Optimization and Kinetic Studies on Biodiesel Production from Kusum (*Schleichera triguga*) Oil Using Response Surface Methodology

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Abstract: In the present study, the low-cost non-edible kusum (*Schleichera triguga*) oil with a substantial amount of free fatty acid (FFA) was utilized for biodiesel synthesis. In pretreatment step, FFA was reduced by the acid catalyzed esterification method. Then, response surface method (RSM) in conjunction with centre composite design (CCD) containing 30 experimental runs were statistically employed for process optimization and kinetic study for the base catalyzed transesterification process. A statistical model predicted highest fatty acid methyl ester (FAME) yield of 97.37% at the optimal values of process parameters as follows: sodium methoxide concentration 0.9 wt% of oil, Methanol to oil molar ratio 9:1, temperature 58.9°C and reaction time 58.5 min. Using these optimal parameters under experimental conditions in three independent replicates an actual FAME content of 98.14% was obtained which was in reasonable agreement with predicted one. The developed kinetic model suggested a 1.8th order reaction with activation energy of 31.42 kcal mol⁻¹ and frequency factor of 5.53 × 10⁷ L mol⁻¹ min⁻¹. Furthermore, Important fuel properties of kusum oil biodiesel (KOB) was compared with ASTM 6751 and DIN EN 14214.

The viscosity was found to be 5.34 Cst at 40°C and the flash point was 152°C.

**Key words:** *S. triguga* oil, esterification, transesterification, response surface methodology, optimization, kinetics

1 Introduction

Depletion of natural resources, increased crude oil prices and negative environmental impact of petroleum fuel has stimulated the search of an alternative renewable fuel such as biodiesel. Biodiesel is renewable, clean as well as environmentally acceptable as it is derived from vegetable oils and animal fats. Biodiesel is a mixture of mono alkyl esters of long-chain fatty acids. The conventional process for industrial biodiesel production is transesterification method using acid or base catalysts. The process takes a triglyceride molecule and breaks the fatty acid bond within the glycerin molecule using an alkali catalyst. Once, a fatty acid is broken off from the glycerin molecule, it bonds with a molecule of methanol and forms biodiesel molecule. After a series of processes, we are left with glycerin and biodiesel molecules. Many authors have studied transesterification of vegetable oil using homogeneous alkali catalysts. Only B20 (20% biodiesel and 80% diesel) blending of biodiesel with diesel has shown great durability of engine parts as well as a considerable reduction in particulate matter and greenhouse gases from the exhaust of Compression Ignition (CI) engine.

The raw material plays a vital role in biodiesel synthesis, which contributes about 60–75% of the total production costs of biodiesel fuel. Therefore, exploring ways to reduce the cost of raw material is the main interest in recent biodiesel research. The choice of raw material depends on its availability, affordability, geographical distribution and physicochemical properties such as iodine value, saponification value and free fatty acid content. Although, edible oils such as soybean oil, Rapeseed oil is the obvious feedstock for global perspective because developing countries have a shortage of edible oils for consumption and cannot afford the use of these oils for biodiesel production. So, Non-edible oils (low cost feedstock) have a greater potential, as they were easily available and very economical compared with edible oils. Literature showed that few non-edible oils have been already utilized for biodiesel synthesis such as Jatropha oil, Karanj oil, Rubber seed oil, Tobacco seed oil. In the present study, kusum oil was explored for biodiesel synthesis. Kusum (*Schleiche-
era triguga) oil is wild tree growing in the sub-Himalayan region, throughout southern and central India, Burma, Cylon, Java, Timor. It belongs to the family of Sapindaceae. It contains cynogenic lipids, which releases cyanide upon hydrolysis. Hence, it saponified only after pretreatment. The estimated availability of kusum seed is about 25,000 tons/annum. Kusum seed kernels contain 40.3% yellowish brown colored oil. It is being used as a medicinal oil, a hair dressing and raw material for soap production. Fatty acid composition of kusum oil has earlier been reported in the literature. The major constituents of kusum oil are Myristic, Palmitic, Oleic, Linoleic, Arachidic and Erucic, which contribute about 90% of total fatty acids present in kusum oil as shown in Table 1.

The aim of this study has been focused on process optimization and kinetic study for CH₃ONa catalyzed biodiesel production from kusum oil using response surface methodology for process optimization and kinetic modeling.

## Materials and Methods

### Materials

Kusum (Schleichera triguga) oil used for this study was supplied by S.K. oil Industries Jharkhand, India. All chemicals, including methanol (99.5%), n-hexane (95%) and sulfuric acid (99%) of analytical reagent (AR) grade was purchased from Merck Limited, Mumbai, India. Magnesium sulfate dry and sodium hydroxide (NaOH) in pellet form was procured from Fisher Scientific, Mumbai, India. Antioxidant 2,6-di-tertiarybutyl hydroxytoluene (BHT) was procured from M/s Ratnagiri Chemicals Pvt. Ltd., Mumbai, India. The standards required for quantification of esters were procured from Sigma-Aldrich Co. Ltd., Mumbai, India and were chromatographically pure.

Experiments were conducted in two steps as kusum oil had a high acid value. Acid catalyzed reaction to reduce the acid value of kusum oil to the desirable limit followed by alkaline catalyzed reaction to produce biodiesel. In case of esterification, experimental setup consists of 1L, three-necked round bottom flasks equipped with a condenser and magnetic stirrer. Stirring and heating was provided simultaneously by Rota-mantle (Remi, India), while transesterification was carried out in Gyrotory water bath shaker (Remi, India).

### Determination of oxidation stability

Oxidation stability of kusum oil is determined by using Rancimat test method and is shown in Fig. S2. In the Rancimat test method, the oxidation is induced by passing a stream of air at the rate of 10 L/h through biodiesel sample (5 mL), kept at constant temperature 110°C. The vapors released during the oxidation process, together with the air, are passed into the flask containing 60 mL of demineralized water, and contains an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. It indicates the end of IP when the conductivity begins to increase rapidly. This accelerated increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. When the conductivity of this measuring solution is recorded continuously, an oxidation curve is obtained whose point of inflection is known as the IP. Data for all analytical measurements are means of triplicate. Subsequent analysis showed no statistically significant difference among the measurements.

### Acid catalyzed Esterification

The acid value of kusum oil was determined by acid base titration technique, except that a standard solution of NaOH was used instead of the standard solution of KOH, as further reactions were carried out using NaOH. Kusum oil had an initial acid value of 21.65 mg NaOH/g corresponding to the free fatty acid (FFA) level of 10.83%, which was far above the safer limit (i.e., 1%) for transesterification reaction using an alkaline catalyst. Therefore, kusum oil was first treated with acid to lower its FFA value to safer limit. In this process, Raw oil (500 mL) was taken into 1 L three necked round bottom flask equipped with a condenser and magnetic stirrer. Sulfuric acid (1% v/v) as a catalyst in
methanol with 6:1 molar ratio (alcohol to oil) was added into the flask. Stirring and heating at 50°C was provided simultaneously by Rota-mantle (Remi, India). After the reaction completion, the mixture was neutralized by addition of 0.05 M NaOH solution and kept in separating funnel for phase separation. The bottom layer was (water and methanol) were removed from the product. The organic layer was washed three-four times with hot distilled water to remove all traces of acid and passed through anhydrous magnesium sulfate (MgSO₄) to remove the residual traces of moisture. Finally, the acid value of product was measured. The final product having an acid value lower than 1 mg NaOH/g was used for the transesterification reaction.

2.4 Alkali catalyzed Transesterification

In this study, sodium methoxide (NaOCH₃) was used as an alkali catalyst to produce biodiesel, which was prepared by dissolving NaOH in methanol. When NaOH was being completely dissolved in methanol, it produces NaOCH₃ and water. As the moles of NaOH used was very small, it produces very small quantity of water. Hence, there was negligible effect of water molecule on the reaction. The transesterification was carried out with a known amount of pretreated kusum (Schleichera triguga) oil, which was added to the 100 ml volumetric flask. The calculated amount of sodium methoxide mixture was then added to the pretreated oil flask. The flask was kept in water bath shaker with temperature range 50–60°C for desired time interval of (50-70 min).

After completion of reaction, the product containing unreacted reactants, catalyst, glycerol, and biodiesel was kept in separating funnel. After few hours, phase separation occurs. Catalyst and glycerol settled at the bottom which were subsequently removed, and residual methanol was removed by vacuum evaporator. The process was continued until the loss in weight of ester was constant thus confirming the complete removal unreacted methanol. The top product layer was washed with dilute sulfuric acid (0.05 M, H₂SO₄) and hot distilled water for three-four times. After water washing, the final product was centrifuged and passed through anhydrous magnesium sulfate (MgSO₄) to remove the residual traces of moisture.

The variables affecting the alkali-catalyzed transesterification such as alcoxide catalyst concentration (0.7–1 wt%), MeOH/oil molar ratio (6:1 to 10:1 v/v), temperature range (50–60°C), reaction time (50–70 min) was investigated.

2.5 Experimental Design

A five-level four-factor Central Composite Design (CCD) was employed in this study to examine the effect of independent variables such as catalyst concentration (A), methanol to oil molar ratio (B), temperature (C) and reaction time (D) on the FAME content. The experimental values used for the employed levels are shown in Table 2.

The model was explained with 30 experimental runs $\left(2^3 + 2k + m\right)$ where, $k$ is the number of factors, and $m$ is number replicated center points six factorial points ($2^6$), eight axial points ($2k$), and six replicated center points ($m = 6$). The Design Expert™, Version 8.0 of Stat-Ease Inc. (USA) software was used for regression analysis on the data obtained. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). Once the experimental data obtained was fitted with a second-order model in order to correlate the response variable to the independent variable. The general form of second order polynomial equation:

$$
Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} \sum_{j=i+1}^{k} b_{ij} x_i x_j + e
$$

Where, $Y$ is response (% FAME content), $b_0$, $b_i$, $b_{ij}$ and $b_{ij}$ are the regression coefficients obtained for constant, linear, quadratic and interaction terms, respectively. $x_i$ and $x_j$ are independent variables, whereas $i$ and $j$ are the linear and quadratic coefficients, respectively. $b$ is the regression coefficient, $k$ is the number of factors studied and optimized in the experiment and $e$ is random error.

2.6 Analysis

Experimental samples were analysed by gas chromatograph (model GC-2010 plus, Shimadzu Corp., Tokyo, Japan) equipped with MXT-Biodiesel TG capillary column (15 m x 0.32 mm x 1 μm) and a flame-ionization detector. Nitrogen was used as a carrier gas at a flow rate of 2.75 mL min⁻¹. Hexanoic acid was used as an internal standard. Column oven temperature was initially maintained at 100°C for 3 minutes, then increases to 250°C at the rate of 30°C min⁻¹ and held here for 3 minutes. The injector and detector temperature were maintained at 270°C. A sample

| Table 2 | Coded and uncoded levels of variables used for CCD. |
|---------|-----------------------------------------------|

| Variables | Symbols | Range and levels |
|-----------|---------|-----------------|
| Catalyst concentration (wt%) | A | 0.55 0.7 0.85 1 1.15 |
| Methanol to oil molar ratio (v/v) | B | 4 6 8 10 12 |
| Temperature (°C) | C | 45 50 55 60 65 |
| Reaction time (min) | D | 40 50 60 70 80 |
3 Results and Discussion

3.1 Acid catalyzed esterification pretreatment

Kusum (Schleicher'a triguga') oil has a high content of FFA (i.e., more than 10%). It was observed that the pretreatment stage considerably reduced the acid value from 21.65 to below 1 mg NaOH/gm. The effect of acid value on reaction time is shown in Fig. 1. Sivakumar et al.\(^{20}\) suggested that the acid catalysis esterification occurs in three stages i.e. fast, slow and stationary. In the first stage, the rate of the reaction was fast for which the acid value drop down from 21.65 to 2.18 in 30 minutes and the reduction in acid value was 89.93%. After 30 minutes, the rate of the reaction slows down up to 50 minutes, the reduction in acid value was 95.56%. In the stationary stage the esterification reached equilibrium after 50 minutes. The acid value was observed less than 1 mg NaOH/gm at 50 minutes, but it was desirable to keep a longer reaction time of 60 min.

Table 4 shows the regression analysis of the RSM in which the three linear terms (A, B, C), one cross products (AD) and the four quadratic terms (A\(^2\), B\(^2\), C\(^2\), D\(^2\)) were all significant model terms at 95% confidence level as the significance determined by p value i.e., (p<0.05). The term D was not found to be the significant and null hypothesis in FAME content but it was included into the analysis for the sake of maintaining the hierarchical structure of the model terms\(^{15, 20}\). The linear effects of A and C, the interactive effects of AD and the second-order effects of A\(^2\), D\(^2\) were most significant, all having p-value<0.0001. The Analysis of variance (ANOVA) as shown in Table 4 shows the model F value 47.67 with low probability value (p-value<0.0001) implies a high significance for the regression model. The coefficient of determination (R\(^2\)) measures the goodness of the fit of the model, greater than 0.80 was desirable\(^{21}\). The R\(^2\) value of 0.9780 which means that model could explain 97.8% of the variation in FAME content, which is attributed to the independent variables, and only 2.2% of the total variation is not explained by the model. It indicates the fitness of the model. The predicted R\(^2\) of 0.8832 was in reasonable agreement with the adjusted R\(^2\) of 0.9575 indicating that the regression model could be used to analyze trends of responses. The adjusted R\(^2\) value is particularly useful when comparing models with a different number of terms. This comparison was, however, done in the background when model reduction was taking place\(^{22}\). Apart from that, the lack of fit F-value of 4.36 implies that lack of fit was not significant relative to pure error. Hence, there is only a mere 5.89% chance that a lack of fit F-value this large could occur due to noise factor such as human errors or experimental errors\(^{23}\). The non-significant lack of fit shows the model is significant and indicates that the model equation is adequate for predicting FAME content under any sets of combination of the variables\(^{24}\). The low coefficient of variation (3.94%) shows the reliability of experiments conducted\(^{25}\). Adequate precision measures the signal to noise ratio. Adequate precision of >27 indicates an adequate signal as a ratio greater than 4 was desirable to navigate the design space excellently\(^{22}\).

Multiple regression analysis of the experimental data gave the following second-order polynomial equation in terms of coded variables:

\[
Y = 95.19 + 3.92A + 2.92B + 3.17C + 1.01D + 1.24AB - 0.42AC - 5.98AD - 0.31BC - 1.49BD - 1.17CD - 12.97A^2 - 2.05B^2 - 2.77C^2 - 4.09D^2
\]

where, \(Y\) represents percentage FAME content. Positive sign in front of the terms indicates the synergistic effect in increased FAME content, whereas a negative sign indicates the antagonistic effect\(^{20}\). Model Eq. (3) with linear term A, B, C, D and cross product term AB had a positive effect on FAME content whereas AC, AD, BC, BD, CD and all qua-
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Table 3  Five-level four-factor response surface analysis with experimental and predicted values for oil to ester FAME content.

| Sr. No. | Catalyst conc. $A$ (wt%) | Molar ratio $B$ | Temp. C ($^\circ$C) | Reaction Time D (min) | % FAME content |
|---------|--------------------------|----------------|---------------------|----------------------|----------------|
|         |                          |                |                     |                      | Experimental Value | Predicted Value |
| 1.      | 0.7                      | 6              | 50                  | 50                   | 53.18           | 54.17          |
| 2.      | 1                        | 6              | 50                  | 50                   | 72.56           | 72.31          |
| 3.      | 0.7                      | 10             | 50                  | 50                   | 59.92           | 61.11          |
| 4.      | 1                        | 10             | 50                  | 50                   | 82.47           | 84.23          |
| 5.      | 0.7                      | 6              | 60                  | 50                   | 64.1            | 64.3           |
| 6.      | 1                        | 6              | 60                  | 50                   | 79.53           | 80.77          |
| 7.      | 0.7                      | 10             | 60                  | 50                   | 71.42           | 70.01          |
| 8.      | 1                        | 10             | 60                  | 50                   | 88.12           | 91.46          |
| 9.      | 0.7                      | 6              | 50                  | 70                   | 72.96           | 73.45          |
| 10.     | 1                        | 6              | 50                  | 70                   | 71.42           | 70.01          |
| 11.     | 0.7                      | 10             | 50                  | 70                   | 74.83           | 74.43          |
| 12.     | 1                        | 10             | 50                  | 70                   | 70.01           | 73.64          |
| 13.     | 0.7                      | 6              | 60                  | 70                   | 79.83           | 78.91          |
| 14.     | 1                        | 6              | 60                  | 70                   | 68.83           | 71.47          |
| 15.     | 0.7                      | 10             | 60                  | 70                   | 74.59           | 78.67          |
| 16.     | 1                        | 10             | 60                  | 70                   | 76.35           | 76.2           |
| 17.     | 0.55                     | 8              | 55                  | 60                   | 35.23           | 35.46          |
| 18.     | 1.15                     | 8              | 55                  | 60                   | 56.04           | 51.14          |
| 19.     | 0.85                     | 4              | 55                  | 60                   | 82.11           | 81.13          |
| 20.     | 0.85                     | 12             | 55                  | 60                   | 96.5            | 92.81          |
| 21.     | 0.85                     | 8              | 45                  | 60                   | 80.26           | 77.76          |
| 22.     | 0.85                     | 8              | 65                  | 60                   | 92.62           | 90.45          |
| 23.     | 0.85                     | 8              | 55                  | 40                   | 78              | 76.81          |
| 24.     | 0.85                     | 8              | 55                  | 80                   | 84.3            | 80.83          |
| 25.     | 0.85                     | 8              | 55                  | 60                   | 92.2            | 95.19          |
| 26.     | 0.85                     | 8              | 55                  | 60                   | 96.5            | 95.19          |
| 27.     | 0.85                     | 8              | 55                  | 60                   | 94.3            | 95.19          |
| 28.     | 0.85                     | 8              | 55                  | 60                   | 96.21           | 95.19          |
| 29.     | 0.85                     | 8              | 55                  | 60                   | 95.3            | 95.19          |
| 30.     | 0.85                     | 8              | 55                  | 60                   | 95.3            | 95.19          |

Drastic terms $A^2$, $B^2$, $C^2$, $D^2$ had a negative effect on FAME content. The Variance Inflation Factor (VIF) did not exceed 1.05 for any of the terms in the quadratic equation. This reflects that there is no problem of multi-collinearity (since VIF < 10). In addition, the leverage for each response 0.583 was less than twice the average leverage and hence is acceptable.

3.3 Effect of parameters
The model was then further processed to generate the response surface plots using Matlab Version 8.3 (R2014a) and analyzed to understand the interactions among the variables followed by optimization of each variable for maximization of FAME content. Deterministic models enable researchers to predict and describe the dynamics of a system over space and time. The 3D response surface plots are generally the graphical representations of the regression (Eq. 3) which are shown in Fig. 2(a-c).

Statistical analysis of the experimental data identified catalyst concentration ($A$) as the most important variable in
the response analysis. Table 4 shows the catalyst concentration and methanol to oil molar ratio, and reaction time have a significant effect on the FAME content. Figure 2(a), 2(b) and 2(c) depicts the FAME content increases with the increasing sodium methoxide concentration from 0.7 to 0.9 (wt %) and further addition of catalyst found negative effect on FAME content. This may be due to fact that addition of an excess amount of catalyst, give rise to the formation of an emulsion, which has increased the viscosity and led to the formation of gel\(^{27}\). Chin et al.\(^{19}\) found that higher catalyst concentration may make the reactant mixture more viscous, which would increase the mass transfer resistance to the reaction system.

The effect of different reaction time and catalyst concentration on FAME content at fixed value of molar ratio 8:1 and temperature 55°C is shown in Fig. 2(a). It can be seen from Fig. 2(a), at one axis, there is a linear increase in FAME content, while at the other axis, there is increase only up to an extent, which decreases thereafter. This indicates that a critical point for catalyst concentration is involved up to which reaction is favored and not so after that critical point. The percentage FAME content is lower at shorter times and increases as the time is increased to 60 min. Increasing the reaction time above 60 min showed no significant effect on the FAME content. Our results are not in agreement with Sharma and Singh\(^{10}\) who investigated an optimum reaction time of 1h (50°C) for production of biodiesel by transesterification of kusum (Schleicheria triguga) oil using KOH as a catalyst. The variations in our analysis might be due to the different catalyst type and concentration as well as the varied nature of kusum oil used.

The simultaneous dependence of FAME content on the molar ratio and catalyst concentration is shown in Fig. 2(b). While, the other two process parameters are maintained at their zero levels. At lower value of molar ratio, FAME content is less even at higher catalyst concentration. As the molar ratio increased from 6:1 to 9:1, FAME content also increased with increase in catalyst concentration. However, the maximum FAME content is obtained at molar ratio of 9:1 and catalyst concentration of 0.9 (wt%). The stoichiometric ratio of methanol/oil (3:1) offered the FAME

Table 4 Analysis of Variance (ANOVA) for fitted quadratic model for FAME content as a function of Independent variables.

| Source       | Sum of Squares | df | Mean Square | F Value | p-value |
|--------------|----------------|----|-------------|---------|---------|
| Model        | 6264.29        | 14 | 447.449     | 47.6686 | < 0.0001 significant |
| A-Catalyst Concentration | 368.95 | 1 | 368.95      | 39.3058 | < 0.0001 |
| B-Molar Ratio | 204.517       | 1 | 204.517     | 21.788  | 0.0003  |
| C-Temperature | 241.427       | 1 | 241.427     | 25.7203 | 0.0001  |
| D-Reaction Time | 24.2808     | 1 | 24.2808     | 2.58674 | 0.1286  |
| AB           | 24.7506       | 1 | 24.7506     | 2.63679 | 0.1252  |
| AC           | 2.80562       | 1 | 2.80562     | 0.29889 | 0.5926  |
| AD           | 571.688       | 1 | 571.688     | 60.9043 | < 0.0001 |
| BC           | 1.50062       | 1 | 1.50062     | 0.15987 | 0.6949  |
| BD           | 35.5216       | 1 | 35.5216     | 3.78426 | 0.0707  |
| CD           | 21.8089       | 1 | 21.8089     | 2.32339 | 0.1482  |
| A\(^2\)      | 4614.5        | 1 | 4614.5      | 491.602 | < 0.0001 |
| B\(^2\)      | 115.62        | 1 | 115.62      | 12.3175 | 0.0032  |
| C\(^2\)      | 210.362       | 1 | 210.362     | 22.4107 | 0.0003  |
| D\(^2\)      | 459.249       | 1 | 459.249     | 48.9257 | < 0.0001 |
| Residual     | 140.8         | 15 | 9.38666    |         |         |
| Lack of Fit  | 126.311       | 10 | 12.6311    | 4.35894 | 0.0589 non significant |
| Pure Error   | 14.4888       | 5  | 2.89775    |         |         |
| Cor Total    | 6405.09       | 29 |           |         |         |

R\(^2\) = 0.9780  Adj R\(^2\) = 0.9575  Pred R\(^2\) = 0.8832  CV = 3.94%  Adeq. precision = 27.57  S = 3.06
content of 80.26 %. Higher quantities (beyond 9:1) of methanol to oil molar ratio exhibits negative effect on FAME content, as it was clear by decreasing response with the increase in the molar ratio from 9:1 to 12:1. This is because, at molar ratios of methanol/oil higher than 9:1, separation of esters from glycerol was problematic. A molar ratio of 6:1 is generally considered the most appropriate for methanol. Although, in this work, we found molar ratio 9:1 to be best for methanolysis of kusum oil. This is because, there may be the predominance of the esterification reaction at the initial phase, to transesterify the remaining FFA acids present in the oil sample which can consume the methanol present in the reaction mixture at the initial stage of reaction and hence the amount of methanol available for the transesterification may not be sufficient to drive the reaction forward for the longer time. The second possible reason may be the evaporation of methanol during the reaction stage, which was condensed back to the reaction mixture. Hence, every time the same amount of methanol was not available for the reaction to happen in forward direction. Nevertheless, the results are quantitatively similar to those of literature where author reported rapeseed oil methanolysis using KOH catalyst. Thaiyasuit et al. also reported 10.5:1 methanol/oil molar ratio for rubber seed oil biodiesel production.

The response surface of percentage FAME content as a function of catalyst concentration and temperature at the central levels of methanol to oil molar ratio 8:1 and reaction time of 60 min is shown in Fig. 2 (c). Figure 2 (c) depicts that FAME content increases with an increase in catalyst concentration at low value of temperature. This is due to the fact that catalyst concentration is the significant parameter. However, temperature is less effective at higher levels (above 60°C), which is in agreement with the previous literature studies. This was probably due to increased evaporation rate of methanol and formed a large number of bubbles, which inhibited the reaction on the phase interface. Meher et al. suggested that temperature above the boiling point of alcohol was avoided as high temperature tends to accelerate the saponification of glycerides by the alkaline catalyst before completion of the alcoholysis.

The optimal values of the combination of four process parameters were estimated by solving the regression equation (Eq. 3) using Design Expert software. The optimum conditions obtained as follows: catalyst concentration (A) = 0.9 (wt %), methanol to oil molar ratio (B) = 9:1, temperature (C) = 58.9°C, and reaction time (D) = 58.5 min. For these optimum conditions, model predicted biodiesel FAME content of 97.37 %. So, experimental runs were carried out in a flask under predicted conditions to validate the model. FAME content of 98.14 % was obtained and shows the high degree of similarity between predicted and experimental values showing validity of RSM model.

3.4 Kinetic Study

The data required for developing the kinetic model of the transesterification of kusum (Schleicheria triguga) oil was generated using the model equation developed from the analysis of variance (ANOVA) in the optimization process (Eq. 2). This reaction kinetic is a function of the concentration of oil (Triglyceride, [TG]) and reaction temperature. The stoichiometry of the transesterification process is given as follows:

$$\text{TG} + 3 \text{MeOH} \rightarrow 3 \text{RCOOCH}_3 + \text{Glycerol}$$

(3)

To determine the rate of reaction per unit time, r, the following equation was used:
\[ r = \frac{dX}{dt} = k(T)f(x) \]

Assuming a simple nth order kinetics,

\[ f(x) = (1 - x)^n \]

\[ r = \frac{dX}{dt} = k(1 - x)^n \]

\[ \frac{dx}{(1 - x)^n} = kt \]

In order to determine the value of k, integral method was used to solve Eq. (7). Rearranging and integrating Eq. (7),

\[ \frac{(1 - (1 - x)^{1-n})}{(1 - n)} = kt \text{ for } n \neq 1 \]

The value of global reaction rate constant k was determined by trial and error, using variable n(n + 1)value until the plot of left-hand side of Eq. (8) consisting of a straight line with a high correlation coefficient \( R^2 \) for all the data point obtained from the conversion vs. time curve for temperature range of 50-60°C. The rate constant and \( R^2 \) values are as shown in Table 5 and Fig. 3. The value of n found to be 1.8 as we did not consider the excess methanol in our reaction system. Even, though, we have used three times more the molar ratio than stoichiometric amount. It is limiting one because of the higher percentage of saturation in oil, which causes the reaction mass transfer limiting.

### Table 5 Rate constant at different temperature for transesterification of kusum oil.

| Temperature (°C) | Rate Constant (L mol\(^{-1}\) min\(^{-1}\)) | \( R^2 \) |
|------------------|---------------------------------|---------|
| 50               | 0.029                           | 0.976   |
| 55               | 0.07                            | 0.995   |
| 60               | 0.126                           | 0.976   |

3.5 Determination of activation energy

The influence of temperature on the global reaction rate constant was determined fitting k to the Arrhenius equation,

\[ k(T) = A e^{(-\frac{E_a}{RT})} \]

on integrating,

\[ \ln k = \ln A - \frac{E_a}{R} \]

Where, A is the frequency factor in min\(^{-1}\), \( E_a \) is activation energy in cal mole\(^{-1}\), R is universal gas constant 1.987 cal K\(^{-1}\) mole\(^{-1}\) and T is temperature in K.

The activation energy was estimated by plotting \( \ln k \) as a function of reciprocal temperature \( 1/T \). Thus, the slope and the intercept of the plot would be equivalent to \( -\frac{E_a}{R} \) and \( \ln A \) respectively. Figure 4 shows the Arrhenius plot used to obtain the activation energy from the temperature dependence of the initial rates for the methanolysis of kusum oil using the NaOCH\(_3\) solution as a catalyst. The activation energy and frequency factor for the transesterification reaction was calculated as 31.42 kcal mole\(^{-1}\) and \( 5.53 \times 10^{19} \) L mole\(^{-1}\) min\(^{-1}\), respectively. This activation energy is slightly higher than those studies by different authors\(^{18, 30, 31} \). This may be due to the higher viscosity as well as the higher saturated fatty acid profile of kusum oil comparative with the other oils. Wang and Briggs\(^{32} \) reported that higher activation energy value indicated a more rapid change in viscosity with temperature. This is caused because of higher saturated fatty acids composition present in oil. The similar trend is observed in our case. The positive value of the activation energy indicates endothermic reactions, whereby energy \( (\text{heat}) \) is required for the reactions to take place.

With the kinetics parameters obtained, a mathematical model was proposed for the base catalyzed transesterification of kusum oil.

![Fig. 3](image-url) Plot between \([(1-(1-x)^{1-n})/(1-n)]\) verses time to determine kinetic constant.

![Fig. 4](image-url) Arrhenius plot between \( \ln k \) and \( 1/T \) to determine activation energy and frequency factor.
\[ r = \frac{dx}{dt} = 5.53 \times 10^{19} e^{(-31.43/RT)} (1 - x) 1.8 \quad (11) \]

The goodness of fit of the proposed model was determined by predicting the conversion at temperature of 338 K and at different reaction times. Comparison with the actual (experimental) vs. predicted conversion at the same reaction temperature was made to determine the errors between the predicted and the actual values. Eq. (11) was plotted using Excel 2007 whereby the data for the actual curve was obtained experimentally. Figure 5 shows the comparison between the actual and predicted conversion at different times. The smooth line indicates the conversion obtained by the proposed model, while the dotted points indicate the experimental conversion with an error less than 10%. This shows that the models developed (model from ANOVA and kinetics model) are highly reliable in representing the whole experimental data and also accurate in predicting the kinetics of the base catalyzed transesterification of kusum oil.

3.6 Properties of Biodiesel fuel produced from Kusum (*Schleicheria triguga*) oil

If kusum oil is a potential source of biodiesel, the product must meet the ASTM standards with respect to diesel quality. Table 6 compares the properties of biodiesel from kusum oil, raw kusum oil, ASTM, and EN-14214 biodiesel standard. Most of the fuel properties are found to be in reasonable agreement with ASTM and DIN EN 14214 biodiesel standard except oxidation potential. According to ASTM/DIN-EN standard, kusum oil biodiesel did not meet the given limit of 3h (ASTM standard) and 6h (EN-14214 standard) for oxidation potential.

Biodiesel oxidation stability is one of the major issues as it cannot be stored beyond a period. Rancimat test is the specified standard method for oxidation stability testing for biodiesel sample in accordance to ASTM/DIN-EN standard. A minimum oxidation stability of 6 h is defined for biodiesel samples. It is already discussed in various literature reports mentioned above that it is very difficult to meet this limit for biodiesel fuels derived from various vegetable oils, unless antioxidants are added to the biodiesel. In the present study, phenolic antioxidant 2,6-ditertiarybutyl hydroxytoluene was used. Antioxidant 2,6-ditertiarybutyl hydroxytoluene was doped to the kusum oil biodiesel (KOB).

Table 6  Fuel properties of Kusum oil, Kusum oil biodiesel, ASTM and DIN EN 14214.

| Sr. No. | Properties       | Kusum oil (Kg/L) | Kusum oil Biodiesel | ASTM standard | DIN-EN 14214 |
|---------|------------------|------------------|--------------------|---------------|--------------|
| 1       | Density at 15℃   | 0.9              | 0.857              | –             | 0.86-0.9     |
| 2       | Viscosity at 40℃ | 40.75            | 5.34               | 1.9-6.0       | 3.5-5.0      |
| 3       | Flash Point      | 240              | 152                | >130          | >120         |
| 4       | Pour Point       | 2                | –2                 | –             | –            |
| 5       | Acid value       | 21.65*           | 0.42*              | <0.8          | <0.5         |
| 6       | Calorific value  | 36.25            | 37.595             | –             | –            |
| 7       | Cetane number    | 40               | 42.47              | Min. 47       | Min. 47      |
| 8       | Water content    | 0.05             | 0.021              | Max. 0.05     | Max. 0.05    |
| 9       | Carbon Residue   | 0.05             | 0.039              | Max. 0.05     | Max. 0.05    |
| 10      | Sulphur          | –                | <0.005             | Max. 0.05     | Max. 0.05    |
| 11      | Total Glycerin   | –                | 47                 | –             | –            |
| 12      | H/C Ratio        | –                | 1.81               | –             | –            |
| 13      | Oxidation stability | – | 0.86h             | Min. 3h       | Min. 6h      |

* g of NaOH/g
samples with varying concentrations (ppm), and corresponding oxidation stability were measured with the Rancimat test method to observe the effectiveness of antioxidant.

Figure 6 shows the effect of antioxidant loading on oxidation stability of biodiesel. The oxidation stability of KOB has been found to increase with increase in dosage of antioxidant. Finally it is found that minimum dosing of 500 ppm of 2,6-diteriarybutyl hydroxytoluene was needed to improve the oxidation stability of neat KOB from 0.86 h to above 6 h as required by ASTM/DIN-EN standard specifications for biodiesel oxidation stability.

4 Conclusions

Kusum (Schleichera triguga) oil, a non-edible low cost feedstock was found to be promising raw material for the production of biodiesel.

A five-level four-factor central composite design was conducted to study the interaction effects of process variables on the transesterification of kusum oil. All the variables except reaction time significantly affected the FAME content, the amount of catalysts and temperature being the most effective, followed by methanol/oil molar ratio. Using response surface methodology, a quadratic polynomial equation was obtained for FAME content by multiple regression analysis. The predicted and experimental FAME contents were found to be 97.37% (wt) and 98.14% (wt), respectively.

The developed kinetic model suggested a 1.8<sup>th</sup> order reaction with activation energy of 31.42 kcal mol<sup>-1</sup> and frequency factor of 5.53×10<sup>19</sup> L mole<sup>-1</sup> min<sup>-1</sup>. The activation energy obtained in our case is higher than the previously reported literature. This concludes that the higher viscosity as well as higher saturated fatty acid content in oil has relative effects on activation energy.

Supporting Information

This material is available free of charge via the Internet at http://dx.doi.org/jos.64.10.5650/jos.ess.15069

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