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Pyrolysis of Mahua seed (*Madhuca indica*) – Production of biofuel and its characterization

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ABSTRACT

The thermal pyrolysis of Mahua seed (*Madhuca indica*) has been carried out in the present study to verify its potentiality for biofuel production. Pyrolysis was conducted in a semi-batch reactor at various temperatures from 450 to 600 °C under 30 mL/min nitrogen flow rate and at 20 °C/min constant heating rate. At an optimum temperature of 525 °C, the maximum bio-oil yield of 49% was obtained along with 18% of bio-char. Both the products were further physically and chemically characterized, and their results demonstrated their efficiency and potentiality as beneficial energy resources. The chemical characterizations through FTIR, ^{1}H NMR, and GC–MS showed that the bio-oil consisted of significant number of aliphatic compounds than aromatics. The obtained calorific value of bio-oil was found to be 39.02 MJ/kg which is closer to the calorific values of the conventional petroleum fuels. Moreover, the morphological characteristics of bio-char was carried out using SEM and BET analysis which revealed their macroporous surface with a low surface area of 13.2 m^2/g. Bio-char had calorific value of 26.053 MJ/kg which is more than that of fossil fuel coal. Such favorable outcomes endorse the Mahua seed biofuel as a promising candidate to be used as hydrocarbon fuel and chemical feed stock.

1. Introduction

The widespread availability of biomass has not only offered an alternative to the declining oil reservoirs and fossil fuel sources but has also earned the recognition of being an attractive biofuel source for clean energy production. Biomass doesn't release CO_2 to the environment unlike the fossil fuels and is mainly composed of carbohydrate compounds (cellulose, hemicellulose, lignin and minor amounts of other organics) containing very high energy [1]. Biomass like non-edible seeds are very useful feedstock for biofuel production. Approximately 23.7 million hectares of land in India is occupied by the oilseed crops and a productivity of just about 1 ton/ha is reached. The rich forest resources and the favorable climatic conditions of India have promoted the harvesting of around 300 non-edible oil bearing plant species across the country, among which Mahua (*Madhuca Indica*) tree is an important economic plant yielding significantly high quantity of oil [2]. The plant is extensively cultivated in central and southern India for its oil bearing seed which have 35% oil content, 16% protein, and desirable levels of oleic and stearic acids which are comparatively devoid of creating toxic effects. The annual production of Mahua seed in India is around 0.50 million tons with seed yield ranging from 20 to 200 kg per tree every year [3–5]. Such properties of Mahua seed can favor the higher production of bio-oil.

The thermochemical biomass energy conversion process, in comparison to other biochemical processes, is preferred presently because of the production of more fuel to feed ratio in the former case [6,7]. Thermochemical process like, pyrolysis is the thermal decomposition of biomass in an inert atmosphere to produce various product such as liquid fuel, solid residue and gas. These products have potential application in boiler and diesel engine for power generation, and also it can be used as a source of pure chemicals [8].

Previously, numerous research work has been done by various researches to produce different products from pyrolysis of seeds that has been summarized in Table 1.

Such results urged us to carry out the pyrolysis of Mahua seed and characterize the bio-oil and bio-char obtained from it to determine if it can be a good candidate as it is widely available and cheaper source for renewable energy production. This work presents the production of the bio-oil and bio-char obtained from conventional pyrolysis of Mahua seed in a semi-batch reactor at 450–600 °C temperature range and 20 °C/min heating rate under

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Table 1
Comparision studies of pyrolytic product yield from different biomass resources.

Biomass	Author	Temperature (°C)	Bio-oil (%)	Bio-char (%)	Gas (%)	Aqueous fraction (%)
Tamarind seed	Kader et al. [8]	400	45	39–40	10–15	n/a
Sal seed	Kumar et al. [9]	600	52.8	23–25	20–25	n/a
Neem Seed	Kumar et al. [10]	475	38	30–32	32–35	n/a
Mahua seed	Shadangi and Mohanty [5]	525	34.64	20–30	20–21	19–20
Cotton seed	Panda et al. [11]	550	58.6	25–30	12–15	n/a
Lin seed	Kumar et al. [2]	550	68	20–23	10–12	n/a
Karanja seed	Kumar et al. [12]	500	57	25–30	10–25	n/a
Castor seed	Singh and Shadangi [13]	550	64.4	18–24	10–15	n/a
Pomegranate seeds	Uçar and Karagöz [14]	500	21.98	29.83	16.13	32.06
Kanar seed	Panda et al. [15]	600	79	10–11	9–10	2.2

n/a: Not available.

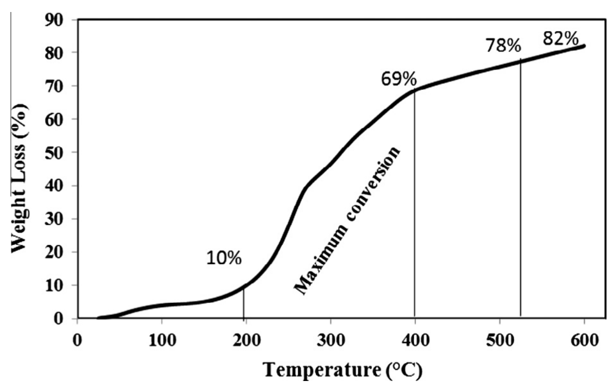

Fig. 1a. TGA plot of Mahua seed.

inert atmosphere. The effect of temperature on product yield were studied. The bio-oil obtained was characterized for its various physical and chemical properties. Further the obtained bio-char after pyrolysis of Mahua seed was also characterized for their physical and chemical properties.

2. Materials and methods

2.1. Materials

Mahua seeds were obtained from National Institute of Technology Rourkela, India. The high grade chemicals used during the chemical analysis are KCl, chloroform-d and n-hexane which were obtained from Fisher scientific, Merck, and Sigma Aldrich.

2.2. Feedstock preparation

Fresh Mahua seeds were dried in sun for 10 h and then crushed and sieved to get particles of 0.55–1 mm size. Before performing pyrolysis, the powdered seeds were preheated at 110 °C in hot air oven for 2 h to remove free moisture content and they were stored in airtight plastic containers.

2.3. Proximate and ultimate analyses

The proximate analyses of the Mahua seed and bio-char were performed according to the ASTM D 3172-07a to evaluate for its moisture, volatile, fixed carbon and ash contents. The ultimate analyses for carbon, hydrogen, nitrogen, sulfur and oxygen weight percentages of Mahua seed, bio-oil and bio-char were determined from CHNSO elemental analyzer (Variael CUBE Germany). The major constituent of Mahua seed are hemicellulose, cellulose, lignin and oil content which were also determined [3,16].

2.4. Characterization of feedstock

2.4.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of Mahua seeds was done using a SHIMADZU model DTG-60/60H. Approximately 12.30 mg of powdered seeds of <100 μm size were taken in an Al_2O_3 crucible and heated up to 600 °C at 20 °C/min heating rate. High purity nitrogen gas at around 100 mL/min flow rate was used as an inert purge gas to displace air in the pyrolysis zone for avoiding unwanted oxidation of the sample.

2.4.2. Thermal pyrolysis of feedstock

The feedstock is fed into the stainless steel semi-batch reactor of 17.5 cm length with the inside and outer diameter 4.7 and 5 cm respectively. Air was purged from reactor with a nitrogen flow rate of 30 mL/min for 15 min to create an inert atmosphere to perform all the experiments. The reactor was heated by electrical furnace and the temperature of the pyrolysis reactor was measured with Cr-Al (K type) thermocouple (error ±2 °C) and controlled by using high sensitive PID controller. The temperature was maintained from 450 to 600 °C in steps of 25 at constant heating rate of 20 °C/min and the maximum yield of the liquid product was obtained at 525 °C. The volatiles from the pyrolysis reactor outlet pipe were condensed with a water-cooled condenser maintained at 25 °C. After pyrolysis, the reactor was cooled down to room temperature and weighed to estimate the weight percentage of bio-char (solid residue). The weight percentage of gas (non-condensable volatiles) was determined from the material balance. The total liquid product consisted of two phases i.e., aqueous and oil phase. Separation of pyrolysis oil from the aqueous phase was done by centrifuging at 5000 rpm and then both were weighed individually. The optimum temperature for maximum pyrolytic oil produced from Mahua seed thermal pyrolysis was decided on the basis of highest weight percentage yield of the pyrolytic oil.

2.5. Characterization of Mahua bio-oil

2.5.1. Water content and pH analysis

Water content in the bio-oil was estimated using Aquamax KF Oil Evaporator model 51000 as per ASTM method (D6304). 0.5 g bio-oil was mixed in 10 mL dried hexane and shaken well till it dissolved. 1.0 mL aliquot was injected into the base oil of the oil evaporator. The liberated moisture was transferred into the titration vessel by the carrier gas where it was titrated coulometrically.

The pH of the pyrolytic oil was determined by using Eutech water proof pH 510 (pH Spear) pH meter.

2.5.2. Density, viscosity and calorific value estimation

The density determination of the pyrolytic oil was done by introducing a small volume (approximately 0.6 mL) of bio-oil sample into an oscillation U shaped tube in a thermal bath at 15 °C as