



Optimization of two step karanja biodiesel synthesis under microwave irradiation

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ABSTRACT

The free fatty acid of crude karanja oil (*Pongamia pinnata*) was reduced and biodiesel was synthesized from pretreated oil under microwave irradiation. The process variables such as irradiation time, methanol–oil ratio and sulfuric acid concentration for pretreatment step; irradiation time, methanol–oil ratio and KOH concentration were optimized through the Box–Behnken experimental design. The free fatty acid of crude karanja oil was reduced to $1.11 \pm 0.07\%$ with an optimal combination of 190 s irradiation time (180 W), 33.83 (w/w)% methanol–oil ratio and 3.73 (w/w)% sulfuric acid concentration. An optimal combination of 150 s irradiation time, 33.4 (w/w)% methanol–oil ratio and 1.33 (w/w)% KOH concentration yielded $89.9 \pm 0.3\%$ biodiesel. The model was validated by conducting experiments at optimal design conditions. The present work confirmed that the microwave energy has a significant effect on esterification and transesterification reaction.

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1. Introduction

Biodiesel is a mixture of fatty acid methyl ester (FAME) compounds derived from oil sources which exhibits fuel properties similar to that of diesel fuel. The physico-chemical properties and availability of the oil vary considerably with location, according to climate and seasons [1]. Use of edible oil for biodiesel production in countries like India, where edible oil is imported, makes the process expensive. Hence non-edible and low cost oils are of major focus in biodiesel synthesis and it includes unconventional oils like green seed canola oil [2], rubber seed oil [3], *Pongamia* oil [4], and *Jatropha* oil [5].

Karanja oil (*Pongamia pinnata*), a non-edible oil grown in the Indian subcontinent in large quantity, is a good feedstock for biodiesel synthesis [4]. For the biodiesel to be marketable it needs to conform with standard fuel specifications such as ASTM, which restricts acid value of biodiesel to 0.5 mg KOH/g [6]. The karanja oil has high free fatty acid (FFA) and necessitates a pretreatment step to reduce FFA. The FFA needs to be reduced below 1% in order to obtain high biodiesel yield through alkali catalyzed transesterification [7]. Free fatty acid of crude oil is generally reduced through an acid catalyzed esterification reaction under conventional heating and is well documented [5]. Microwave assisted free fatty acid reduction of crude oil is a novel technique and rarely any literature is available.

Several techniques have been used for the synthesis of biodiesel which includes conventional heating [4], lipase catalyzed method [8,9], supercritical methanol [10], ultrasonic method [11] and

microwave irradiation [12,13]. Efficiency of microwave heating is significantly higher when compared to the conventional method of transesterification reaction. Microwave assisted biodiesel production requires less time for reaction as well as for separation of products [13]. The yield and quality of biodiesel produced via microwave irradiation is the same as that produced by conventional heating [12].

The major factors that affect the esterification and transesterification are reaction time, temperature, methanol–oil ratio and catalyst concentration. In conventional method of biodiesel synthesis the reaction time and temperature are 30 min–2 h and 55–65 °C respectively [4,14,15]. Theoretical methanol–oil molar ratio is 3:1, but a higher molar ratio is used in order to shift the equilibrium reaction towards completion and the optimal methanol–oil molar varies from 6:1–9:1 [5,15]. KOH is preferred as the homogeneous catalyst for transesterification of triglycerides and it depends upon the %FFA present in the oil [7]. In order to reduce %FFA in oil, oil is pretreated through esterification reaction catalyzed, generally, by sulfuric acid [5,7]. Intensity of mixing has negligible effect beyond 300 rpm in comparison with above mentioned parameters [4,16].

The present work discusses the synthesis of biodiesel through microwave assisted two step synthesis and parameter optimization through response surface methodology. Karanja oil, having high FFA, was pretreated (esterification) and then transesterified under microwave irradiation. To minimize the %FFA and maximize biodiesel yield parameters were optimized through Box–Behnken experimental design. The variables considered were microwave irradiation time (at 180 W), methanol–oil ratio and catalyst concentration (pretreatment: sulfuric acid, transesterification: KOH). Further this report also describes the advantages of microwave irradiation on two step biodiesel synthesis and quality of biodiesel.

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2. Materials and methods

2.1. Materials

Analytical reagent grade chemicals such as methanol, sulfuric acid were used. Karanja oil was obtained from a local departmental store. Experiments were conducted in a modified domestic microwave oven (Samsung M183DN) as shown in Fig. 1. Carousel plate was replaced with a fixed Teflon base. A 100 ml glass round bottom flask with Teflon agitator was used as reactor. A hole of 10 mm was made in microwave oven above the carousel axis and a condenser was provided for refluxing of methanol.

2.2. First step: microwave assisted pretreatment

The crude karanja oil had an initial FFA of 8.8% which corresponds to acid value of 17.5 mg KOH/g, a value far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst. Therefore, a pretreatment step was carried out to esterify FFAs with methanol using a sulfuric acid catalyst. Experiments were carried out with 25 g oil as basis. The reaction mixture was irradiated for a different time irradiation (at 180 W) with constant stirring (300 rpm). Upon treating the oil, the mixture was separated and FFA content of the lower layer was measured. The FFA content was determined by standard titrimetry method [17]. The product having FFA less than 1% was used for the next step of transesterification.

2.3. Second step: microwave assisted transesterification

The transesterification reaction was carried out in the same microwave reactor. Methanolic KOH was added to the pretreated oil and irradiated (180 W) for various time intervals. A constant stirring rate was maintained at 300 rpm. Thus the product obtained was allowed to settle into two phases in a separating funnel. The upper biodiesel layer was washed 3–4 times with warm water. The product phase was dried over anhydrous sodium sulfate and filtered. The quality of biodiesel and triglyceride in karanja oil were analyzed

through thermogravimetry [18]. Biodiesel yield was calculated using the following relationship;

$$\% \text{ EsterYield} = \frac{\% \text{ Purity of Biodiesel} \times \text{Mass of Biodiesel Layer}}{\% \text{ Triglyceride in Karanja oil} \times \text{weight of oil}} \times 100 \quad (1)$$

Biodiesel properties such as density at 15 °C [6], kinematic viscosity at 40 °C [6], acid value [17], saponification value [17], iodine value [17], oxidation stability [6], copper strip corrosion [6] and cetane index [19] were determined.

2.4. Experimental design

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response [20]. The experimental design was formulated using Box–Behnken design and the process variables for pretreatment and transesterification steps were optimized through the response. A three-level-three-factor Box–Behnken design was employed consisting of 15 experiments, including 3 centre points, in pretreatment and transesterification step separately [20]. Time of irradiation (T_p or T_T), methanol–oil ratio (M_p or M_T) and catalyst concentration (C_p or C_T) were the independent variables selected to be optimized. Sulfuric acid and KOH were chosen as catalysts for pretreatment step and transesterification step respectively. The coded and uncoded levels of all variables are given in Table 1. The experiments were conducted in a randomized order.

The experimental data obtained by following the above procedures were fit to second order polynomial equation [20]:

$$y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_i x_j \quad (2)$$

Where y is the response (%FFA or %FAME Yield); x_i and x_j are uncoded independent variables and β_0 , β_i , β_{ii} and β_{ij} are intercept, linear, quadratic and interaction constant coefficients, respectively. The aim was to minimize %FFA in pretreatment step and to maximize percentage yield of FAME in transesterification step. Minitab v15 software package was used for regression analysis and analysis of variance (ANOVA). Stepwise elimination of insignificant terms was carried out to obtain statistically significant reduced fit models. Optimal conditions obtained were validated by conducting experiments.

Table 1

Independent variables and levels used for experimental design in pretreatment and transesterification step.

Variables	Levels ^a		
	-1	0	+1
<i>Pretreatment step</i>			
Irradiation time, T_p (sec)	60	210	360
Methanol–oil ratio, M_p (%w/w)	10	30	50
H ₂ SO ₄ Concentration, C_p (%w/w)	0.5	2.75	5.0
<i>Transesterification step</i>			
Irradiation time, T_T (sec)	60	180	300
Methanol–oil ratio, M_T (%w/w)	10	30	50
KOH concentration, C_T (%w/w)	0.5	1.0	1.5

^a Transformation of variable levels from coded (X) to uncoded could be obtained as: $T_p = 210 + 150X$; $M_p = 30 + 20X$; $C_p = 2.75 + 2.25X$; $T_T = 180 + 120X$; $M_T = 30 + 20X$; $C_T = 1 + 0.5X$ where X can be -1, 0 or +1.

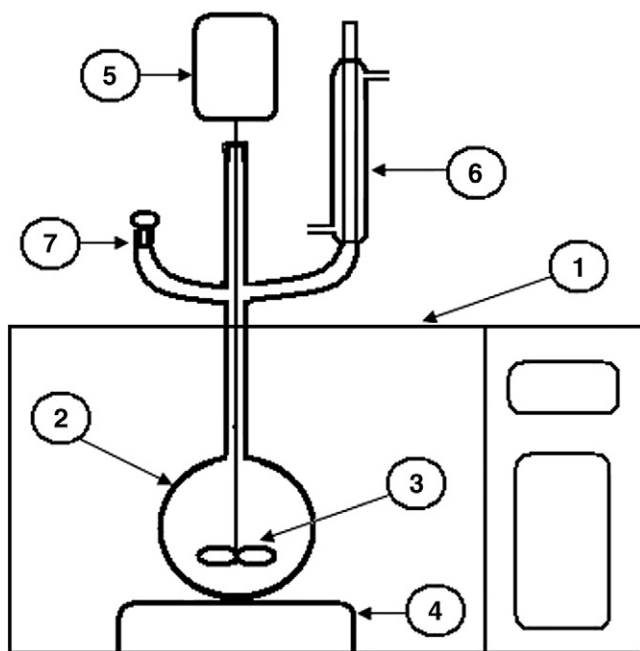


Fig. 1. Schematic diagram of domestic microwave oven modified for batch experiments. 1: Microwave oven, 2: round bottom flask, 3: Teflon stirrer, 4: base, 5: motor, 6: condenser, and 7: feed neck.

3. Results and discussion

3.1. Effect of FFA and microwave power on biodiesel yield

In order to study the effect of free fatty acids and microwave power, experiments were conducted to synthesize biodiesel from crude (single step method) and pretreated (two step method) karanja oil at different microwave power. In the two step method the FFA of crude karanja oil was reduced by an acid catalyzed pretreatment step. A 40 (w/w)% methanol–oil ratio was used in all the experiments. Catalyst (KOH) concentration was kept constant, 3 (w/w)% for single step method and 1 (w/w)% for two step method [5,7]. The initial FFA in single and two step methods were found to be 8.8% and 1.6% respectively.

The results, as shown in Fig. 2, indicate that microwave power has considerable effect on single step method at high FFA level (8.8%). But at reduced FFA level (upon pretreatment, FFA 1.6%) microwave power seems to have a negligible effect on FAME yield. Higher FFA content leading to saponification reaction caused the single step method to yield less amount of biodiesel [7]. Pretreated karanja oil yielded up to 90% biodiesel in 4 min at 300 W and 180 W where as in single step method the maximum yield of 80% was obtained at 4–5 min at 300 W. Under conventional heating mechanism biodiesel yield plummets to less than 10% when FFA content is beyond 5% [21]. In the present case of microwave assisted synthesis very high yields were obtained for oil with FFA beyond 5%. In case of single step method, along with reduction in yield, final FFA content of biodiesel was beyond the standard limits. The final FFA of single step biodiesel was 7.8% which is far beyond the standard limits. Single step microwave assisted synthesis seems to be a better approach, but in order to synthesize biodiesel conforming to standard limits, a two step method is preferred. The yields obtained at 180 W and 300 W of microwave powers are almost the same. Hence optimization of two step process parameters was conducted at 180 W microwave power.

3.2. Optimization of microwave assisted pretreatment step

The experimental design with uncoded variables, experimental and predicted % FFA are given in Table 2a. The experimental data were fit to quadratic polynomial equation through least square technique and statistical analyses were carried out. Upon step wise elimination of insignificant terms, the significant terms were fit to reduced model. Thus obtained coefficients are shown in Table 2b. The table shows that linear and quadratic terms of T_p , M_p and C_p are significant model terms in reducing FFA. Interaction terms have no effect on reduction of FFA. High coefficient of determination 0.916

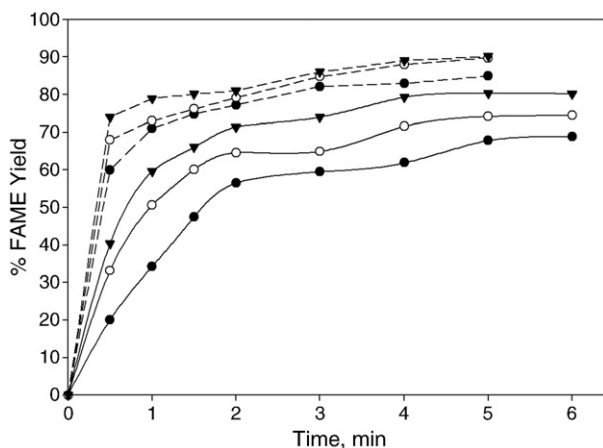


Fig. 2. Influence of FFA and microwave power on % FAME yield. Single step method (—) and two step method (---) at microwave powers 100 W (●), 180 W (○) and 300 W (▼).

Table 2a

Box–Behnken experimental design and response for pretreatment of karanja oil to reduce free fatty acids.

Std. Order	Levels of variables Uncoded (coded)			Response:% FFA	
	T_p	M_p	C_p	Experimental	Predicted
1	60 (-1)	10 (-1)	2.75 (0)	1.97	1.944
2	360 (+1)	10 (-1)	2.75 (0)	2.08	2.211
3	60 (-1)	50 (+1)	2.75 (0)	1.98	1.739
4	360 (+1)	50 (+1)	2.75 (0)	1.87	2.006
5	60 (-1)	30 (0)	0.5 (-1)	1.92	2.05
6	360 (+1)	30 (0)	0.5 (-1)	2.43	2.318
7	60 (-1)	30 (0)	5.0 (+1)	1.47	1.608
8	360 (+1)	30 (0)	5.0 (+1)	2.03	1.875
9	210 (0)	10 (-1)	0.5 (-1)	2.09	1.929
10	210 (0)	50 (+1)	0.5 (-1)	1.58	1.724
11	210 (0)	10 (-1)	5.0 (+1)	1.43	1.486
12	210 (0)	50 (+1)	5.0 (+1)	1.32	1.281
13	210 (0)	30 (0)	2.75 (0)	1.04	1.073
14	210 (0)	30 (0)	2.75 (0)	1.12	1.073
15	210 (0)	30 (0)	2.75 (0)	1.06	1.073

and small standard error 0.17 shows that model is highly significant. Also the insignificant lack fit data shows that the predicted model is a good fit. The predicted model in terms of uncoded variables can be represented by Eq. (3).

$$\%FFA = 3.544 - 0.011T_p - 0.046M_p - 0.381C_p + 0.00003T_p^2 + 0.00068M_p^2 + 0.051C_p^2 \quad (3)$$

The optimized values of independent variables were found to be as follows: Time of irradiation (T_p) 190 s, methanol–oil ratio (M_p) 33.83 (w/w)%, H_2SO_4 concentration (C_p) 3.73 (w/w)%. Few experiments were conducted at optimal condition to validate the model. The final FFA value at this condition was determined to be $1.11 \pm 0.07\%$. This value is reasonably close to the predicted FFA of 1.01% and thus validates the model. Nayak et al. reported the acid catalyzed esterification reaction time of 15–30 min for karanja oil having 10% FFA under conventional method and obtained acid value decreased up to 3.4 ± 0.3 mgKOH/g [21]. In the present work use of microwave irradiation decreased the time of reaction and also the %conversion of FFA increased.

Fig. 3a–c shows the interaction plots at constant time of irradiation (190 s), methanol–oil ratio (33.83 w/w%) and H_2SO_4 concentration (3.73 w/w%). Presence of lesser quantity of alcohol and lower reaction time may not decrease the FFA to a great extent [7]. Moderately higher coefficients are obtained for linear and quadratic terms of C_p which indicate that catalyst concentration is the most significant term with

Table 2b

Regression coefficients of predicted quadratic polynomial after step wise elimination for pretreatment of karanja oil to reduce free fatty acids.

Terms	Regression coefficient ^a	SE
Intercept		
β_0	+ 3.544**	0.269
Linear		
β_1	- 0.011**	0.001
β_2	- 0.046*	0.013
β_3	- 0.381*	0.098
Quadratic		
β_{11}	+ 3E-005**	4E-006
β_{22}	+ 6.8E-004*	2.2E-004
β_{33}	+ 0.051*	0.018

^a $R^2 = 0.916$, $S = 0.17$, F -value = 21.01, P (lack of fit) = 0.055.

** Significant at 99% confidence level.

* Significant at 95% confidence level.

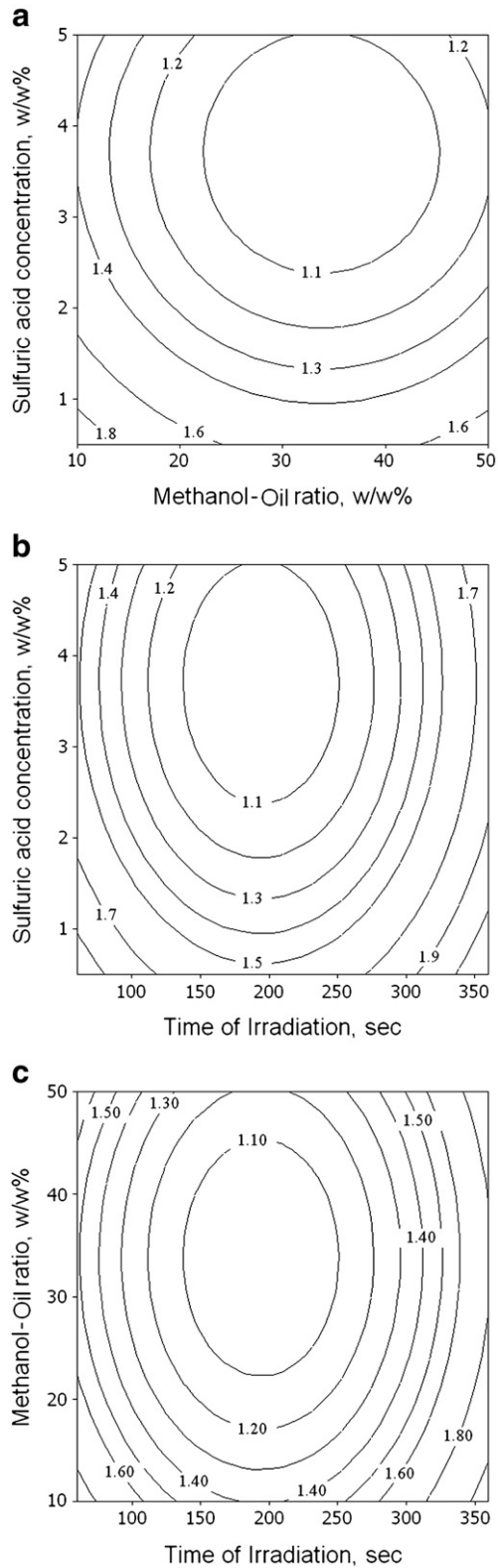


Fig. 3. Contour plots of pretreatment step:%FFA predicted from the quadratic model at constant a) microwave irradiation time (190 s), b) methanol-oil ratio (33.83 w/w%) and c) sulfuric acid concentration (3.73 w/w%).

negative effect. Fig. 3a and b also indicates reduction in response (% FFA) at lower methanol-oil ratio and irradiation time as catalyst concentration is increased. But at higher methanol-oil ratio (Fig. 3a) reduction in %FFA is not much affected by an increase in catalyst concentration. The reduction in FFA is very low beyond irradiation

Table 3a

Experimental design and response for transesterification of pretreated karanja oil.

Std. Order	Levels of variables			Response:% FAME yield		
	Uncoded	(coded)		Experimental	Predicted	
1	60	(-1)	10 (-1)	1.0 (0)	83.9	86.1
2	300	(+1)	10 (-1)	1.0 (0)	97.6	79.3
3	60	(-1)	50 (+1)	1.0 (0)	99.2	85.3
4	300	(+1)	50 (+1)	1.0 (0)	95.8	88.4
5	60	(-1)	30 (0)	0.5 (-1)	91.6	87.1
6	300	(+1)	30 (0)	0.5 (-1)	95.8	84.1
7	60	(-1)	30 (0)	1.5 (+1)	94.7	90.2
8	300	(+1)	30 (0)	1.5 (+1)	93.2	87.3
9	180	(0)	10 (-1)	0.5 (-1)	98.7	79
10	180	(0)	50 (+1)	0.5 (-1)	94.9	84
11	180	(0)	10 (-1)	1.5 (+1)	89.2	85.6
12	180	(0)	50 (+1)	1.5 (+1)	89.1	89.1
13	180	(0)	30 (0)	1.0 (0)	99.3	89.9
14	180	(0)	30 (0)	1.0 (0)	94.4	90.6
15	180	(0)	30 (0)	1.0 (0)	88	90.3

time of 300 s (Fig. 3b and c); this could be due to the formed water preventing esterification reaction in forward direction.

3.3. Transesterification step

The experimental design for three independent variables, experimental and predicted %FAME yield are given in Table 3a. The experimental data was fit to quadratic model through stepwise elimination procedure to obtain reduced fit equation (Eq. (4)). The coefficients of significant terms are shown in Table 3b. High correlation coefficient (R^2) 0.973 and low standard error 0.85 indicate the predicted model fits the experimental data very well. The insignificant lack of fit data (F -value: 7.82, P value: 0.117) also support the predicted model. Two linear terms (M_T and C_T) and all three quadratic terms (T_T^2 , M_T^2 and C_T^2) found to be significant along with one interaction term ($T_T * M_T$). Even though the linear term T_T is insignificant it cannot be excluded from model as the quadratic and interaction terms were significant. All three quadratic terms found to have a negative effect on yield, whereas the alone interaction term ($T_T M_T$) has positive effect.

$$\%FAME \text{ Yield} = 70.7458 - 0.0067T_T + 0.5375M_T + 18.2667C_T + 0.0001T_T^2 - 0.0103M_T^2 - 6.8833C_T^2 + 0.001T_T M_T \quad (4)$$

Table 3b

Regression coefficients of predicted quadratic polynomial after step wise elimination for transesterification of pretreated karanja oil.

Terms	Regression coefficient ^a	SE
<i>Intercept</i>		
β_0	+70.7458**	2.386
<i>Linear</i>		
β_1	-0.0067	0.013
β_2	+0.5375**	0.075
β_3	+18.2667**	3.593
<i>Quadratic</i>		
β_{11}	-1E-004*	3E-005
β_{22}	-0.0103**	0.001
β_{33}	-6.8833*	1.771
<i>Interaction</i>		
β_{12}	+0.001**	1.8E-004

^a $R^2 = 0.973$, $S = 0.85$, F -value = 7.82, P (Lack of fit) = 0.117.

** Significant at 99% confidence level.

* Significant at 95% confidence level.

An optimal predicted yield of 91.4% was obtained at 150 s irradiation time, 33.4 (w/w)% methanol–oil ratio and 1.33 (w/w)% catalyst KOH concentration. The optimal methanol–oil ratio is equivalent to 9.3:1 molar ratio based on 893 as karanja oil molecular

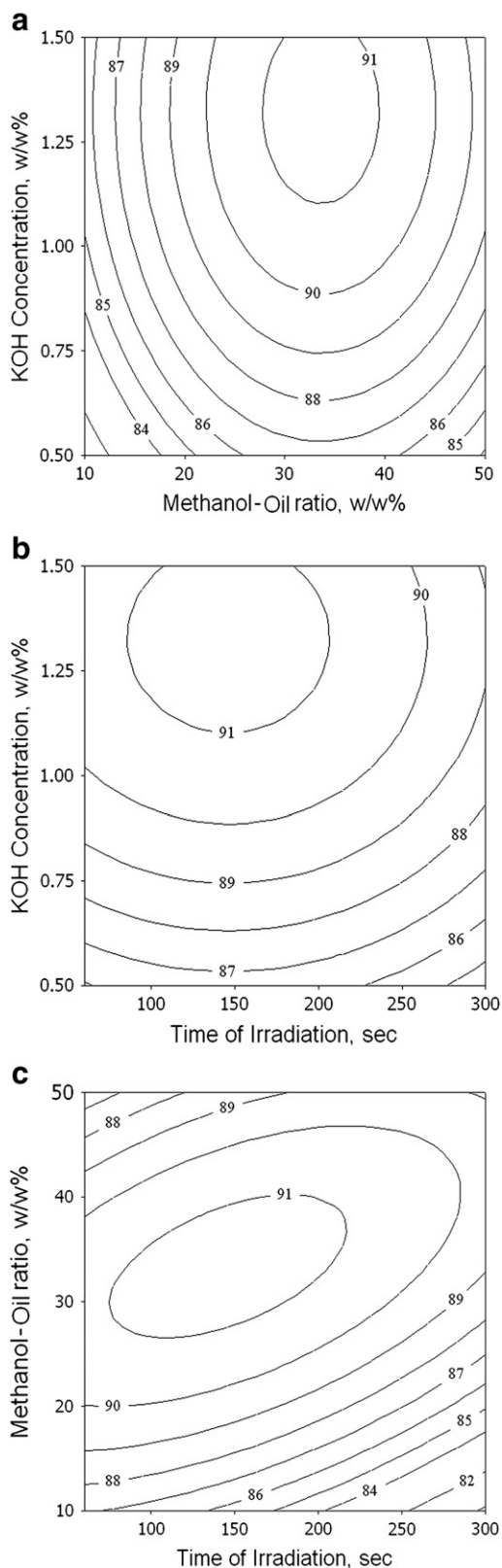


Fig. 4. Contour plots of transesterification step: %FAME yield predicted from the quadratic model at constant a) microwave irradiation time (150 s), b) methanol–oil ratio (33.4 w/w%) and c) KOH concentration (1.33 w/w%).

Table 4
Properties of karanja oil and karanja biodiesel.

Properties	Crude Karanja Oil	Karanja Biodiesel ^a	Biodiesel Standard	
			ASTM D6751–09	EN14214
Density (kg/m ³)	940	887	–	860–900
Kinematic viscosity (mm ² /s)	42	4.3	1.9–6.0	3.5–5.0
Acid value (mg KOH/g)	17.5	0.405	<0.5	<0.5
Saponification Number (mg KOH/g)	210	195	–	–
Iodine Value (g I ₂ /100 g)	85	83	–	<120
Cetane Index	53.2	56.3	>47	>51
Flash point (°C)	–	145	>93	>101
Oxidation Stability (hour)	–	7.5	>3	>6
Copper strip corrosion	–	No. 2	No.3 max	Class 1

^a Karanja biodiesel synthesized under optimal conditions of two step process.

weight [22]. Experiments conducted at this process condition to validate the model yielded $89.9 \pm 0.3\%$ fatty acid methyl ester.

Contour plots at constant time of irradiation (T_T : 150 s), methanol–oil ratio (M_T : 33.4 w/w%) and KOH concentration (C_T : 1.33 w/w%) are shown in Fig. 4a–c respectively. Yield of FAME increased as KOH concentration increased at moderate levels of methanol–oil ratio (Fig. 4a). As the time or methanol–oil ratio increased biodiesel yield did not improve with increasing KOH concentration (Fig. 4a and b). It signifies that catalyst concentration has strong positive effect on yield and is supported by high coefficient (β_3) for linear term in model equation. Beyond 200 s of irradiation FAME yield did not improve significantly (Fig. 4b and c). This could be either due to the formation soap during prolonged time of reaction or due to equilibrium nature of reaction [7,13]. At higher methanol–oil ratio separation of glycerol layer becomes difficult, eventually reducing yield [7]. Microwave irradiation seems to have strong effect on speed of reaction rather than yield of biodiesel. The rate of reaction increased drastically which reduced time of reaction to 2–3 min from 1–2 h as in case of conventional heating [13].

3.4. Properties of biodiesel

The properties of biodiesel such as density, kinematic viscosity, saponification number, iodine value and cetane index [19] were determined for biodiesel synthesized at optimal condition and are summarized in Table 4. The properties were compared with ASTM standard [6] and analyzed to be in good agreement. Microwave irradiation accelerates the process without altering the physical properties of biodiesel. Application of microwave energy also improves the product recovery from reaction mixture [12,16]. The static separation time required for separation of glycerol layer was reduced by at least 90% which is in good agreement with available literature results [13]. The purity of biodiesel synthesized was analyzed using thermogravimetry. The biodiesel was found to contain more than 98% FAME which is well above the EN 14214 limits of 96.4% [23].

4. Conclusion

The crude karanja oil with high FFA (8.8%) was reduced to 1.1% by pretreating the oil with methanol (33.83 w/w% methanol–oil ratio) using H_2SO_4 catalyst (3.73 w/w%) and irradiating for 190 s at 180 W. The pretreated oil was used to synthesize biodiesel through alkali catalyzed transesterification. The optimal reaction condition was methanol–oil ratio 33.4 (w/w)%, KOH catalyst concentration 1.33 (w/w)% and microwave irradiation time of 150 s at 180 W. The predicted FAME yield 91.4% was validated experimentally. The experimental investigation resulted in producing karanja biodiesel with high purity and satisfying the major biodiesel properties.

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