



## Physicochemical and thermal characterization of nonedible oilseed residual waste as sustainable solid biofuel



Pooja Doshi\*, Gopal Srivastava, Gauri Pathak, Madhurima Dikshit

Biochemistry Division, Department of Chemistry, University of Pune, Pune 411007, MS, India

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### ABSTRACT

The present study aims to investigate the potential of nonedible oilseed *Jatropha* (*Jatropha curcas*) and *Karanja* (*Pongamia pinnata*) defatted residual biomasses (whole seed, kernel, and hull), as solid biofuel. These biomasses showed good carbon contents (39.8–44.5%), whereas, fewer amounts were observed for sulfur (0.15–0.90%), chlorine (0.64–1.76%), nitrogen (0.9–7.2%) and ash contents (4.0–8.7%). Their volatile matter (60.23–81.6%) and calorific values (17.68–19.98 MJ/kg) were found to be comparable to coal. FT-IR and chemical analyses supported the presence of good amount of cellulose, hemicellulose and lower lignin. The pellets prepared without any additional binder, showed better compaction ratio, bulk density and compressive strength. XRF analysis carried out for determination of slagging–fouling indices, suggested their ash deposition tendencies in boilers, which can be overcome significantly with the optimization of the blower operations and control of ash depositions. Thus, overall various chemical, physical properties, thermal decomposition, surface morphological studies and their high biofuel reactivity indicated that residual biomasses of *Jatropha* and *Karanja* seeds have high potential to be utilized as a solid biofuel.

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### 1. Introduction

Energy is considered as prime agent in the generation of wealth and a significant factor in economic development. The energy resources have been split into three categories: fossil fuels, renewable resources and nuclear resources. There are many alternative for new and renewable energy sources which can be used instead of the fossil and conventional fuels (Demirbas, 2000). As, the conventional or fossil fuels are becoming exhausted and contributing to greenhouse gas (GHG) emissions, leading to many negative effects on the global environment (Anon, 2005; Prasad et al., 2007; Singh et al., 2010; Zhao et al., 2009), the dominance of fossil fuels is gradually diminishing in favor of renewable sources of energy, including agricultural biomass (Serio et al., 2003; Xiao et al., 2001).

Lignocellulosic biomass represents a source of renewable energy. This biomass can be converted into liquid, solid and gaseous fuels with the help of some physical, chemical and biological conversion processes (Campbell, 1983; Ravindranath and Hall, 1995). Biomass has attracted attention as renewable energy sources with the highest potential to contribute to energy needs worldwide because of the ease of production and availability advantages as well as environmental benefits. In many developing countries, fraction of the biomass energy consumed is ranged from 40% to 50%, since

these countries have large agriculture and forest areas (Ko and Bin, 2004). In addition to their sustainable favorability, they are, in general, more evenly distributed over earth's surface than fossil fuels or uranium and may be exploited using less capital-intensive technologies (Naik et al., 2010). Hence, they increase the scope for diversification and decentralization of energy supplies and the achievement of energy self-sufficiency at a local, regional and national level (Sudo et al., 1989). The Indian approach to biofuels is based solely on non-food feed stocks to be raised on degraded or wastelands that are not suited to agriculture, thus avoiding a possible conflict of fuel vs. food security (Mathiyazhagan et al., 2011). In India, a few states have created Boards, Authorities and Departments for the promotion and use of biofuels. Some have announced 'Minimum Support Price' for non feed oilseeds such as *Karanja*, *Jatropha*, *Jajoba*, *Kusum*, and *Mahua* (Kumar, 2010; Srivastava and Prasad, 2004).

Recently, *Jatropha* (*Jatropha curcas*) and *Karanja* (*Pongamia pinnata*) plants are receiving a great deal of attention (Achten et al., 2008; Kumar and Sharma, 2008; Openshaw, 2000) and were selected as the most suitable for production of biodiesel in India. *Jatropha* seed oil has been recognized as a source for medium viscosity pure plant oil that is easily converted to biodiesel with good product properties (Agarwal, 2007), based on its ability to thrive in a variety of agro-climatic conditions, a low gestation period, and high seed yield relative to other plants with oil-bearing seeds (Planning Commission, Government of India, 2003). It is apparent

\* Corresponding author. Tel.: +91 9545588772; fax: +91 02025691728.

E-mail address: [pdoshi@chem.unipune.ac.in](mailto:pdoshi@chem.unipune.ac.in) (P. Doshi).

that extraction of biocrude or oil from the *Jatropha* seeds will generate huge quantity of residual deoiled seed cake. *Jatropha* production is forecasted about 2500 kg seeds/hectare under Indian conditions, and considering 40–50% oil in it, the extraction will generate approximately 1000 kg seedcake per hectare crop. Similarly, *Karanja* belonging to the *Leguminaceae* family is prominent species having nonedible oilseed that can be grown easily in available wastelands. In India, 0.93 million hectares of wastelands is covered with *Karanja* plantations in eight states (Kumar, 2010). The yield of oilseeds per tree is reported between 8 and 24 kg. The typical oilseed has oil 30–33% (Padhi and Singh, 2011). The availability of *Karanja* oilseeds and defatted oilseed cake in India is estimated to be around 0.20 and 0.145 million metric tonnes per annum respectively, before introduction of 'Biodiesel Programme' in the country (Radhakrishna, 2003).

One of the major problems arising in coming years will be disposal of defatted cake left over after expelling oil from these oilseeds (Chandra et al., 2006). Since *Jatropha* and *Karanja* are nonedible crops and the seeds are toxic (Akintayo, 2004; Gubitz et al., 1999), these cakes cannot be used as cattle feed, unlike in other parts of the world where the vegetable oil from rape seed and soy, are used for biodiesel and their cake is used for cattle feed. Therefore, their safe disposal or meaningful utilization is very important. This residual waste, may be used either as animal feed after detoxification (Vinay and Sindhu Kanya, 2008) as organic nitrogenous fertilizers (Sanderson et al., 1996) or for biogas production (Chandra et al., 2006). Apart from these uses there is utmost need for development of its alternative applications. Thermal applications such as pellets and biofuels, are much more profitable as they are easier to materialize, require less financial investments and have a smaller environmental impacts (Gronalt and Rauch, 2007). Characterization of biomass is imperative as the chemical composition of biomass affects the combustion processes differently (Sanderson et al., 1996). From the chemical point of view this residual biomass is composite material, constituted by a mixture of hemicellulose, cellulose, lignin, inorganic matter (ash) and extractives, with proportion and chemical structure affected by variety (Theander, 1985; McKendry, 2002). The characterization techniques developed for other fuel like coal can also be applied for the biomass fuel (Carpenter, 2008). This characterization includes proximate analysis (moisture content, ash content, volatile matter), ultimate analysis (C, H, N, O, S), calorific value measurement, ash analysis and organic matter analysis. Therefore, knowledge of the influences of properties of final ash materials can make it possible to avoid fuel combinations with unwanted properties, or even to design an ash material for a certain application (Fernández et al., 2006; Theis et al., 2006). Several studies have dealt with co-combustion of biomass and coal (Amand et al., 2001; Werther et al., 2000; Okasha et al., 2006), as this fuel is attractive due to relatively high combustion efficiency, moderate NO<sub>x</sub> emissions and "intrinsic" sorbent retention capability. Eutectics of low melting point are created by absorption and chemical interaction between silica (SiO<sub>2</sub>) and potassium compounds, e.g. K<sub>2</sub>O or KCl of the ash biomass (Miles et al., 1996; Baxter et al., 1998; Ghaly et al., 1994). Also, researchers have confirmed and mentioned the formation of low melting point compounds like silicates in the combustion and gasification of lignocellulosic biomass (Lin and Dam-Johansen, 1999; Nordin et al., 1996; Ergudenler and Ghaly, 1992).

Further, these biomass materials are often preferred in densified form (briquettes, pellets, or cubes) than baled forms, which involve a lot of handling, transportation and storage costs, whereas, densification improves the effective bulk density of the biomass. Thus, the basic objectives of the present study was to evaluate the potential of residual biomasses left over after oil extraction from *Jatropha* and *Karanja* oilseeds for the production of solid biofuel. Hence, the defatted whole seed, kernel and hull biomasses

were evaluated for their physicochemical characteristics and thermal decomposition as well as pelletization properties.

## 2. Materials and methods

### 2.1. Sample preparation

The dried whole seeds of *Jatropha* and *Karanja* were obtained from 'Agharkar Research Institute', Pune, Maharashtra, India as well as 'Indian Biodiesel Corporation', Baramati, Pune, Maharashtra, India. The whole seeds of both the seed samples were separated manually to obtain kernel and hull. Then, whole seed, kernel and hull were ground separately, using a mechanical grinder followed by laboratory defatting with solvent hexane using Soxhlet apparatus. These defatted residual biomasses were dried in oven at 70–80 °C overnight for removal of residual solvent, grounded, sieved (<250 μm) and stored in a separate air tight plastic containers till further used for characterization and pellet preparation.

### 2.2. Chemical characterization of residual samples

#### 2.2.1. Proximate analysis

It involved moisture, ash, volatile matter and fixed carbon contents determination. To determine the moisture content, samples were introduced into hot oven at 105 °C till constant weight was achieved (ASTM 871-82, 2006).

The ash contents were determined using laboratory muffle furnace (Fourtech, Mumbai, India) as per the reported procedure (ASTM-D 3174-04, 2009). Briefly, 1.0 g of each residual biomass sample was taken in crucible and placed in muffle furnace and maintained at 600 ± 10 °C for 4 h. After cooling, the crucibles were removed from the furnace and placed in the desiccators. The above process of heating and cooling was repeated until constant weight was obtained, which allows the removal of volatiles and unburnt carbon.

The volatile matter was determined by the procedure given in ASTM-D 3175-07 (2009). The residual biomass samples (1.0 g each) were taken in crucible and placed in muffle furnace maintained at 950 ± 10 °C for 7 min. Then the crucibles were removed from the furnace and placed in the desiccators. The loss of weight was expressed as the volatile matter in the samples. The percentage of fixed carbon was determined by difference from 100, taking into account the percentile amounts of moisture, volatile matter and ash.

#### 2.2.2. Ultimate analysis

The equipment used in this analysis was an elemental analyser (Vario EL III, Germany) available at ARI, Pune, with an automatic injector and the option of analyzing the C, H, N and S elements, simultaneously. The amount of oxygen was obtained by subtracting the sum of the C, H, N and S contents and the ashes from 100.

#### 2.2.3. Biofuel reactivity

The biofuel reactivity was obtained from the proximate and ultimate analysis by dividing the volatile matter (VM) and fixed carbon (FC) contents in the sample along with the information provided by the molar ratios H/C and O/C (Miranda et al., 2008, 2009; Shafizadeh and DeGroot, 1976).

#### 2.2.4. Chemical analysis

This involved cellulose, hemicellulose and lignin content determination in the residual biomass samples. The neutral detergent fiber (NDF) and acid detergent fiber (ADF) were determined using

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