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Optimization of biodiesel production from mixture of edible and nonedible vegetable oils

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ABSTRACT

In the present study, optimization of biodiesel production from mixture of edible and nonedible vegetable oils with low to high free fatty acid (FFA) has been investigated. The selection of oils was based on richness of particular fatty acid in it. The combination of oils has been optimized to get suitable mixture for production of biodiesel. The mixture was analyzed in terms of physical properties and accordingly two step esterification process was applied. For optimization study, the response surface methodology (RSM) based central composite design (CCD) was used in Design of Experiments (DOE) software to optimize the various process variables such as reaction time, methanol to oil molar ratio, reaction temperature and catalyst concentration for biodiesel production . A quadratic model was created for the prediction of the Biodiesel yield. The R^2 value of the model was 0.96 which indicates the satisfactory accuracy of the model. The optimum conditions were obtained as follows: reaction temperature of 43.50 °C, methanol to oil molar ratio of 8.8:1, catalyst concentration of 1.9 g/100 cc feed, reaction time of 58.4 min. At these reaction conditions, the predicted and observed biodiesel yield was 97.02% and 97.00%, respectively. These values experimentally satisfied the accuracy of the model. GC and FTIR analysis of biodiesel was also done for biodiesel characterization.

1. Introduction

Due to the continuous high energy demand and the increasing environmental and health concerns, it is necessary to develop renewable fuel for production of energy (Chen et al., 2015; Royon et al., 2007). In this regard, Biofuels have been gaining much popularity because of their renewability and environmental friendly nature (Kwon et al., 2012). Biodiesel (biomass-based fuel), one of the most common biofuels is produced from biological resources such as vegetable oils and animal fats (Kilic et al., 2013a, 2013b; Issariyakul et al., 2014). In the open literature, biodiesel was produced by transesterification process from edible oils such as soybean oil, castor oil, palm oil , linsed oil (Abrahamsson et al., 2015; Al-Mulla et al., 2015; Meneghetti et al., 2006; Al-Zuhair et al., 2007; Hameed et al., 2009; Demirbas, 2009) and non edible oil resources like Karanja oil and Thumba oil (Agarwal et al., 2013; Naik et al., 2008; Karnwal et al., 2010;). The edible oils were primary feedstocks of biodiesel production because they gave high biodiesel yield with alkali catalyst due to low FFA content (Ardebili et al., 2011; Acevedo et al., 2015). The major disadvantage of edible oils is high cost, and can lead to imbalance between the food supply and biodiesel production. Therefore, the use of alternative sources such as animal fats and nonedible oils has been gaining importance as they can minimize the dependency on edible oils and having low price can reduce cost of production of biodiesel (Agarwal et al., 2012b; Yang et al., 2014; Kumar et al., 2011). The use of nonedible oils for biodiesel production is more significant in developing countries, as nonedible oils are not suitable for human consumption due to presence of toxic components in them (Shah and Gupta, 2007). But the high FFA content, high viscosity, non availability in sufficient quantity, and their use in industries as a source of bio-lubricants may lead to self sufficiency problem in nonedible oils for biodiesel production (Ashraful et al., 2014). Therefore to overcome these problems, the production of biodiesel from a mixture of edible and non-edible oils needs to be explored. The use of mixture of oils in place of specific oil for biodiesel production can reduce competition for food, may utilize excessive available oils efficiently, leading the process to be economical. Few studies have been carried out for the production of biodiesel from mixture of oils. It was reported (Jena, et al., 2010) that when mixture of mahua and simarouba oils with high FFA was used for

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biodiesel production (using two step process) biodiesel yield of 98% with 90% conversion was obtained. In another study, it was found that biodiesel yield varied from 81.7% to 88% when mixture of soybean oil, waste frying oil and lard was used (Dias et al., 2008). Martínez et al., 2014 investigated on the effects of fatty acid composition on fuel properties of biodiesel obtained from vegetable oils and their mixtures revealed that density, kinematic viscosity, iodine number and higher heating value were strongly dependent on the fatty acid composition of oils used. Therefore, proper selection of oils for mixture to provide high yield of biodiesel with better properties need to be investigated. Many researches are available, where characteristics of oil have not been taken as variable because of single oil and constant physical properties of oil (Rashid et al., 2011; Santos et al., 2013). In this paper, all characteristic has been taken as variable due to use of oil mixture for biodiesel production instead of single oil. In order to get optimum/suitable mixture for biodiesel production from various oil mixtures, variation in oil characteristics placed important in all final biodiesel properties.

The catalyst has a significant role in biodiesel production. Various homogeneous and heterogeneous catalysts were used for biodiesel production. Heterogeneous catalyst have many advantages such as reusability, easier separation from liquid product and can be designed to give higher activity; selectivity and longer life time (Nizah et al., 2014; Nur et al., 2014; Feyzi et al., 2014; Granados et al., 2007). But heterogeneous catalysts also have many disadvantages such as mass transfer resistance, time consumption, fast deactivation and inefficiency (Agarwal et al., 2012a; Leung et al., 2010). Therefore, the use of homogeneous catalyst is gaining attention because of its good catalytic activity, faster reaction rate and moderate reaction conditions (Vicente et al., 2007; Georgogianni et al., 2009).

The optimization study for biodiesel production process is essential in development of mass production facilities. Optimization study by using Design of Experiments (DOE) allows quantifying the effects of changes in transesterification process conditions on the quality and performance of produced biodiesel (Leung and Guo, 2006). Response surface methodology (RSM) is a combination of statistical techniques for planning experiments, developing models, defining optimum conditions and appraising the various factors. Optimization with RSM provides quick screening of wide experimental field and also explains the role of each of the process variables. The main focus of this research is to optimize the operating conditions for maximizing the biodiesel yield from a mixture of oils by transesterification process. In the present work, production of biodiesel was studied from mixture of edible and nonedible oils by using KOH catalyst. Central composite design (CCD) and Response surface methodology (RSM) were used to examine the effects of four transesterification process variable such as reaction temperature, catalyst concentration, alcohol to oil molar ratio and reaction time on biodiesel yield.

2. Materials and methods

2.1. Materials

Thumba oil, karanja oil, linseed oil and palm oil were purchased from local market of Jaipur and Jodhpur (India) and were used as such without further purification. Reagents like analytical grade methanol (99.9% purity, Merck), potassium hydroxide (85% purity, Merck) in pellet form, sulphuric acid (95–97% purity, Merck) were procured from a local vendor of Jaipur.

2.2. Characterization of oils

Various oils have been distinguished in terms of fatty acid content, and four oils, thumba oil (highest linoleic acid 52%), karanja oil (oleic acid 44.5–71.3%), linseed oil (linolenic acid 35–60%) and palm oil (32–45% palmitic acid) were selected and mixed in different proportions to get mixture of oil having suitable fatty acid composition for biodiesel production. The qualities of edible and nonedible oils are expressed in terms of the physicochemical properties such as density, acid value and FFA. These properties of oils were measured as per ASTMD6751 standard and are shown in Table 1.

2.3. Selection of suitable oil mixture

Various blends containing different proportions of four oils were chosen for biodiesel production through two step transesterification process at similar operating conditions (temperature 65 °C, time 60 min, 6:1 M ratio of methanol to oil, catalyst loading 1 gm/100cc). The blend giving highest yield and better biodiesel properties was selected for further studies.

2.4. Design of experiments

RSM was adopted to study the impact of reaction temperature, methanol to oil molar ratio, catalyst concentration and reaction time on the yield of biodiesel. Four known independent variables are: (A) methanol to oil molar ratio (3–9 M ratio), (B) temperature (35–65 °C), (C) Time (10–60 min), (D) catalyst loading (0.5–2 wt%). The response decided fatty acid methyl ester (FAME) yields which were obtained from the transesterification reaction. A 2^4 full factorial CCD for four independent variables at 3 level was employed and total number of experiments was 30 ($=2^k+2k+6$) where k is the total number of independent variables (Yuan et al., 2008). Table 2 shows the parameters and their levels. The complete design matrix corresponding to the central composite design in terms of real and coded independent variables is presented and results are given in Table 3.

2.5. Statistic analysis

The experimental results collected from central composite design were investigated using response surface methodology. The data were then fitted to the following second order polynomial equation in Eq. (1)

$$Y_{yield} = b_0 + \sum_{i=1}^{4} bi\ Xi + \sum_{i=1}^{4} bii\ Xi^2 + \sum \sum_{i=1}^{4} bij\ Xi\ Xj \qquad (1)$$

Where Y_{yield} is the predicted methyl ester yield, b_0 is the constant term, b_i is the linear effect, b_{ii} is the squared effect, b_{ij} is the interaction effect of x_i (the ith independent variable) and x_j (the jth independent variable). The data were analyzed using Design Expert program (version 9.0.6) and the coefficients were interpreted using F-test. Analysis of variance (ANOVA), regression analysis and plotting of contour plot were employed to set the optimum conditions for the yield of biodiesel from oil blend.

2.6. Transesterification experiments

In the initial step, the esterification reaction was carried out for reducing FFA at 60–70 °C by acid catalyst. The reaction was carried out in 250 ml 2 neck round bottom flask equipped with a reflux condenser, temperature controller and magnetic stirrer. 100 ml of blend 4 was preheated to the set temperatures (60 °C) before starting the reaction. A fixed amount (1–2 ml) of acid catalyst (H_2SO_4) was dissolved in requisite amount of methanol (20 ml)