oil (MJ/kg) | Pyro-char yield (%) | Calorific Value of Pyro-char (MJ/kg) | Gas yield (%) | Combined Energy yield (%) |
|-------------------|------------------------------------|--------------------|-------------------------------------|---------------|--------------------------|
| 41.8              | 37.82                              | 28.36              | 28.75                               | 29.84         | 58.42                    |

**Conclusion**

The pyrolysis of cashew nut shell was carried out and the products of the process were quantified and characterized. The physio-chemical analysis of raw biomass showed a higher volatile and fixed carbon content of 71.55 and 25.92%, respectively which confirmed the potential of the feedstock for its suitability for pyrolysis process. The pyrolysis experiments were carried out in the pyrolysis reactor at 500°C and 30 min residence time. The yield of pyro-char was found to be 29.50% with an energy content of 28.75 MJ/kg. The pyro-oil yield was observed as 41.8% with an energy content of 37.82 MJ/kg. The combined energy yield of the process was calculated as 58.42%. These results confirmed the potential of CNS to produce higher energy fuels and chemicals through pyrolysis process.

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