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Process optimization and kinetic modeling of biodiesel production using non-edible *Madhuca indica* oil

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HIGHLIGHTS

- Non-edible mahua oil is utilized for biodiesel production.
- RSM was used to optimize the transesterification process variables.
- Catalyst, methanol and temperature had significant effect on mahua biodiesel yield.
- Biodiesel production follows first-order kinetics.
- Mahua biodiesel satisfied the ASTM standards.

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ABSTRACT

Optimization and kinetic modeling of biodiesel production from non-edible *Madhuca indica* oil were investigated in this study. Type of catalyst, catalyst concentration, methanol amount, and reaction temperature were optimized by the univariate method. KOH was found as a better catalyst for conversion of mahua oil to biodiesel. Response surface methodology (RSM) was employed to determine the optimal level of KOH (%), methanol amount (v/v), temperature (°C) and time (min). Maximum biodiesel yield of 91.76% was predicted at the optimal level of KOH as catalyst (1.5%), methanol amount (0.32% v/v), temperature (60 °C) and time (90 min). Biodiesel yield (88.71%) was obtained in the validation experiments and fitted 96.6% with the RSM predicted results. Kinetic studies were performed at different temperatures and observed that the conversion of mahua oil to biodiesel follows the first order reaction. The kinetic rate constants and activation energy were calculated. The physiochemical properties of mahua biodiesel were determined using standard methods and the mahua biodiesel properties are in accordance with the ASTM D6751 standards.

1. Introduction

An image on fuel consumption represents the oil demand in India. According to the Petroleum Planning and Analysis Cell, India is Asia's third-largest country consumes about 15.48 million tons of fuel by the year 2015. On putting the country's track on fuel demand, it requires 300,000 barrels per day and the need surpass the China in an incremental growth [1]. According to U.S. Energy Information Administration (EIA), India's demand will be more than double to 8.2 million bbl/d by 2040 while domestic production will remain at 1 million bbl/d. The country mainly depends on imported crude oil to meet the petroleum demand. Due to these reasons, the need for an alternative to traditional petroleum arises. In search of an alternative source of energy which reduces the carbon emission to environment and dependency on fossil fuel is the major key factor which drives towards the production of biodiesel. Biodiesel is mono-alkyl esters of fatty acid derived from transesterification reaction between oil and alcohol in the presence of catalyst [2]. Biodiesel has similar properties with conventional petroleum fuel and has several advantages over it such as low CO_2 emission, safe and easy to handle, nontoxic, high fuel efficiency [3,4]. Nowadays >95% of biodiesel produced from the edible oils by transesterification with alcohol and catalyst. It will be difficult for large scale production of biodiesel because it imbalances the global food demand and diminishes the line between the food and fuel as both if the fields strive to gain from the same oil

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resources. The use of low-cost feed stock will decrease the production cost, research on biodiesel production from non-edible oils such as jatropha [5], rapeseed [6], karanja [7], palm [8], mahua [9], *Hodgsonia macrocarpa* seed [10], *Cerbera odollam* [11], moringa [12] and rubber seed [13] are increasing nowadays.

Mahua oil is a non-edible vegetable oil obtained from seeds of *Madhuca indica* tree found in many parts of India. Mahua oil is an excellent source of fuel comparable with diesel. It possesses a high content of free fatty acids (FFA) and, therefore it makes as a good initiator for transesterification process and can be transesterified into methyl esters, ethyl esters and butyl esters based on treatment with methanol, ethanol and butanol respectively. It has been reported that the methyl esters of mahua oil is closer to the properties of diesel and also having less carbon emission [14]. Methanol is used rather than other alcohols due to its high efficiency, increased thermal efficiency; low stoichiometric air to fuel ratio (6.42:1), recovery of biodiesel from final product is easy. To construct an economically attainable bioprocess, the operating parameters must be optimized perfectly. Using an effective experimental design, the combined interaction of processing parameters can be optimized to produce the desired product. Response Surface Methodology (RSM) is a promising tool for designing the experiments, constructing models, analyzing the effects of factors and scrutinizing the optimum conditions [15]. Ghadge and Raheman employed RSM for optimizing the acid pre-treatment parameters for biodiesel production using mahua oil [16]. In this study, process variables for transesterification of mahua oil were optimized using RSM and kinetic modeling of transesterification was studied.

The present study reports an approach based on the use of mahua oil as low-cost feed stock and the influence of various operating parameters such as catalyst type, catalyst concentration, methanol to oil molar ratio, and temperature on the yield of fatty acid methyl esters (FAMEs). Kinetic constant, as well as activation energy for the transesterification reaction have also been determined at optimum operating conditions. The properties of synthesized biodiesel are analyzed in order to compare with ASTM standards.

2. Materials and methods

2.1. Materials

Mahua oil was obtained from a private oil company. Methanol, NaOH, KOH, $BaCl_2$, Na_2CO_3, $K_2Cr_2O_7$ were purchased from Himedia, India. All the chemicals used in this study were of analytical grade.

2.2. Methods

2.2.1. Pre-treatment and acid esterification

The crude oil is very denser, and it was heated at 60 °C for an hour to remove the traces of water, and it was filtered to remove the dust particles. The free fatty acid profile of treated oil was analyzed, and it is given in Table 1. The oil had an initial acid value of about 36 mg KOH/g corresponding to the FFA level of 18% which is far behind the limit for transesterification reaction (1 and 2%). Single step acid pre-treatment was carried out to reduce the FFA of the oil. The reaction was carried out in a 500 ml beaker using magnetic stirrer. The methanol was initially charged in the beaker (0.40 v/v oil) and sulphuric acid (1% w/w oil) was added by constantly stirring. The acid was thoroughly mixed with methanol and then pre-heated oil was added. The mixture was stirred at a constant speed at 55 °C for 1.5 h. The reaction mixture was then poured in separating funnel and allowed to settle for 2 days. The top layer had unreacted methanol and water whereas the bottom layer had oil and fatty acid methyl esters (FAMEs) [17].

2.2.2. Determination of acid value

The acid esterified oil is titrated against 0.1 N KOH using phenolphthalein indicator to estimate the FFA content. The acid transesterification was repeated for two times to achieve FFA of about 0.8% which is suitable for transesterification reaction. This acid treated oil with less FFA% was stored and used for further experiments [8].

2.2.3. Transesterification

For transesterification reaction, pre-treated oil was heated at 55 °C and the methanol containing dissolved catalyst was added. The reaction was performed in temperature controlled magnetic stirrer at a constant speed for 1.5 h and the reaction temperature was monitored routinely using thermometer. After this step, the mixture was poured in separating funnel and allowed to settle for a day. Two layers were obtained, the top layer comprised of biodiesel and the bottom layer comprised of glycerol. The biodiesel layer was separated and washed with an equal amount of warm distilled water to remove the soap contents and other impurities. The washing was continued until the clear biodiesel without soap contents were obtained. The washed biodiesel is dried by heating at 100 °C for an hour to remove the traces of water. The yield of biodiesel was then calculated using following formula,

$$\text{Biodiesel yield } (\%) = \frac{\textit{Weight of biodiesel produced } (\text{g})}{\textit{Weight of oil } (\text{g})} \times 100 \quad (1)$$

2.3. Univariate optimization

The initial optimization of the different operating parameters for biodiesel production was done one-variable at a time approach. Type of catalyst (NaOH, KOH, $BaCl_2$, Na_2CO_3, $K_2Cr_2O_7$), catalyst concentration (1, 2, 3, 4% w/w), methanol amount (0.20, 0.30, 0.40, 0.50% v/v) and temperature (30, 40, 50, 60 °C) were optimized to obtain the maximum biodiesel yield.

2.4. Statistical optimization by RSM

In this investigation, RSM was used for the optimization of the process variable to improve the transesterification of Mahua oil with central composite design (CCD). CCD is a successful design for fitting a quadratic surface model in sequential experimentation. CCD avoids a large number of unusual design points and allows a sensible amount of information for testing the lack of fit. The regression model was proposed and the experimental results were analyzed using Design expert 7 software. Catalyst, methanol

Table 1
Free fatty acid profile of treated mahua oil.

S. No.	Parameters	Carbon atom number	Method	Units	Results
1	FFA as ricinoleic acid	18:1	IS 548 (Part-1) (RA. 2006)	%	15.93
2	FFA as oleic acid	18:1		%	15.08
3	FFA as palmitic acid	16:0		%	13.69
4	FFA as lauric acid	12:0		%	10.69