

RESEARCH ARTICLE

Optimization of pretreatment of *Jatropha* oil with high free fatty acids for biodiesel production

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Abstract A central composite rotatable design and response surface methodology were used in order to investigate the individual and combined effects of the ethanol-to-oil ratio, H_2SO_4 concentration, temperature and time of reaction on the reduction of free fatty acid (FFA) in *jatropha* oil. A quadratic polynomial model relating the reaction variables with FFA reduction was developed, presenting a good coefficient of determination ($R^2 = 0.893$). For reducing FFA to less than 1%, the optimal combination was found to be $0.62 \text{ v} \cdot \text{v}^{-1}$ ethanol-to-oil ratio ($14.9 \text{ v} \cdot \text{v}^{-1}$ ethanol-to-FFA ratio), $1.7\% \text{ v} \cdot \text{v}^{-1}$ H_2SO_4 concentration, and 79 min reaction time at a reaction temperature of 54°C . These results are of great relevance to maximize methyl esters formation by transesterification using an alkaline catalyst.

Keywords biodiesel, biofuel, esterification, free fatty acids, *jatropha curcas* oil

1 Introduction

Biodiesel produced from renewable feedstocks is receiving an increased interest worldwide as an alternative diesel fuel [1]. This biodegradable and non-toxic biofuel is composed of simple alkyl esters of fatty acids obtained by transesterification of triglycerides with low-molecular weight alcohols, such as methanol and ethanol [2]. Biodiesel can be used unmixed or blended at various percentages with conventional fossil diesel fuel in diesel engines or as a heating fuel [3].

Notwithstanding these attributes, the high cost of the most commonly-used feedstocks (partially or fully refined and edible-grade vegetable oils) affects the cost of

biodiesel production up to 60%–75%, being the major bottleneck that greatly limits its widespread commercialization [4]. Therefore, using less expensive feedstocks such as non-edible oils, animal fats, waste cooking oils and byproducts of vegetable oil refinery can be regarded as an effective way of reducing production costs, particularly in developing countries [5].

In this sense, *Jatropha curcas* L. oil can be considered as a potential cheap feedstock for biodiesel production in comparison with refined and edible oils such as those obtained from rapeseed, soybean and sunflower that are commonly used in Europe and USA [2]. However, *jatropha* oil is prone to gradual deterioration due to unsuitable handling and improper storage conditions. Furthermore, increasing free fatty acid (FFA) concentration has been found in this oil when exposed to atmospheric air and sunlight for long time [5,6]. It has been reported that *jatropha* oil may contain up to 14% FFA, which is well above the limit of 1% FFA required for a satisfactory conversion into biodiesel by base catalyzed transesterification [7].

High levels of FFA have significant effects on the transesterification of triglycerides as FFA reacts with the alkali catalyst to form soaps, resulting in serious emulsification and separation problems. Thus, the additional washing step required to remove the soap from the biodiesel to maintain its quality leads to lower yields of product formation [8]. Hence, a suitable procedure must be developed in order to reduce the content of FFA [9].

Some studies have shown that high yields of biodiesel can be attained by using a two stage process, i.e., an initial pretreatment (esterification) with acid catalyst followed by transesterification with base catalyst [10]. Esterification catalyzed by homogeneous acids, such as sulfuric, phosphorous, and sulfonic acids, is a conventional and useful procedure to reduce the content of FFA, which can turn the oils transesterifiable by an alkali catalyst [11].

Therefore, the objective of this work was to optimize the conditions of esterification for reducing the FFA content of jatropha oil. Assays were carried out according to central composite rotatable design (CCRD) and response surface methodology (RSM) in order to understand the interaction of the factors affecting FFA reduction.

2 Materials and method

2.1 Materials

Refined jatropha oil was supplied by ATMI (Akademi Teknik Mesin Indonesia), Surakarta, Indonesia. Some physical and chemical properties of this oil are shown in Table 1. Jatropha oil presented a greenish yellow color and had an initial acid value of 8.3 ± 0.3 mg KOH/g corresponding to a FFA level of $4.15 \pm 0.15\%$, which is higher than the 1% limit for satisfactory transesterification reaction using alkaline catalyst [7].

Table 1 Fatty acid composition and physical properties of jatropha oil used in this study

Fatty Acid /%	0.04
Caprylic	0.06
Capric	0.02
Lauric	0.09
Myristic	0.82
Palmitoleic	14.09
Palmitic	0.23
Margaric	75.82
Oleic	7.93
Stearic	0.09
Linoleic	0.04
Linolenic	0.15
Eicosenoic	0.33
Eicosanoic	0.09
Eicosenoic	0.08
Eicosapentaenoic	0.03
Behenic	0.01
Docosatrienoic	0.04
Decahexanoic	< 0.001
Teracosanoic	42.765
Kinematic viscosity $/(40^\circ\text{C}, \text{mm}^2 \cdot \text{s}^{-1})$	0.2
Water content $/(\text{vol} \cdot \%)$	0.9184
Specific gravity at 60/60°C	374
Flash point PMcc $/^{\circ}\text{F}$	1.052
Conradson carbon residue $/(\text{wt} \cdot \%)$	182
Saponification value $/(\text{mg} \cdot \text{g}^{-1})$	0.61
Peroxide value	

All chemicals used in the experiments were of analytical reagent (AR) grade. Ethanol (99.5%), sulfuric acid (96% – 98%) and potassium hydroxide were purchased from Panreac, Spain. Potassium hydrogen phthalate was purchased from Riedel de Haen, Germany.

2.2 Equipment

Esterification of FFA in jatropha oil was performed in 125 mL rounded glass flasks equipped with a spiral condenser. A magnetic stirrer was used to homogenize the solution and a controlled water bath was employed to maintain a constant temperature throughout the experiment.

2.3 Esterification

Jatropha oil was poured into the rounded flask and heated up to the desired temperature. Then, ethanol and sulfuric acid were mixed with the oil and time was started to count. At the end of the experiment, the reacting mixture was transferred into a separation funnel. The oil phase was separated and centrifuged at 5000 rpm during 5 min. The FFA content of the oil phase was then determined by standard titration using potassium hydroxide (KOH) [12].

2.4 Experimental design and optimization by response surface methodology

A three-level-four-factor CCRD leading to 29 sets of experiments was employed in this study to establish the influence of the variables: ethanol-to-oil ratio (EtO), acid catalyst concentration (Ac), temperature (Te) and time of reaction (Ti) on the FFA reduction of jatropha oil. For statistical analysis, the independent variables were coded according to Eq. (1), where each independent variable is represented by x_i (coded value), X_i (real value), X_0 (real value at the center point) and ΔX_i (step change value). The coding facilitated the computation for regression analysis.

$$x_i = (X_i - X_0) / \Delta X_i \quad (1)$$

The range and levels of the variables are given in Table 2.

The experiment in the central point was replicated five times to provide sufficient degrees of freedom for estimating the purely experimental uncertainty variance.

Table 2 Levels and range of the independent variables used in the esterification process according to CCRD

Independent variable	Symbol	Levels and range		
		-1	0	1
Ethanol-to-oil ratio $/(\text{v} \cdot \text{v}^{-1})$	EtO	0.3	0.5	0.7
H_2SO_4 concentration $/(\text{vol} \cdot \%)$	Ac	1	2	3
Time /min	Ti	50	70	90
Temperature $/^{\circ}\text{C}$	Te	45	55	65

The experimental results were fitted with a second-order polynomial equation by multiple regression analysis. The quadratic model for predicting the optimal point was expressed according to Eq. (2), where \hat{y}_i represents the response variable, b_0 is the interception coefficient, b_i , b_{ii} and b_{ij} are the regression coefficients, n is the number of studied variables, and X_i and X_j represent the independent variables. Where possible, the model was simplified by elimination of statistically insignificant terms.

$$\hat{y}_i = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j. \quad (2)$$

The quality of the fitted polynomial model was expressed by the coefficient of determination R^2 , and its statistical significance was checked by the F -test. The

significance of the regression coefficients was tested by t -value. Results were analyzed by the Experimental Design Module of the Statistica 8.0 software (Statsoft, USA). The model permitted evaluation of the effects of linear, quadratic and interactive terms of the independent variables on the chosen dependent variables.

3 Results and discussion

Previous studies have reported that alkaline transesterification of jatropha oil containing more than 1% FFA presents significant drawbacks due to the formation of fatty acid salts (soap). The soaps promote the formation of stable emulsions that prevent separation of the methyl ester layer from the glycerin during processing and also reduce the

Table 3 Observed and predicted values of the reduction of FFA content in jatropha oil according to the full-factorial CCRD

Run	H ₂ SO ₄ /(vol-%)	Ethanol: oil /(v·v ⁻¹)	Time /min	Temperature /°C	FFA reduction	
					Experimental	Predicted
17	1	0.5	70	55	3.80	3.14
1	1	0.3	50	45	2.56	2.29
2	1	0.3	50	65	3.09	2.67
3	1	0.3	90	45	2.93	2.58
4	1	0.3	90	65	2.98	2.16
5	1	0.7	50	45	3.35	3.13
6	1	0.7	50	65	3.59	3.45
7	1	0.7	90	45	3.55	3.05
8	1	0.7	90	65	3.37	2.57
19	2	0.3	70	55	3.03	2.71
21	2	0.5	50	55	3.66	3.26
23	2	0.5	70	45	3.54	3.08
29 (C)	2	0.5	70	55	3.62	3.17
25 (C)	2	0.5	70	55	3.60	3.17
26 (C)	2	0.5	70	55	3.64	3.17
28 (C)	2	0.5	70	55	3.66	3.17
27 (C)	2	0.5	70	55	3.64	3.17
24	2	0.5	70	65	3.31	2.87
22	2	0.5	90	55	3.58	3.08
20	2	0.7	70	55	3.85	3.23
9	3	0.3	50	45	2.60	2.49
10	3	0.3	50	65	2.89	2.55
11	3	0.3	90	45	3.69	3.01
12	3	0.3	90	65	2.93	2.27
18	3	0.5	70	55	3.43	3.18
13	3	0.7	50	45	3.38	3.11
14	3	0.7	50	65	3.42	3.11
15	3	0.7	90	45	3.48	3.27
16	3	0.7	90	65	3.25	2.47

ester conversion rate [5]. On the other hand, an acid-catalyzed esterification of the FFA followed by base-catalyzed transesterification appears to be an effective and efficient method to obtain biodiesel from high FFA feedstocks [13].

Esterification of FFA with an alcohol is a reversible reaction, which is catalyzed by acids to produce fatty acid alkyl esters and water [12], as shown below:



The rate and conversion efficiency of acid esterification can be affected by several factors, among which, alcohol type, alcohol-to-oil ratio, acid catalyst concentration, reaction temperature, and reaction time have been regarded as the most important [2,5]. Thus, a number of studies on the esterification [11,14–16] have been performed by changing one of these factors separately at a time (COST). However, reaction system influenced simultaneously by more than one factor can be poorly understood with the COST-approach [17].

Therefore, our study evaluated the simultaneous effect of ethanol-to-oil ratio, H_2SO_4 concentration, temperature and time of reaction on the reduction of FFA of jatropha oil by using CCRD. According to Canacki et al. [13], a higher rate of esterification can be obtained by using ethanol rather than methanol due to its higher solubility in oils and fats. In addition, Marchetti and Errazu [15] employed ethanol instead of methanol for the esterification of FFA with sulfuric acid, since ethanol is less toxic and safer to handle.

3.1 Statistical analysis of FFA reduction

The experimental results obtained for the reduction of FFA of jatropha oil under different operational conditions

according to the 2^4 CCRD are shown in Table 3. It can be noted that FFA decreased under all the evaluated conditions, however, the reduction strongly varied according to the levels employed for the independent variables.

Due to the large difference observed in the FFA reduction, a statistical analysis was carried out to identify the variables that had the greatest influence on this process. Table 4 shows the Student's t -test and p -values used to determine the statistical significance of the independent variables (ethanol-to-oil ratio, H_2SO_4 concentration, temperature and time of reaction) on the response variable (reduction of FFA). According to this analysis the ethanol-to-oil ratio was the only variable with significant (at 95% confidence level) individual effect on FFA reduction. Such effect had a positive signal, indicating that FFA reduction increased by increasing the initial ratio between ethanol and oil. Interaction effects between ethanol-to-oil ratio and time and between time and temperature were also significant at 95% confidence level.

After identification of the variable affecting the reduction of FFA of jatropha oil, a multiple regression analysis was performed to fit the experimental data to a polynomial equation, obtaining the coefficients given below.

$$\begin{aligned} \text{FFA reduction (\%)} = & -9.550 + 0.438\text{Ac} - 0.012\text{Ac}^2 \\ & + 8.803\text{EtO} - 4.974\text{EtO}^2 + 0.056\text{Ti} + 0.299\text{Te} \\ & - 0.002\text{Te}^2 - 0.272\text{AcEtO} + 0.003\text{AcTi} - 0.008\text{AcTe} \\ & - 0.023\text{EtOTi} - 0.007\text{EtOTe} - 0.001\text{TiTe}, \end{aligned} \quad (4)$$

where Ac = acid catalyst concentration (% $\cdot \text{v}^{-1}$), EtO = ethanol-to-oil ratio ($\text{v} \cdot \text{v}^{-1}$), Ti = time of reaction (min) and Te = temperature ($^{\circ}\text{C}$). The quality of the fitted polynomial model was expressed by the coefficient of determination (R^2). Variables with no significant effects at $p < 0.05$ were

Table 4 Effect estimates, standard errors, t -test and p -values for the reduction of FFA content in jatropha oil according to the full-factorial CCRD

Variables and interactions ^{a)}	Estimated effects	Standard errors	t -value	p -value
Ac (L)	-0.019	0.075	-0.248	0.808
Ac (Q)	-0.024	0.192	-0.124	0.903
EtO (L)	0.504	0.076	6.676	0.000
EtO (Q)	-0.398	0.198	-2.005	0.065
Ti (L)	0.136	0.076	1.806	0.092
Ti (Q)	-0.042	0.198	-0.210	0.836
Te (L)	-0.027	0.076	-0.356	0.727
Te (Q)	-0.421	0.198	-2.121	0.052
Ac EtO	-0.109	0.080	-1.357	0.196
Ac Ti	0.102	0.080	1.270	0.225
Ac Te	-0.161	0.080	-2.005	0.065
EtO Ti	-0.186	0.080	-2.327	0.035
EtO Te	-0.029	0.080	-0.359	0.725
Ti Te	-0.279	0.080	-3.482	0.004

a) (L): linear; (Q): quadratic

maintained in the model to not decrease the value of R^2 . As can be noted, the model explains nearly 90% of the variability observed in the response ($R^2 = 0.893$). The high R^2 value means that the model accurately represents the data in the experimental region studied. The values predicted by the model are displayed in Table 3 along with the observed values. Comparison of these values indicates that there is a good agreement between the model and experimental data for the range of experimental values tested.

The relation between independent variables and FFA reduction can be best visualized by examining the contour plots presented in Fig. 1.

Figure 1(a) clearly shows that increasing the ethanol-to-oil ratio resulted in higher FFA reduction for an acid catalyst concentration between 1% and 3%, with maxima values of reduction ($\geq 3.6\%$) being achieved when the ratio was higher than 0.5 (ethanol-to-FFA ratio > 12.0). It can also be observed in Fig. 1(b) that ethanol-to-oil ratios higher than 0.5 lead to the highest reduction of FFA of jatropha oil when the time of reaction was between 50 and 90 min. These results are in agreement with those reported by Azhari et al. [14]. According to these authors, FFA concentration decreases sharply after 60 min of reaction by using an alcohol (methanol)-to-oil ratio higher than 0.5. Deng et al. [2] also demonstrated that FFA of jatropha oil can be reduced from 3.21% to 0.605% as methanol-to-oil ratio is increased from 0.16 to 0.40 (5.0 to 12.5 methanol-to-FFA ratio).

The reduction of FFA of jatropha oil increased as the temperature was raised from 45°C up to 60°C using H_2SO_4 concentrations between 1 and 3% (Fig. 1(c)). This result confirms the earlier findings of Marchetti and Errazu [15] where the final FFA conversion increased as temperature increased from 35°C to 55°C. According to these authors, the reaction was typically endothermic. On the other hand, the lower FFA reductions observed at temperatures higher than 60°C can be related to a higher evaporation of ethanol.

The statistical model (Eq. (3)) predicted that the highest reduction of FFA can be obtained for the following optimized reaction conditions: an ethanol-to-oil ratio of 0.62 (ethanol-to-FFA ratio of 14.9), an acid catalyst concentration of 1.7%, temperature of 54°C and a reaction time of 79 min. Thus, additional experiments were carried out to validate the equation using these optimal values. The experimental value of FFA reduction (3.45%) obtained by using the optimized conditions agreed well with the predicted value (3.20%), and thus confirmed the adequacy of the predicted model.

4 Conclusions

The high FFA level of jatropha oil was reduced to less than 1% by its pretreatment with ethanol-to-oil ratio of 0.62 (ethanol-to-FFA ratio of 14.9) using H_2SO_4 (1.7%) at 54°C

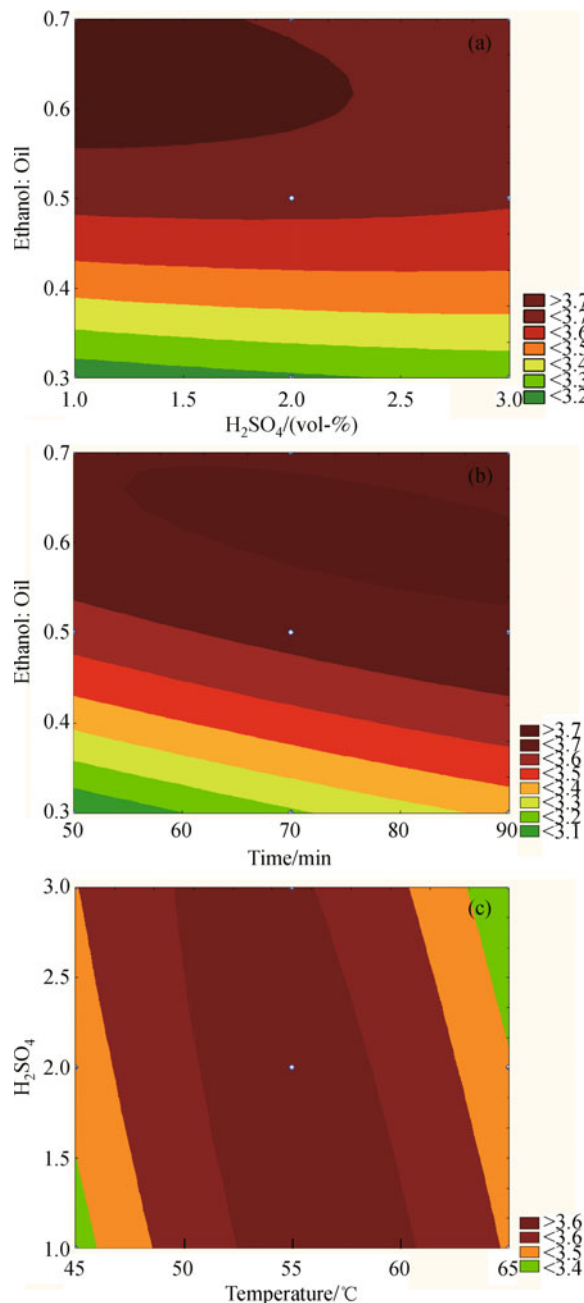


Fig. 1 Contour plots of FFA reduction (%) as a function of (a) ethanol-to-oil ratio and acid catalyst concentration, (b) ethanol-to-oil ratio and time, and (c) acid catalyst concentration and temperature, predicted from the quadratic model.

during 79 min. The quadratic polynomial model presented in this study was found to be highly significant with a coefficient of determination of 0.893. These results are of great relevance to maximize methyl esters formation by transesterification using an alkaline catalyst.

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