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Characterization of the liquid product obtained by pyrolysis of karanja seed

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HIGHLIGHTS

- This paper highlights the chemical recycling of karanja seeds by thermal pyrolysis.
- Utilization of agricultural wastes.
- Production of the bio-oil from biomass.
- The results of thermal pyrolysis of different seeds carried out by different researchers.
- Suitability of liquid product obtained after thermal pyrolysis of karanja seed as an alternate fuel.

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ABSTRACT

Karanja (*Pongamia glabra*) seeds were pyrolyzed in semi-batch mode at a temperature range of 450–550 °C and at a heating rate of 20 °C/min. FTIR (Fourier transform infrared spectroscopy) analysis of the liquid product indicates the presence of alkanes, alkenes, ketones, carboxylic acids and aromatics rings. GC–MS (Gas chromatography–Mass spectrometry) demonstrated the presence of hydrocarbons with between 14 and 31 carbon atoms in a chain. The physical properties of the pyrolysis liquid were close to mixture of diesel and petrol.

1. Introduction

The recovery of energy from biomass and solid wastes has centered on biochemical and thermo-chemical processes. Of the thermo-chemical processes, pyrolysis is of interest, because it can lead to the production of fuels and useful chemicals. Products from the pyrolysis of biomass include residue chars, tars, and volatile gaseous components (Sharma et al., 2004). For many biomass systems, the products of pyrolysis can be controlled by regulating the heating and gas flow rates, pressure, sample size, and inorganic salts (Baliga et al., 2003). The liquid product of pyrolysis (pyrolysis oil) has the potential to be used as a fuel oil substitute. Liquid products are comprised of molecules derived from depolymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemicellulose, lignin, protein and lipids. In contrast to petroleum fuels, liquid products contain a large amount of oxygen, usually 45–50 wt% (Piskorz et al., 2000). Seeds can be a source of pyrolysis products. For example, slow pyrolysis of pomegranate seeds was carried out by Suat and Selhan (2009) and a maximum liquid yield was obtained at 500 and 600 °C. The bio-chars had high bulk densities and calorific values. Beis et al. (2002) studied pyrolysis of safflower seed in a fixed-bed pyrolyzer to determine the effects of pyrolysis temperature, heating rate, particle size and sweep gas flow rate on product yields and their chemical compositions. The authors obtained a maximum oil yield of 44% at 500 °C at a particle size range of +0.425 to 1.25 mm, with a heating rate of 5 °C/min and sweep gas (N_2) flow rate of 100 cm^3/min. Rapeseed pyrolysis was performed by Onay and Kockar (2006) in a free-fall reactor at atmospheric pressure under nitrogen atmosphere and a maximum pyrolysis conversion of 78% was achieved at 700 °C. A liquid product yield of 75% was obtained at a final pyrolysis temperature of 600 °C, particle size range of 0.224–0.6 mm and a sweep gas flow rate of 100 cm^3/min. Karanja seeds, produced by *Pongamia glabra*, a tree adaptable to various climatic conditions and soil types, are another type of seeds that might be suitable

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for the production of pyrolysis liquids. Therefore, the present study focused on the characterization of liquid products obtained from thermal pyrolysis of karanja seeds at different temperatures in a semi-batch mode.

2. Methods

2.1. Raw material

Karanja seeds were purchased in the market in Rourkela, Orissa, India, dried in a hot air oven for 24 h at 50 °C and directly used for pyrolysis. Moisture, ash, volatile matter and fixed carbon contents were determined according to ASTM D3172-07a method on a dry, ash-free basis.

Ultimate analysis was carried out using a CHNSO elemental analyzer (Variael CUBE Germany).

The calorific value was determined for both seed and char using a bomb calorimeter (Model: AC-350, LECO Corporation, USA). Thermo-gravimetric analysis (TGA) of the sample seed was done using a DTG60 instrument. Around 20–30 mg of seeds was taken and heated to 600 °C for 1 min. TGA was performed in air atmosphere, at a heating rate of 20 °C/min.

2.2. Experimental procedure

The experiment was conducted in a reactor-furnace system in which the temperature was maintained using a PID (proportional-integral-derivative) controller. The karanja seeds (25 g) were placed into the 300-ml reactor and the reactor was heated in the furnace to the desired temperature and the temperature was maintained for the desired length. Vapors were condensed in a condenser at the outlet of the reactor and the condensed liquid was collected in a jar as shown in the previous study (Agrawalla et al. 2011).

2.3. Characterization of char obtained after pyrolysis

Proximate analysis, ultimate analysis and determination of the calorific value of the char were carried out according to ASTM D3172-07a. Scanning electron microscopy (SEM) images of the obtained char were taken with a JEOL (JSM-6480 LV) microscope with an acceleration voltage of 15 kV.

2.4. Characterization of liquid product

Density, specific gravity, viscosity, conradson carbon, flash point, fire point, pour point, cloud point, calorific value, sulfur content and cetane index of the liquid product was determined using the standard test methods.

FTIR of the pyrolysis oil obtained at 500 °C was done in a Perkin-Elmer Fourier transformed infrared spectrophotometer with a resolution of 4 cm^{-1}, in the range of 400–4000 cm^{-1} using Nujol mull as reference. GC/MS-QP 2010 SHIMADZU, equipped with flame ionization and mass spectrometry detection (GC–FID–MS) was used to determine the chemical compounds present in the oil. A capillary column coated with a 0.25 μm film of DB-5 with length of 30 m and diameter 0.25 mm was used. The GC was equipped with a split injector at 200 °C with a split ratio of 1:10. Helium gas of 99.995% purity was used as carrier gas at flow rate of 1.51 ml min^{-1}. The oven initial temperature was set to 70 °C for 2 min and then increased to 300 °C at a rate of 10 °C/min and maintained for 7 min. All the compounds were identified by means of the NIST library. Mass spectrometer was operated at an interface temperature of 240 °C with ion source temperature of 200 °C of range 40–1000 *m*/*z*.

3. Results and discussion

3.1. Characterization of karanja seed and char

3.1.1. Proximate and ultimate analysis of karanja seed and obtained char

As observed in Table 1, the karanja seed had a very high volatile matter content of 73.8% which was reduced drastically to 32% after pyrolysis. As a result of the decrease in volatile matter content, fixed carbon increased significantly. The ultimate analysis presented in Table 2 shows significant variation in carbon and oxygen content whereas there were slight variations in hydrogen, nitrogen and sulfur content.

3.1.2. SEM analysis of karanja char

Images are of karanja seed char taken at 80× and 200× magnifications are presented as Supplemental Fig. S1. The char exhibited a heterogeneous distribution of pores and a rough texture. The average size of pores on the surface was 43.3 μm. Pyrolysis temperatures and heating rate influenced the size and shape of particle through a general increase in size and proportion of voids and a decrease in cell wall thickness. The fast volatile release during

Table 1
Proximate and ultimate analysis on daf basis of karanja seed and char produced.

Properties	Karanja seed	Karanja char
Moisture content	15.2	0.0
Volatile content	73.8	32.0
Ash content	3.9	8.9
Fixed carbon	7.1	59.1
C	52.79	68.32
H	6.26	3.16
N	3.88	6.53
S	0.06	0.04
O	37.01	21.95
C/H Molar ratio	0.70	1.80
C/N Molar ratio	15.85	12.21
Empirical formula	$C_{23.47}H_{33.39}N_{1.48}S_{0.01}O_{12.34}$	$C_{45.56}H_{25.28}N_{3.73}S_{0.01}O_{10.97}$
Gross calorific value (kcal/kg)	5350	6050

Table 2
Physical properties of karanja seed pyrolytic oil.

Properties	Karanja seed pyrolytic oil	Methods
Appearance	Dark brownish oil	
Density at 15 °C (kg/m^3)	0.9384	ASTM D1298-99
Specific gravity at 15/15 °C	0.9393	ASTM D1298-99
Kinetic viscosity at 40 °C in centistoke	27.9	ASTM D445-11
Kinetic viscosity at 100 °C in centistoke	4.4	ASTM D445-11
Viscosity index	Plus 34	
Conradson carbon residue	4.30%	ASTM D189-06(2010)e1
Pour point	Plus 16 °C	ASTM D5853-09
Cloud point	28 °C	ASTM D1310-01(2007)
Flash point by Abel method	40 °C	ASTM D6450-05(2010)
Fire point	58 °C	ASTM D1310-01(2007)
Gross calorific value in kcal/kg	8113	ASTM D5468-02(2007)
Sulfur content	0.05%	IS:1448 P:33
Calculated cetane index	29	ASTM D4737-10
Initial boiling point	96 °C	ASTM D2887-08
Final boiling point	376 °C	ASTM D2887-08