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In-situ alkaline transesterification of castor seeds: Optimization and engine performance, combustion and emission characteristics of blends

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An optimization of methyl esters synthesis from castor seed by using three-level-four factor central composite design (CCD) was carried out. The biodiesel was produced by *in situ* alkali-catalyzed transesterification process. Influence of four variables, such as reaction time, oil to methanol molar ratio, catalyst concentration and reaction temperature on maximum methyl ester conversion has been optimized. From RSM study, the optimal conditions inferred were 3 h, 1:200 molar ratio, 1.19 wt.% catalyst and 30 °C. Under this optimal condition, the methyl ester conversion could reach as high as 97% ± 0.4% with higher desirability of 0.99. The estimated fuel properties of diesel, COME and its blends with diesel (COME5, COME10 and COME15) revealed that blending decreases density and viscosity and also reaches to diesel value, but showed insignificant effect on other fuel properties. Engine performance tests have been carried out for diesel and blends of COME with diesel. Among three blends, B10 gave best brake thermal efficiency of engine at maximum load. The ignition delays calculated for standard diesel, B5, B10 and B15 fuels were 16, 14, 14 and 14°CA, respectively. The exhaust gas emission was found with reduction in CO (26–36%), NOx (14–20%) and HC (17.5–50%) gases with increase of COME blending percentage compared to conventional diesel.

1. Introduction

The present trend of climate change towards the global warming has resulted in different changes in the geological, climatology, social, economical and biological processes worldwide. The emission from the means of transport is one of the causes for global warming. Bhasha et al. (2009), have reported that India is paying an enormous amount of foreign currency on fuel and on its import more than 80% of its fuel demand [1]. So, there is an urgent need to find out an alternative to petro-diesel [2]. Biodiesel is one of the alternate fuels which is eco-friendly, renewable, non-hazardous and can be obtained from transesterification of vegetable oils and animal fats [3]. It can be readily used in most diesel engines without any change [4]. Owing to the "food verses fuel" crisis, it may not be feasible to use an edible oil as a fuel source for transportation, so the non-edible oils can be used for biodiesel production [3]. Castor is a crop which can be well adapted to different soil qualities and with the seeds of high oil content (45%) among the non-edible crops like jatropha, karanja, tobacco, rubber and cotton [5].

Conventional method for the production of biodiesel from vegetable oil involves extraction of oil from seeds, refining of oil and then transesterification. This method constitutes the cost of vegetable oil about seventy percentage of the production cost of biodiesel [6]. The reduction in production costs and improvement of biodiesel yield can be achieved by *in-situ* transesterification or reactive extraction in which biodiesel is produced directly from the oil bearing raw materials [4]. Biodiesel can be produced by transesterification with methanol or ethanol using acid or base catalysts [7]. The use of acid catalyst can provide high conversion rates but required longer processing time than alkaline catalysts [8]. Optimization of reaction conditions has the capacity to decrease the reagent use and increase the yield [9]. The conventional approach for optimizing analytical methods is the one-factor-at-a-time approach, is time consuming and requires huge number of experiments [3]. Alternatively, factorial designs involve simultaneous optimization of all factors at once. It offer an efficient, simple, and statistically valid method for optimizing analytical methods and is widely used to optimize the processes in various fields like food industry, research and development, and natural and medical sciences (contamination studies) [10]. There are several reports on the conventional

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approach for optimization of reactive extraction using various edible and non-edible seeds [11]. On the other hand, optimizations of reactive extraction have also been investigated by using RSM (Response Surface Methodology) design technique with the feed stocks such as castor [3], Jatropha [12] and coconut waste [13]. One of the previous studiestreats this subject matter with greater details. The preliminary results of the study showed highest FAME yield using KOH compare to NaOH as a catalyst. In continuation separate study was carried out on optimization by RSM design technique with KOH as a catalyst [3]. Most of the literature published in the area of reactive extraction employs KOH as homogeneous catalyst. Relatively very few papers have addressed intensification of NaOH catalyzed biodiesel synthesis with reactive extraction. Recently, biodiesel fuel has been attracting the world as a blending component or direct fuel in diesel vehicle engines. The low level blends do not need any engine modifications. Generally, the blends of biodiesel up to B20 are preferred due to their compatibility in terms of storage and distribution equipment [14]. Previous study, they found reduction of NOx emissions with lower blends of B10 and B20; while increase of NOx emissions with increasing the blending to B30 [15]. To date, reports on the use of these non-edible oil methyl esters for engine study are scanty while that of castor oil are limited. There are no reports available on the engine study using the methyl ester produced via reactive extraction (directly from oil seeds).

To the best of our knowledge, recently there is no published report pertaining to the optimization of reactive extraction process by RSM design technique especially on "methyl ester "using NaOH as a catalyst. Therefore, present study is focussed on to optimize the reactive extraction of castor seeds by RSM design technique and to examine the physico-chemical properties of diesel, COME and their blends. In addition, an attempt has been made to evaluate the performance of prepared blends of COME in diesel engine.

2. Materials and methods

2.1. Materials and reagents

All the chemicals such as NaOH, KOH, methanol and other reagents used in this study were analytical grade. Castor seeds were purchased from local market in Anantapur, Andhra Pradesh, India. The detailed castor seed preparation methodology for reaction followed is reported elsewhere [16].

2.2. Experimental design

RSM was employed to evaluate the effect of various process parameters on the conversion of castor oil during reactive extraction. The factorial levels were selected on the basis of our preliminary experiments reported elsewhere [16].

A central composite designhas been used to devise the reactive extraction experiments comprising of 30 experiments for four variables [3]. The coded and uncoded levels of the independent variables are given in Table 1. The four independent variables were reaction time (A), oil to methanol molar ratio (B), catalyst concentration (C) and reaction temperature (D). The reactions were carried out at varied reaction time of 2–5 h, oil to methanol molar ratio of 1:150–1:300, catalyst concentration of 0.5–2 wt.% of oil content in seeds and temperature of 30–60 °C.The lowest and highest levels are assigned to be −1 and +1 while all variables at zero level constitute the centre points, respectively. Value of α (alpha) was fixed at level 2 ($\alpha = 2^{4/4}$). A 2^4 full factorial CCD for four independent variables was used by giving a total number of 30 ($=2^n + 2n + 6$) experiments, where 'n' is the number of independent variables. During the optimization study, eight axial experiments and sixteen factorial runs were carried out with six extra replications at the centre of design were used for the estimation of pure error.

2.3. Statistical analysis

Design expert software 8.0.7.1 trial version was used to predict the response of a process as a function of independent variables and their interactions to understand the system performance. The mathematical relationship between the process variables and response was calculated by the following quadratic polynomial expression:

$$Y = \beta_0 + \sum_{i=1}^{n}\beta_i x_i + \sum_{i=1}^{n}\beta_{ii}x_i^2 + \sum_{i=1}^{n}\sum_{j>1}^{n}\beta_{ij}x_i x_j \quad (1)$$

where Y is the response i.e., COME conversion, X_i and X_j represent the independent variables, β_0 is constant, β_i is linear term coefficient, β_{ii} is quadratic term coefficient, β_{ij} is cross term coefficient and 'n' is the number of process variables studied and optimized during the study. Analysis of variance (ANOVA) was carried out to estimate the effects of process variables and their possible interaction effects on the COME conversion in the response surface regression procedure. The best fit of the model was evaluated by regression coefficient R^2. Response surface and contour plots were drawn based on the obtained quadratic polynomial equation from regression analysis by keeping the two of independent variables at central value (0) and by varying other two variables to assess the interaction among the operational factors and to determine the optimal values of each parameter.

2.4. Production of COME, blends preparation and characterization

Reactive extraction was carried out in a three-neck 250 ml round bottom flask equipped with a reflux system, magnetic stirrer and heater. Flow sheet for the process was given in Fig. 1.

Castor seeds (20 g) were macerated in a mixer grinder and mixed with methanol in which NaOH had been dissolved. When the alkali alcohol mixture (methanol with NaOH) reached the desired temperature (under reflux), reaction was started and continued up to required reaction period. The reaction mixture was filtered to separate the meal and the liquid mixture by normal filtration. The solid residue was washed repeatedly with methanol to recover some product that adhered to the seed and the excess methanol was removed using a rotary evaporator. After complete evaporation of methanol, two layers of biodiesel rich upper layer

Table 1
Independent variables and levels for response surface design.

Independent variables	Symbol	Unit	Coded levels		
			−1	0	+1
Reaction time	A	h	3	4	5
Oil to methanol molar ratio	B	–	200	250	300
Catalyst concentration	C	wt.%	0.5	1	1.5
Temperature	D	°C	30	40	50