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Optimization and kinetic studies on biodiesel production from underutilized *Ceiba Pentandra* oil

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HIGHLIGHTS

- C. *Pentandra* oil is non-edible, which has been used as a novel source for the first time for biodiesel production.
- This study gives an overall view of extraction and process parameter optimization for biodiesel production.
- Kinetic studies were established for the production of biodiesel for *C. Pentandra* oil.
- Physio chemical characteristics of *C. Pentandra* oil and biodiesel were determined as per standard method.
- The fuel properties of biodiesel obtained from *C. Pentandra* oil were compared with ASTM D6751 standards.

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ABSTRACT

This present work investigates the production of biodiesel from non-edible *Ceiba Pentandra* oil. The process was catalyzed by two-step acid base transesterification. Reaction parameters such as catalyst concentration, methanol to oil molar ratio, reaction temperature and time are studied. The conversion of biodiesel was found to be 99.5% under the optimized conditions of 1.0 wt.% KOH and 6:1 methanol oil molar ratio at 65 °C for a reaction time of 45 min. The kinetic study is carried out in various temperatures. The conversion of triglycerides into methyl esters obeys the first-order mechanism. The reaction rate constants and activation energies were determined. The physical and chemical characteristics of *C. Pentandra* oil and biodiesel were determined as per standard method. The fuel properties complied with the limits prescribed in the ASTM D6751standards.

1. Introduction

Environmental concerns in fossil fuel depletion and fluctuating oil price intensified the search for alternate fuel from renewable resources. Vegetable oil and animal fats were found to be the best alternate energy source that can be used in existing engine. High viscosity and low volatility were the two main reasons for their direct application [1]. Obviously, transesterification meant for displacement of alcohol from an ester by another alcohol and widely used to reduce the viscosity of oils and fats [2]. Portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number and higher biodegradability were the advantages of biodiesel as diesel fuel [3].

The use of edible vegetable oils and animal fats for biodiesel production received great concern because they compete with food materials [4]. The demand for vegetable oils for food has increased tremendously in recent years. It was impossible to justify the use of vegetable oils for fuel purposes such as biodiesel production. Moreover, vegetable oils were more expensive to use as fuel [5]. The uses of non-edible plant oil sources are keeping competition with food edible oil for biodiesel feed stock. Hence, the contribution of non-edible oil from *C. Pentandra* will be significant source for biodiesel production.

In this regard, the oil from tropical plant *C. Pentandra* is non-edible, which has a tremendous potential for biodiesel production. Moreover it grows in wasteland, provides a more attractive feedstock for biodiesel production. *C. Pentandra* is generally drought-resistant tree. Pods from these trees are leathery, ellipsoid, pendulous capsule, 10–25 cm long, and 3–6 cm diameter. Capsules split open into 5 valves, revealing a mass of woolly, yellowish grey and lustrous fiber in which the 120–175 seeds are embedded. Seeds are round and black in color. As its fiber is short natured, they are used for filling mattresses, cushions, and also to make life belts. *C. Pentandra* seeds were reported to have low feeding value due to its high fiber content

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and presence of tannins [6]. The seeds were picked out of the wool and thrown away when it was not needed for planting. At present the *C. Pentandra* oil has only limited application and the natural production of seeds remain under utilized.

Literature shows that no work was established so far on the production of biodiesel using *C. Pentandra* oil. In this present investigation, *C. Pentandra* oil was used as a potential source for biodiesel production. The reaction conditions have been investigated to optimize the process variables that lead to higher yield of biodiesel and to develop a simple kinetic model for transesterification process.

2. Experimental section

2.1. Materials

Pods of *C. Pentandra* were collected from local villages near Chennai, Tamil Nadu, India during the month of July. Sample was identified as *C. Pentandra* and authenticated at Centre for Advanced Studies in Botany, University of Madras, Chennai, Tamil Nadu, India. KOH (97% purity) anhydrous sodium sulphate and concentrated H_2SO_4 (98.4% purity) was purchased from Sisco Research Laboratories, Mumbai, India. Methanol and n-hexane of 99.9% pure were obtained from Merk, Mumbai, India. Other chemical reagents used in the study, were purchased from Rankem, Delhi, India. All solvents and chemicals obtained were used without any further purification.

2.2. Extraction

The *C. Pentandra* pods were disrupted and seeds were removed manually from the fiber. The collected seeds were dried under sun, ground to powder, passed through 60 mesh and then the powdered seeds were dried at 105 °C until a constant weight was obtained. The *C. Pentandra* seed powder was mixed with one forth weight of diatomaceous earth for better solvent flow through sample. The mixture was packed inside a thimble in a soxhlet extractor. Extracting medium n-hexane was poured into the round bottom flask. The extraction was conducted at the rate of 6 cycles per hour and continued for 18 h. The extract was filtered through Whatman filter paper No. 4 and rinsed with the same to complete the transfer. The extracted oil was recovered after a solvent evaporation in a rotary vacuum evaporator. The oil yields obtained was expressed in terms of mass percentage of the samples and calculated as

$$\text{Total yield}\%(\text{w/w}) = [\text{Mass of oil extracted}(\text{g})/\text{Mass of seed}(\text{g})] \times 100$$

2.3. Characterization of oil

The acid, saponification and iodine values were determined by titrimetry [7]. Water content was determined using a Karl Fisher auto-titrator. The unsaponifiable fractions of the extracted oils were analyzed in duplicate and the results are presented as mean values [8].

Gas chromatography was used to qualify and quantify various fatty acid profiles present in *C. Pentandra* oil. Fatty acids were initially transformed in to their respective methyl esters [9]. The fatty acid methyl ester profile was detected using gas chromatography. It consists of CHEMITO GC 8610 with flame ionization detector and nitrogen as a carrier gas. Hydrogen and oxygen were used for ignition purpose. Column was packed with BPX-70 (50% cyanopropyl and 50% methylsiloxane). Injection port was maintained at 250 °C and detector port was maintained at 260 °C. The starting temperature of oven was maintained at 160 °C and increased by 7.5 °C per min to a final oven temperature of 240 °C. The data obtained were collected by Win-Chrom software and were identified by comparing with standard methyl esters retention time.

2.4. Reaction setup

Initially, transesterification reaction was carried out in a reactor consists of 250 mL double-necked round bottom flask. Followed by placing the round bottom flask inside the heat jacket. Thermostat, a part of heat jacket which maintain the temperature of the reactant at a desired value with an accuracy of ±1 °C. Methanol has a boiling point of 65 °C, which vaporizes at elevated temperature during the reaction. To prevent the loss of methanol during reaction, a water-cooled condenser was fixed on the side neck. This condenses the vapors and refluxes back into the reactor. The condenser also helps in maintaining atmospheric pressure inside the reactor. A stirrer assembly was inserted through the main neck of the reactor for effective mixing, to achieve a perfect contact among the reactants they are stirred well at constant rate [10].

2.5. Acid catalyzed esterification process

The base catalyzed reaction was reported to be very sensitive to the content of Free Fatty Acids (FFA), which should not exceed a certain limit to avoid deactivation of catalyst by formation of soaps and emulsion [11]. Therefore, FFAs were first converted to respective esters in a pretreatment process with methanol using an acid catalyst (H_2SO_4). It was reviewed from the literature and found that the product having acid value less than 2 mg KOH g^{-1} is used for base catalyzed reaction [12].

The acid catalyzed esterification is a pretreatment process employed to decrease the acid value of the feedstock below 2 mg KOH g^{-1}. Based on the results of Chongkhong et al. (2007) [13] esterification reaction was performed by employing methanol to oil volume ratio as 8:1 at 65 °C with 1.834 wt.% H_2SO_4 as a catalyst. The FFA level of the mixture was checked at different time intervals. When the required FFA level was reached, the mixture was cooled to room temperature and transferred to a separating funnel without agitation leading to separation of two phases. Finally the acid value of the product separated at the bottom was determined.

2.6. Alkali catalyzed transesterification process

Alkali-catalyzed transesterification, the most effective in the transesterification processes used in the commercial production of biodiesel. Even at ambient temperature, the alkali-catalyzed reaction precedes rapidly usually reaching 95% conversion. It is noted that the parameters like catalyst concentration, methanol to oil molar ratio, reaction temperature and reaction time play an important role in production of biodiesel [14]. The effect on varying these parameters such as catalyst concentration (0.25, 0.50, 0.75, 1.0 and 1.25 wt.%), methanol to oil molar ratio (3:1, 6:1, 9:1 and 12:1), reaction temperature (45, 50, 55, 60 and 65 °C), reaction time (15, 30, 45 and 60 min) on the biodiesel yield was studied. The speed of the stirrer was kept constant at 600 rpm for all test runs.

2.7. Downstream process

About 5 mL of sample was drawn at required interval. Ice-cold distilled water was added to the sample immediately to stop the reaction. The mixture was shaken well and centrifuged at 10,000 rpm for 10 min. The top organic layer was separated and dried over sodium sulphate.