



Optimization of process variables on two-step microwave-assisted transesterification of waste cooking oil

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Abstract

Scale-up and commercialization of biodiesel is often delimited by costly feedstock that adds up to the process costs. These underlying issues demand the exploration of unconventional cheap feed to improve the process economics. Conversion of waste cooking oil (WCO) into biodiesel could reduce the process costs by 60–70%. However, the continuous exposure to heat during frying leads to oxidation as well increase in the free fatty acid (FFA) content which intensifies the time and energy required for transesterification. The present study analyzes the effect of parameters over the conversion of WCO (with 8.17% FFA) into biodiesel via two-step acid-alkali-based microwave-assisted transesterification. Response surface methodology (RSM) was used to optimize the oil:methanol volume ratio, microwave power, and reaction time during the acid-catalyzed esterification to bring down the FFA below 1%. Microwave irradiation of 250 W, with methanol:oil molar ratio of 19.57:1 [oil:methanol volume ratio of 1.31 (expressed as decimal)] and reaction time of 35 s, resulted in 0.082% of FFA. Alkali-catalyzed transesterification with methanol:oil molar ratio of 5:1 with 2% sodium hydroxide at 65 °C thereby produced fatty acid methyl esters (FAMES) with the volumetric biodiesel yield of 94.6% in 30 min. Physiochemical properties of the transesterified WCO were well comparable with the biodiesel standards. The study highlights the essentiality of multivariate optimization for the esterification process that could aid in understanding the interactive effects of variables over FFA content. Such studies would benefit in scaling up of the transesterification process at industrial level by improving the economics of the overall bioprocess.

Keywords Waste cooking oil · Biodiesel · Free fatty acids · Optimization · Transesterification · FAME

Introduction

The present era is confronted with the concerns for depleting petroleum fuel reserves and increase in crude oil prices along with population explosion and energy crisis. These problems could be partially sorted out by exploring new non-conventional energy sources (Rangabhashiyam et al. 2017; Behera et al. 2019). Biodiesel is regarded as a renewable, non-toxic alternative fuel, derived from vegetable oils and animal fats that has possibly lower emission profile compared to petroleum fuels (Ajala et al. 2015). In developing countries like India, with people relying more on edible vegetable oil

which accounts to nearly 30 billion tonnes per year, it is irrational to rely on the edible feedstock as raw materials for biodiesel production (Dorni et al. 2018). However, India should tap unconventional resources for energy utilization to meet its demand (Balasubramanian and Karthickumar 2012; Asok et al. 2013). Direct use of vegetable oil/animal fats as raw material for biodiesel increases the production costs by 60% (which is 1.5 times more than the cost of petroleum fuel) making its large-scale commercialization questionable (Bhuiya et al. 2016). The critical issues such as hefty expenditures of raw materials can be averted by the use of waste cooking oil (WCO) which is 2–3 times cheaper compared to other feedstocks (Maddikeri et al. 2012). Large quantities of WCO generated in households and restaurants are disposed inappropriately leading to a multitude of environmental problems and health hazards threatening the aquatic life (Singh-Ackbarali et al. 2017). Direct utilization of WCO in fuel engines is often prohibited by their high viscosity which might lead to the problems of choking due to the presence of carbon deposits (Kraiem et al. 2017). Thus, biodiesel

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production via transesterification is regarded as an energy and cost-effective alternative for the utilization of this waste resource (Qasim et al. 2018).

Several alkali and acid homogenous catalysts, heterogeneous and enzymatic catalysts are used for chemically converting WCO into biodiesel. Alkali-catalyzed transesterification is one of the most preferred routes because of (1) milder reaction conditions (low temperature and atmospheric pressure), (2) less number of reagents involved, and (3) minimal reaction time and costs, as compared to the other counter processes involved (Srivastava et al. 2018). However, the above method is suitable only for oils with less than 6% of free fatty acids (FFA). High FFA often deactivates the catalyst leading to undesirable soap formation, thereby declining its process efficiency (Thoai et al. 2019). Studies have revealed that the long-term exposure to heat (160–190 °C) and oxygen during the course of frying changes the physical and chemical properties of oil resulting in an increase in viscosity, surface tension, and specific heat as well as the FFA (to about 15%). High FFA and water content often manifests the process of saponification, and the soap formed in course of time gels up as semisolid mass making the purification and recovery difficult (Bouaid et al. 2012). Hence, acid-catalyzed transesterification is commonly practiced for feeds like WCO with higher FFA.

The single-step, acid-catalyzed reaction and thereby conversion into biodiesel is 4×10^3 times slower compared to the alkali-catalyzed reaction (Chai et al. 2014). Thus, it is not advantageous to use only the acid catalysts. Researchers have proposed that the acid-catalyzed pre-esterification step could be used to minimize the FFA content, prior to the utilization of base catalysts. However, the combined process is associated with the usage of huge amount of base for neutralization (Mardhiah et al. 2017). Although studies have also proposed alternative techniques like the use of heterogeneous acid catalysts, heteropoly acids, ion exchange resins, green carbon catalysts, and the associated issues with technically critical operating conditions, greater reaction time with low reusability and higher costs has to be resolved (Srivastava et al. 2018; Noshadi et al. 2012). Studies have proposed that the approach of enhancing the diffusion characteristics of the transesterification via augmenting the process with the use of microwave irradiation can increment the efficiency of conversion (Patil et al. 2012).

Recently, electromagnetic energy in the form of microwave irradiation has gained interest among the researchers due to the advantages of producing higher yield of the desired product in shorter time (Thoai et al. 2019). Further, the process is regarded to be environmentally benign compared to other conventional methods with relatively lower energy consumption and relatively less green house gas emissions (Babel et al. 2018). Electromagnetic transfer of heat energy is faster and independent of the thermal conductivity and specific density

of the material (Thoai et al. 2019). The regular heating process is slow due to non-uniform distribution of heat energy and often requires more time for completion resulting in degradation of the desired product (Patil et al. 2012; Vasantha et al. 2017). Consequently, in microwave heating, the random collisions and friction due to oscillations between the reacting molecules and the container result in rapid and uniform heating. Studies concerning the use of microwave irradiation with respect to the transesterification process have been reported by several researchers (Jaliliannosrati et al. 2013; Martinez-Guerra and Gude 2014; Tangy et al. 2017). Modeling and optimization of reaction parameters using different designs have been reported by few studies. Chen et al. (2012) examined the influence of variables on microwave-assisted transesterification of WCO with less than 2% FFA. Babel et al. (2018) studied the microwave transesterification of WCO with potassium hydroxide supplemented carbonized coconut shell. Sajjadi et al. (2014) modeled the effect of parameters on microwave transesterification and reported 98% biodiesel yield with honeycomb monolith-based zirconia catalyst under optimal conditions. Tangy et al. (2017) reported an increase in biodiesel yield from waste frying oil with microwave heating under batch mode of operation. Hong et al. (2016) reported 96.5% yield of biodiesel with continuous microwave power of 600 W after 60-min exposure. Most of the studies reported so far are restricted to the optimization of process conditions for single-step microwave transesterification under alkaline conditions with less initial FFA. Very few studies have been done with regard to the two-step acid-alkali-catalyzed microwave-assisted transesterification, where the reaction is being limited by several influencing factors (Bouaid et al. 2012; Urrutia et al. 2016). The first step of acid-catalyzed esterification influences the FFA of WCO, thereby playing an essential role in deciding the cost and economics of the process at industrial scale (Banani et al. 2015). One variable at a time approach has been utilized by different researchers for optimizing the process parameters for esterification. Suppalakpanya et al. (2011) and Jaliliannosrati et al. (2013) optimized the influencing variables for FFA reduction with crude vegetable oils using microwave irradiation. The reported values are often contradicting; thus, it is difficult to predict the interactive effects of these factors over the output. The study by Bouaid et al. (2012) optimized the esterification process of production of biodiesel from *Jatropha curcas* crude oil. Eventhough researchers (Hong et al. 2016; Tangy et al. 2017) have studied the influence of variables during the microwave-assisted transesterification of WCO, none of the studies have been reported with the optimization of process variables during the microwave-assisted esterification process. This necessitates the use of factorial design with multivariate for optimizing the process conditions and to study the interactive effects resulting in FFA reduction.

The current study focuses on optimizing the influencing factors of two-step acid-alkali-catalyzed microwave-assisted transesterification of the WCO with higher FFA. Experiments were carried out initially at the acid-catalyzed esterification step to optimize the reaction variables like the volume ratio of oil:methanol, reaction time, and microwave power for reducing the FFA of WCO below 1%. Then the alkali-catalyzed transesterification was done to convert the esterified oil into fatty acid methyl esters (FAMES) with a lower heating rate and shorter reaction time. The physiochemical properties of the WCO were compared with that of the biodiesel standards to assess its potential at commercial scale. The outcome of the study would help the industrialists and policy makers to understand the relative influence of parameters and would aid in cost-efficient and easy scale up at the field level.

Materials and methods

Materials and reagents used

One liter of WCO in clean plastic containers was obtained from the hostel mess of C.V Raman Hall of Residence of National Institute of Technology Rourkela (India). The collected WCO was deep brown in color as well it has been used thrice for cooking purpose. All chemicals used in the experiments were analytical grade and were procured from Himedia (India). The oil was filtered to remove any suspended particulate matter present, prior to its characterization.

Analysis of properties of waste cooking oil

Physical properties of WCO such as cloud point, pour point, kinematic viscosity, and density were measured using standard protocols. For cloud point and pour point measurement, AIM 503 apparatus was used which met the requirements of IS:1448 (P:10)-1970 and IP:15/67. Viscosity measurement was done using capillary tube viscometer (Visco-88 Viscometer, Malvern Instrument) through falling ball method. The chemical properties of WCO such as the saponification, acid, and iodine values were measured by titration methods using standard protocols of ASTM D 5558, ASTM D 554, and ASTM D 584 respectively and ash content was measured by gravimetric method using ASTM D 482 standard protocol. The ester value was calculated from saponification value and acid value using Eq. (1). The percentage FFA was determined using Eq. (2).

$$\text{Saponification value} - \text{Acid value} = \text{Ester value} \quad (1)$$

$$\% \text{Free Fatty Acids} = \text{Acid value} \times 0.503 \quad (2)$$

Two-step acid-alkali-catalyzed microwave-assisted transesterification reaction

A two-step acid-alkali catalyzed microwave-assisted transesterification reaction was followed to chemically convert the FFA into biodiesel. The first step represented a pre-treatment step involving acid catalysts to reduce the FFA below 2%. The second step involved the conversion of esterified oil into biodiesel using alkali-catalyzed reaction. The pre-treatment step dictates the FFA constituents as an essential rate-limiting step that further governs the power requirement and time during the alkali-catalyzed transesterification (Banani et al. 2015). Hence, the acid-catalyzed esterification process was optimized to obtain the minimal %FFA.

Experimental procedure for acid-catalyzed esterification

The pre-treatment step involved the use of 1% sulfuric acid as catalyst with variation in parameters like oil:methanol volume ratio (expressed in decimal), time (s), and microwave oven power (W) affecting the percentage (%) of FFA. The reaction was carried out by varying the volume ratio (expressed as decimal) of oil:methanol from 0.1–1, subjecting them to microwave power of 100–400 W for a reaction time of 10–60 s. The reaction mixture was allowed to stand for 20 min in a separating funnel to obtain two distinct layers. The upper layer consisting of methanol and water was removed while the lower layer comprising oil was utilized for further studies. The acid values and thereby FFA of each of the reaction mixture were measured as mentioned in previous section. The effects of these parameters on minimizing the FFA content were studied using response surface methodology (RSM).

Statistical analysis of factors influencing FFA reduction

The effects of influencing factors like the volumetric ratio (expressed as decimal) of oil:methanol, microwave power, and time period were evaluated using Design Expert 11.0.11 (US Stat Ease Inc.). The experimental range of each of the independent variable affecting the response is given in Table 1. The variables were chosen based on the previous literature (Noshadi et al. 2012; Banani et al. 2015; Babel et al. 2018). The simultaneous interactive effects of each of the parameter require a second-order polynomial equation to be assessed. RSM using full-factorial central composite rotatable design (CCRD) with $\alpha = 1.682$ was used to study the change in response with the dependent variable and to identify the significant factors through regression and graphical analysis by fitting the data into the quadratic model. The experimental design matrix included 8 factorial run points, 6 axial run points, and 6 center replicates resulting in a total of 20 experimental runs.

Table 1 Table showing experimental range of parameters taken under consideration

Variables	Symbols	Levels				
		− 1.68197 (− α)	− 1	0	+ 1	+ 1.68197 (+ α)
Oil:methanol volume ratio	<i>A</i>	0.206807	0.1	0.55	1	1.30681
Reaction time (s)	<i>B</i>	7.04482	10	35	60	77.0448
Microwave power (W)	<i>C</i>	2.26892	100	250	400	502.269

The experimental matrix generated has been illustrated in Table 2 with all factors expressed at their actual levels.

A generalized quadratic model was used to study the significant parameters affecting the response. The generalized second-order polynomial equation for analyzing the model is given by Eq. (3) as follows:

$$y = \beta + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_i x_i^2 \quad (3)$$

where y represents the predicted response and x_i shows the level of each of the factors used in the study. Analysis of variance (ANOVA) was used to find the statistical significance of the model based on regression analysis. Fisher (F) test and probabilistic (P) value were used to evaluate the significance of each of the process parameters. 3D response surface graphs and contour plots were used to study and further confirm the interactive effect of the chosen parameters.

Alkali-catalyzed transesterification for conversion to biodiesel

The oil in the lower layer having the least FFA was selected and further subjected to alkali-catalyzed transesterification process using 2% sodium hydroxide as catalyst with methanol:oil molar ratio of 5:1. The mixture was stirred at 100 rpm at 65 °C for 30 min to ensure uniform mixing of reactants. It was then allowed to settle for 30 min until two distinct layers were formed. Biodiesel comprising of FAMES present in the top layer were separated. The biodiesel volumetric yield was obtained using Eq. (4). The physiochemical properties of the obtained biodiesel were determined and compared with the WCO and the existing biodiesel standards.

Volume Yield (%)

$$= [\text{Volume of Product/Volume of oil fed}] * 100 \quad (4)$$

Table 2 Design matrix generated by RSM and experimental values of response

Std. order	Run order	*A: oil:MeOH (unitless)	B: time (s)	C: power (W)	%FFA (Expt.)	%FFA (Pred.)
9	1	− 0.20	35	250	0.1	0.12
13	2	0.55	35	− 2.27	4.50	4.40
16	3	0.55	35	250	1.406	1.68
6	4	1	10	400	1.99	2.15
11	5	0.55	− 7.04	250	3.87	3.80
5	6	0.1	10	400	1.589	1.58
15	7	0.55	35	250	1.7	1.68
4	8	1	60	100	1.354	1.55
7	9	0.1	60	400	1.107	1.20
14	10	0.55	35	502.27	2.69	2.53
18	11	0.55	35	250	1.861	1.68
20	12	0.55	35	250	1.767	1.68
8	13	1	60	400	1.33	1.51
3	14	0.1	60	100	2.48	2.50
19	15	0.55	35	250	1.654	1.68
17	16	0.55	35	250	1.632	1.68
2	17	1	10	100	2.99	3.08
12	18	0.55	77.04	250	2.39	2.19
10	19	1.31	35	250	0.082	0.02
1	20	0.1	10	100	3.76	3.77

*Volumetric ratio of oil to methanol has been given as decimal

GC-MS analysis for determining the biodiesel properties

The biodiesel sample after the transesterification reaction was analyzed by a gas chromatography-mass spectrometry (GC-MS) system [Agilent 5977] equipped with mass selective detector (MSD). The column used was HP 5 ms ultra inert with the dimensions of $30\text{ m} \times 250\text{ }\mu\text{m (ID)} \times 0.25\text{ }\mu\text{m}$. A sample of approximately $1\text{ }\mu\text{L}$ was injected into the GC chamber and helium was used as gas carrier with the flow rate of 1 mL min^{-1} . Splitless mode of injection was performed. The oven temperature program parameters included a start at $80\text{ }^{\circ}\text{C}$ with $10\text{ }^{\circ}\text{C min}^{-1}$ intervals up to $180\text{ }^{\circ}\text{C}$ (1 min) and up to $255\text{ }^{\circ}\text{C}$ with $15\text{ }^{\circ}\text{C min}^{-1}$ intervals (2 min). The peaks of fatty acid methyl esters (FAMES) obtained at different retention time were analyzed.

Results and discussion

Properties of waste cooking oil

The physical and chemical properties of WCO were analyzed through various analytical methods to assess its suitability for direct utilization as engine fuel. The viscosity of WCO at $40\text{ }^{\circ}\text{C}$ was found to be $48.10\text{ mm}^2\text{ s}^{-1}$ and density at $25\text{ }^{\circ}\text{C}$ was 0.910 g cm^{-3} . Pour point and cloud point of WCO was found to be $-21\text{ }^{\circ}\text{C}$ and $-4\text{ }^{\circ}\text{C}$ respectively. The saponification, acid, and iodine value were found to be $193.90\text{ mg KOH g}^{-1}$, $16.24\text{ mg KOH g}^{-1}$, and $193.04\text{ mg KOH g}^{-1}$ respectively. The ash and FFA content were found to be 2.23% and 8.17% respectively. The properties of WCO when compared with that of the different biodiesel standards such as ASTM, European, and ISI showed significant differences, thus discouraging their long-term use as engine fuel. Noshadi et al. (2012), Talebian-Kiakalaieh et al. (2013), and Hamze et al. (2015) also reported similar results with different waste cooking oils. Banani et al. (2015) reported a viscosity of 23.12 (at $40\text{ }^{\circ}\text{C}$) and density of 0.91 g cc^{-1} (at $15\text{ }^{\circ}\text{C}$) with acid value of $32.83\text{ mg KOH g}^{-1}$ for waste frying oil of Gourma from Tunisian restaurants. WCO with acid value of $2.04\text{ mg KOH g}^{-1}$, saponification value of $204.77\text{ mg KOH g}^{-1}$, with density of 0.902 g cc^{-1} and (at $40\text{ }^{\circ}\text{C}$) and viscosity of $51.04\text{ mm}^2\text{ s}^{-1}$ was used in the study by Chuah et al. (2017). The variation in properties might be attributed to the difference in the source and disparities owing to the different operating conditions to which the oil has been exposed. The continuous polymerization and oxidation reactions due to repetitive frying of oil result in the changes in the physiochemical properties which are not considered within the permissible range for the direct use as an engine fuel (Raqeab and Bhargavi 2015). Thus, it is essential to chemically process the oil via transesterification.

Statistical interpretation of the effect of parameters on acid-catalyzed esterification

The experimental sequence was randomized to reduce the effect of uncontrolled factors. Regression analysis was used to correlate the effect of three independent variables on the response using the quadratic polynomial equation, which resulted in the determination coefficients as given by the final model equation in terms of actual factor (Eq. 5).

$$\begin{aligned} \text{FFA} = & +1.68 - 0.0952 A - 0.4794 B - 0.5574 C - 0.0668 AB \\ & + 0.3150 AC + 0.2217 BC - 0.6077 A^2 \\ & + 0.4669 B^2 + 0.6313 C^2 \end{aligned} \quad (5)$$

From Eq. (5), it could be observed that the microwave power (C) and reaction time (B) are the primary influencing factors affecting the response. Coefficients with positive sign indicate the synergistic effect and vice versa. It is well evident from the coefficient of variables (A , B , C) that the increase in either of these will result in a decrease in FFA until a threshold range after which it might not have a desired influence. Even the quadratic effects of all the three variables have a significant effect over the response. The interaction effect between oil:methanol volume ratio (A) and microwave power (C) was more significant followed by the interaction effects of reaction time (B) and microwave power (C), and oil:methanol volume ratio (A) and reaction time (B). The use of statistical analysis and factorial design provided the expression of the yield (%FFA) in terms of the influencing parameters as second-order quadratic model. Similar kind of model for esterification has also been studied and reported by Bouaid et al. (2012) for *Jatropha curcas* crude oil.

Statistical analysis was done using the ANOVA (Table 3) that provided the F and P values to evaluate the goodness of fit and to conclude how well the suggested model fits the experimental data. At 95% confidence interval, F value higher than that of the theoretical value of 3.97 showed adequacy of the model (Bouaid et al. 2012). The model F value of 68.35 and P value < 0.0001 indicated that the quadratic regression model was highly significant. The coefficients for the linear effect of reaction time (B) and microwave power (C) were also found to be significant with P value < 0.05 at 95% confidence level. The microwave power (C) and reaction time (B) had a significant effect on FFA as indicated by the higher F values of 107.92 and 79.84 respectively. The quadratic effect of volumetric ratio of oil to methanol (A^2) with F value of 135.36 was more than that of the microwave power (C^2) and reaction time (B^2) with F value of 146.12 and 79.93 respectively. The interaction effect was observed between the oil:methanol volume ratio (A) and the microwave power (C), with F value of 20.19 followed by that of the interaction between the reaction time

Table 3 ANOVA table for FFA (%) content obtained from transesterification of WCO

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> value	<i>P</i> value	
Model	24.18	9	2.69	68.35	< 0.0001	Significant
A: oil:MeOH vol. ratio	0.1239	1	0.12	3.15	0.1063	
B: time	3.14	1	3.14	79.84	< 0.0001	
C: power	4.24	1	4.24	107.92	< 0.0001	
AB	0.0356	1	0.04	0.91	0.3634	
AC	0.7938	1	0.79	20.19	0.0012	
BC	0.3934	1	0.39	10.01	0.0101	
A ²	5.32	1	5.32	135.36	< 0.0001	
B ²	3.14	1	3.14	79.93	< 0.0001	
C ²	5.74	1	5.74	146.12	< 0.0001	
Residual	0.3931	10	0.04			
Lack of fit	0.2750	5	0.06	2.33	0.1878	Not significant
Pure error	0.1182	5	0.02			
Total	24.58	19				

(B) and microwave power (C) with *F* value of 10.01. Relatively lower *F* values for interaction effects compared to the quadratic effects indicated that the later had a more prominent influence than the former. The non-significant value of lack of fit with *P* value of 0.1878 (> 0.05) implied the adequacy of the model for the selected combination of parameters.

The actual and predicted values of FFA that are shown in Fig. 1a revealed that the experimental values are closely related to the predicted values of response. The experimental regression coefficient (R^2) of 0.9840 invoked the model adequacy. Xiang et al. (2017) postulated that a higher value of R^2 explains the excellent correlation of the selected parameters over the response. However, the higher value of R^2 can be occasionally misleading as in case of inclusion of several extraneous terms in the model (Noshadi et al. 2012). The predicted R^2 of 0.9082, in reasonable agreement with that of the adjusted R^2 having a value of 0.9696, with a difference less than 0.2 indicated that the model did not have any insignificant terms. Relatively lower coefficient of variance of 9.85 (< 10%) indicated that the ratio of standard error of the estimate to the mean value of the observed response thus justified the accuracy and reproducibility of the experimentally collected data (Bouaid et al. 2012). Adequate signal was provided for the model as indicated by the acceptable precision value of 32.82. This value determines the signal to noise ratio, and a value greater than four is desirable to use the model for point prediction across the design space (Bouaid et al. 2012; Xiang et al. 2017).

The plot of residuals, normal probability plot as shown in Fig. 1b, indicated the accuracy of the range of independent variables taken into consideration. The best fit normal distribution plotted against the experimentally obtained studentized residuals exhibited a straight line elucidating the model adequacy (Fig. 1b). The plot of residual versus predicted (Fig. 1c)

showed that the model formulated appropriately describes the process. Similar interpretations were also made in the study by Bouaid et al. (2012) and Xiang et al. (2017) during the optimization study with crude oil.

The use of factorial design thus provides better insights about the multivariable interaction over the %FFA content. This would assist in controlling the factors in the desired range to achieve the requisite output without going for costly experimental analysis at real-time level. The study also provides the optimal conditions that could be used to reduce the FFA content below 1% in a short period, thus decreasing the time and power requirements. The optimization of the first step also reduces the requirement of huge amount of alkali during the second step of transesterification, thus avoiding the catalyst inactivation and undesired soap formation facilitating easier downstream processing.

Graphical analysis of the effect of different independent variables on FFA

Contour plots (Fig. 2a, c, e) and 3D plots (Fig. 2b, d, f) were drawn taking the mid ranges of variables as constants, e.g., 0.55 for the volumetric ratio of oil:methanol [expressed as decimal] (A), 35 s for reaction time (B), and 250 W for microwave power (C) respectively.

Interaction between oil:methanol ratio and reaction time The responses indicated by the interaction effect of volume ratio of oil:methanol (A) and reaction time (B) (Fig. 2a, b) showed that there are two optimum regions, one in the upper left side and the other in the upper right side of the plot with FFA lower than the 1%. The region on the top left side with lower oil:methanol volume ratio but higher reaction time might be discarded due to prolonged

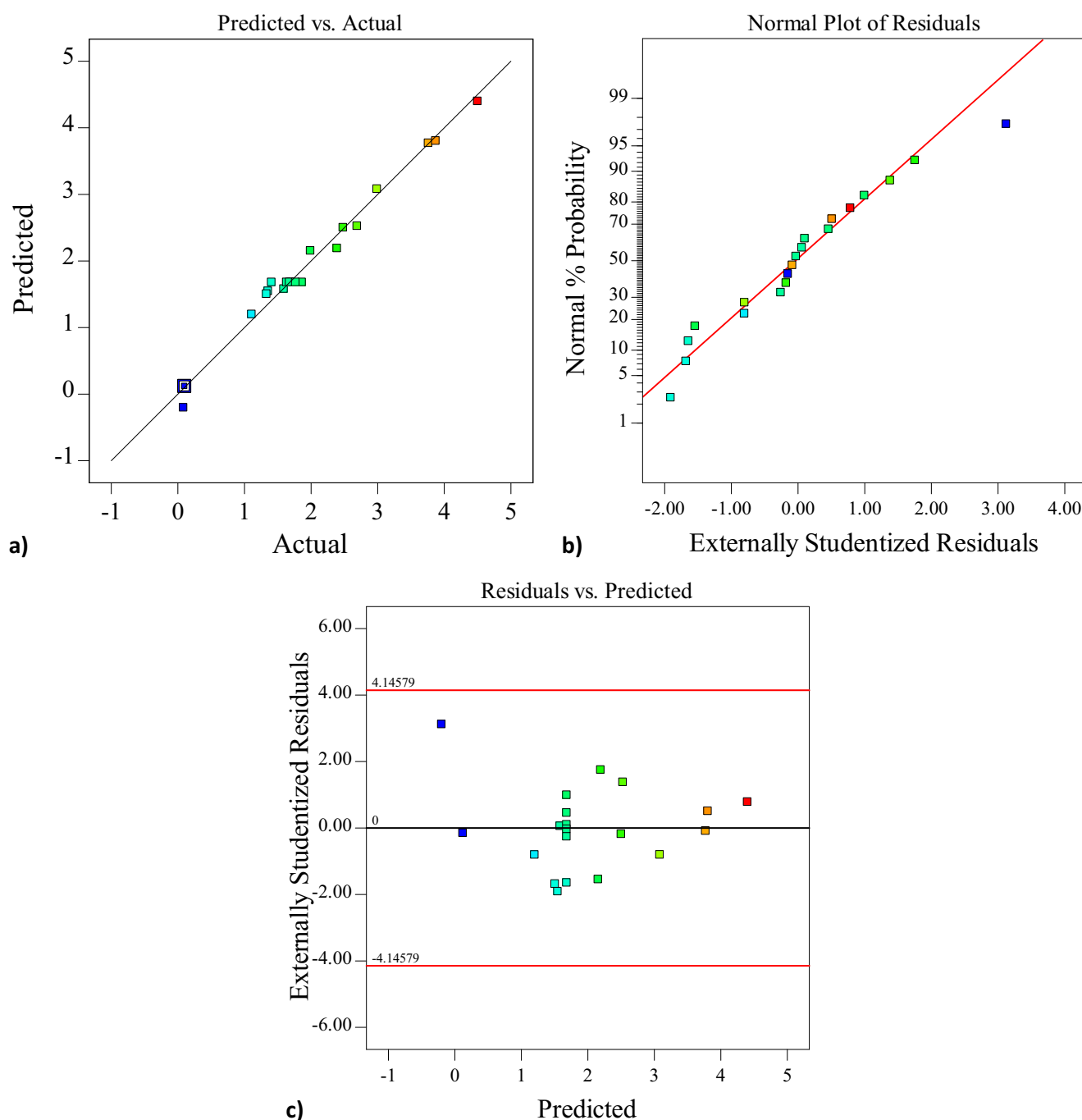


Fig. 1 **a** Predicted versus actual plot for FFA. **b** Normal plot of residuals for FFA. **c** Residuals versus predicted plot for FFA [scale:0.082 4.5]

reaction time as it could increase the energy consumption, thus declining the process efficiency. The region on the top right side of the graph involving higher oil:methanol volume ratio and relatively lower time consumption might be used to decline the FFA content. Antagonistic effects between the oil:methanol volume ratio and time consumption were also seen in the regression equation. Keeping

the acid catalyst at 1% and microwave radiation fixed at 250 W, increasing the oil:methanol volume ratio and the reaction time is expected to drive the process towards reversible reaction, thus declining the yield. Similar conclusions were also obtained during the microwave transesterification of WCO into biodiesel in the study by Hong et al. (2016) and Tangy et al. (2017).

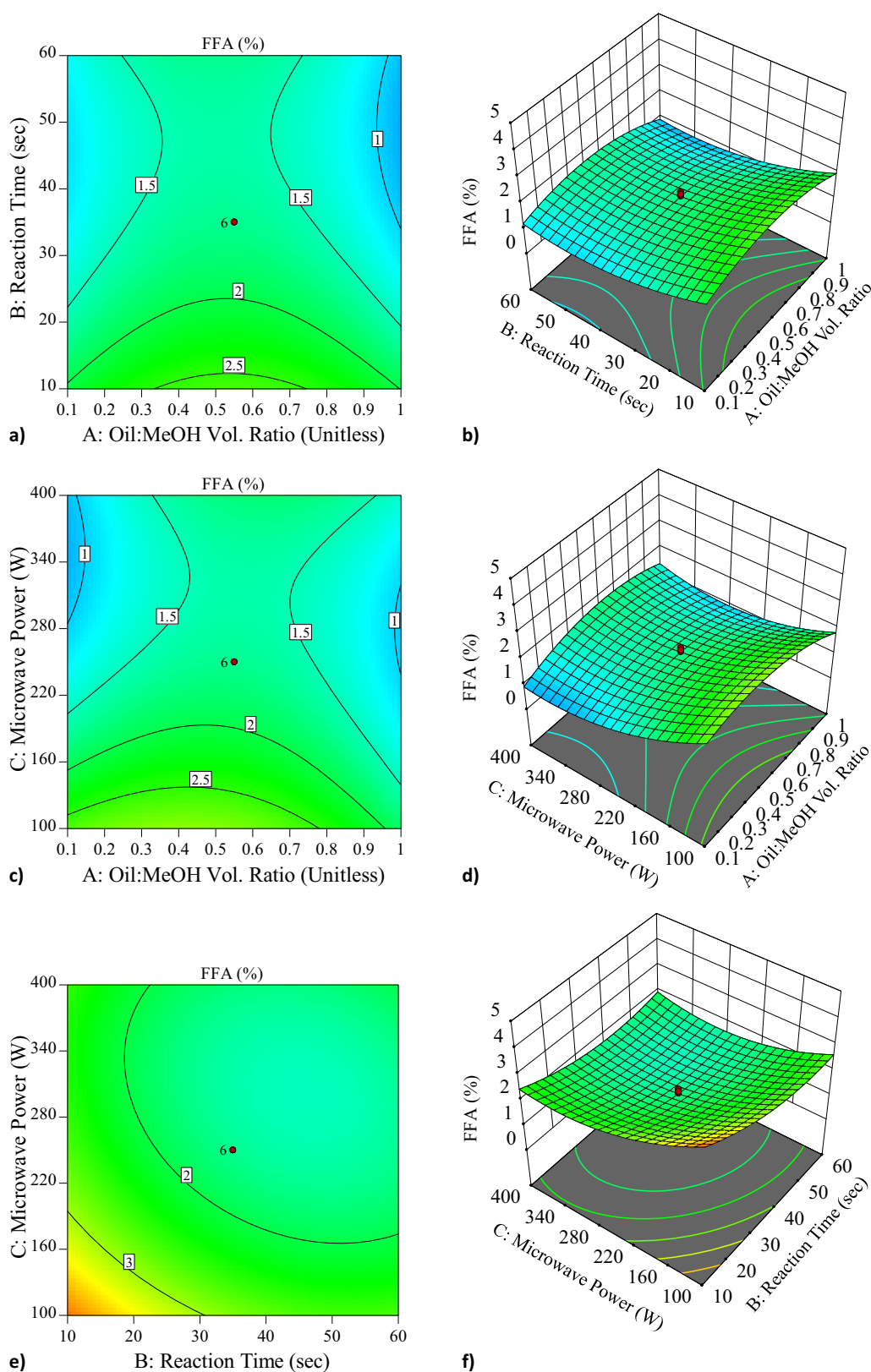


Fig. 2 a Contour plot of volume ratio of oil:methanol (decimal) and time over %FFA. b 3D plot for the oil:methanol volume ratio (decimal) and time over %FFA. c Contour plot of volume ratio of oil:methanol (decimal) and microwave power over %FFA. d 3D plots of volume ratio

of oil:methanol (decimal) and microwave power over %FFA. e Contour plot of microwave power and time over %FFA. f 3D plot of microwave power and time over %FFA [scale:0.082 4.5]

Table 4 Comparison between the experimental and predicted values of the validation studies

Factors	*Oil:MeOH ratio	Time (s)	Power (W)	Response (FFA in %)
Experimental	1.31	35	250	0.095
Predicted	1.31	35	250	0.082

*Oil:MeOH volumetric ratio expressed as decimal

Interaction between microwave power and oil:methanol ratio

Interactive effect of microwave power (*C*) and volume ratio of oil:methanol (*A*) is illustrated in Fig. 2c, d. Increase in both the parameters help in reducing the FFA until a threshold point beyond which it declines. The regression plots for both of these parameters also highlight the similar phenomenon. Esterification is an equilibrium reaction where the increase in oil:methanol volume ratio beyond the optimum might dilute the solution, thereby decreasing the yield by shifting the reaction in the reversible direction. Also intensive microwave power might evaporate the alcohol resulting in inefficient conversion (Gude and Grant 2013). As the microwave power increases, the temperature also rises increasing the rate of reaction; however, the start time and the rate of reversible also consequently increase, thereby declining the yield (Hong et al. 2016). Adequate methanol:oil volume ratio will absorb microwave irradiation resulting in decrease in activation energy because of the increment in dipolar polarization (Tangy et al. 2017). To the best of author's knowledge, none of the previous studies have statistically optimized the first step of esterification of WCO with the use of microwave irradiation. However, studies by Hong et al. (2016) and Tangy et al. (2017) with WCO also reported the presence of optimum amount of microwave irradiation and oil:methanol ratio could improve the biodiesel yield in case of microwave-assisted transesterification.

Interaction between microwave power and reaction time

The plots between the interaction of microwave power (*C*) and reaction time (*B*) (Fig. 2e, f) keeping the volume ratio of oil:methanol [expressed as decimal] at 0.55, the increase in reaction time and power is expected to decrease the FFA content. This is evident from the negative coefficients obtained for both the factors in the regression equation. The positive coefficient of the interactive term showed that increasing both the independent variables, the dependent variables would increase. Adequate reaction time provides sufficient interaction between the microwave irradiation and the reactants. With homogenous catalysts, adequate time period of heating promotes interaction between the

glyceride moieties of oil and methanol. Higher intensity of microwave irradiation applied for longer period of time often results in degradation of the final product and faster progress of reverse reaction. Hong et al. (2016) reported that at lower reaction time, microwave irradiation might not be effective in driving the reaction towards completion. The study by Tangy et al. (2017) reported that the application of microwave irradiation beyond the optimal time showed no appreciable improvements in yields. Thus, the factorial design predicted an optimal region/range for combination of the microwave irradiation and the exposure time to obtain the desired yields.

Optimization and point prediction

The optimum conditions for reducing the FFA using three independent variables such as the volume ratio of oil:methanol, reaction time, and microwave power were obtained using the numerical optimization tool provided in Design Expert 11.0.11. The optimization tool searches a combination of factors/variables that simultaneously fulfills the requirement of desired response. The process variable in combination creates an experimental design space with defined goals for creating optimum working conditions (Bouaid et al. 2012). The goal in the current study was set to minimize the FFA content (%) keeping all other variables in range. The optimization tool predicted a set of 38 possible combinations of factors at which the responses are due within the required limits of the process variables. The predicted values are in accordance with the experimental values at 95% confidence interval, with a standard deviation of 0.009 and standard error of 0.006. From Table 4, it is quite evident that the experimental values and the predicted values are nearly same, with little or no significant difference. Hence, the combination could be successfully implemented to achieve desirable results.

Microwave power provides strong heating and reaction conditions to achieve the desired results with shorter reaction time. Thus, under optimal conditions, with methanol:oil molar ratio of 19.57:1 (volume ratio of oil:methanol is 1.31 [expressed as decimal]), microwave irradiation of 250 W, and reaction time of 35 s, the FFA content was reduced from 8.17 to 0.082%. Similar to the above study, Suppalakpanya et al. (2011) reported a decline in FFA from 7.5 to 2% using 4% sulfuric acid at alcohol:oil molar ratio of 24:1 with

Table 5 Comparison between the properties of WCO and the transesterified biodiesel with different standards

Parameters	WCO ^a	Biodiesel ^a	WCO ^b	Biodiesel ^b	WCO ^c	Biodiesel ^c	ASTM standard	European standard	ISI standard
Viscosity (mm ² /s)	48.10	4.68	49.93	4.53	37.65	3.8	1.9–6.0	3.5–5.0	2.5–6.0
Density (g/cc)	0.910	0.892	0.926	0.883	0.96	0.880	0.86–0.90	0.86–0.90	–
Saponification value (mg KOH/g)	193.9	110.6	206	205	214	–	–	–	–
Acid value (mg KOH/g)	16.24	0.04	7.45	0.272	0.65	0.1	0.50	0.50	–
Iodine value (mg KOH/g)	193.04	112.02	78	81	–	–	–	120	–
Ash content (%)	2.236	1.08	–	–	–	–	–	–	0.02
FFA content (%)	8.1687	0.02	–	–	–	–	1–2	–	–

^a Current study (two-step acid-alkali-catalyzed microwave-based transesterification of the WCO)

^b Noshadi et al. (2012) (transesterification of the WCO with heteropoly acid)

^c Hamze et al. (2015) (transesterification of WCO with three operating parameters: methanol:oil ratio 3:1 to 9:1; KOH catalyst concentration 0.5–1.5 wt%; and reaction temperature of 25–65 °C)

70 W irradiation. Jaliliannosrati et al. (2013) also projected that the FFA content can be decreased from 14% to less than 1% using 110 W microwave power with alcohol to oil molar ratio of 54:1 in 35 min. The variation in the range of optimal variables might be due to the difference in the origin and source of WCO. Nevertheless, the optimal combination could be used to reduce the FFA content as per the permissible limit with less power consumption and in shorter reaction time. This step further reduces the need for using large amount of alkaline catalyst thus preventing unwanted soap formation, thereby increasing biodiesel yield.

Fuel properties of biodiesel obtained via alkali-catalyzed transesterification

The properties of the biodiesel in order to be commercialized must meet the ASTM, European, and ISI standards. The properties of biodiesel obtained after the two-step acid-alkali-catalyzed transesterification were compared to that of WCO, with previous literature and the biodiesel standards (Table 5) to establish its technical and commercial feasibility. Chemical properties such as the saponification value, acid value, and FFA decreased significantly following the transesterification process. Similar kind of declining trend was also seen in case

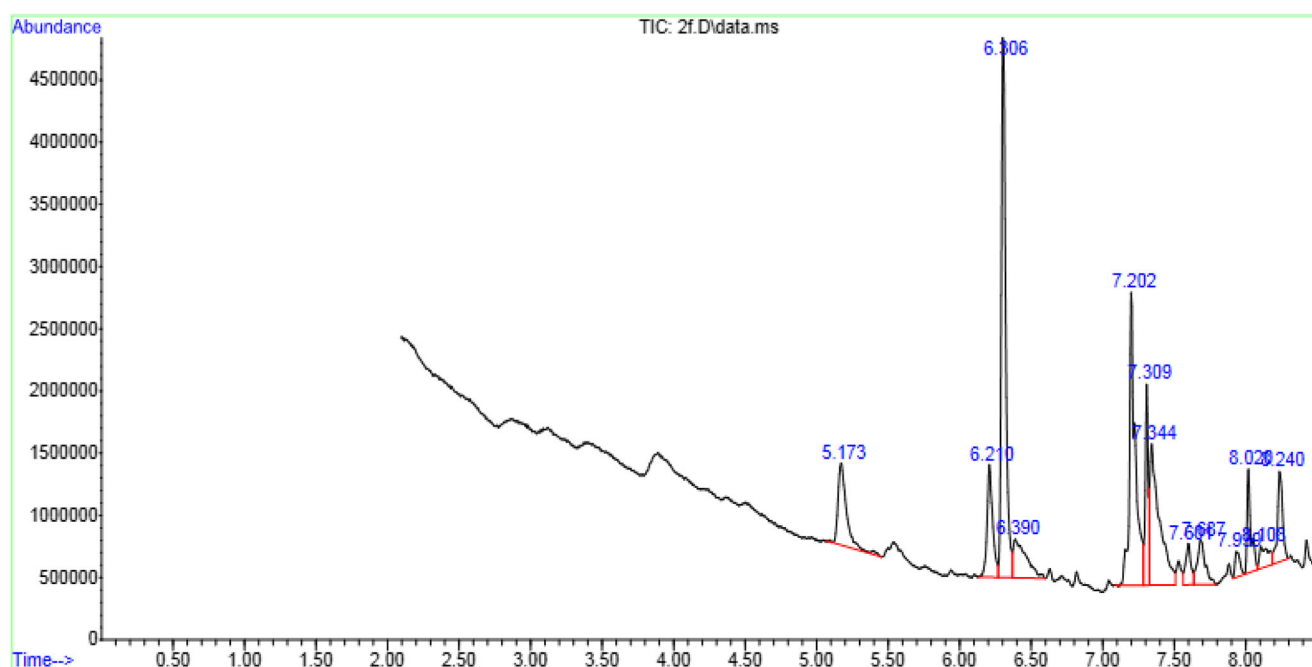


Fig. 3 GC-MS spectrum of the biodiesel obtained through two-step acid-alkali-catalyzed microwave-assisted transesterification of WCO

Table 6 Fatty acid methyl esters obtained via GC-MS analysis

Compound name	% Area	Retention time (min)
Tetradecanoic acid methyl ester (C14:0)	9.41	5.153
Pentadecanoic acid methyl ester (C15:0)	0.71	5.532
9-Hexadecanoic acid methyl ester (C16:1)	5.08	6.212
Hexadecanoic acid methyl ester (C16:0)	32.94	6.300
11-Octadecanoic acid methyl ester (C18:1)	13.68	7.229
9-Octadecanoic acid methyl ester (C18:0)	6.13	7.312

Other compounds constitute 28.8% of the total

of viscosity. The density of the transesterified oil was found to be 0.89 g cm^{-3} . The physical and chemical properties were found to be in accordance with the different biodiesel standards as illustrated in Table 5. This establishes the suitability of the transesterified biodiesel for engine application compared to the direct use of WCO. Properties for transesterified biodiesel reported in the studies by different researchers like Noshadi et al. (2012), Talebian-Kiakalaieh et al. (2013), and Hamze et al. (2015) were also compared in Table 5. Sodhi et al. (2017) reported an acid value of $0.22 \text{ mg KOH g}^{-1}$, viscosity of $3.2 \text{ mm}^2 \text{ s}^{-1}$, and pour point of -3°C for biodiesel obtained from WCO transesterified with 1% potassium hydroxide with 5:1 M ratio of methanol to oil at 60°C . It should be noted that inclusion of microwave heating produced 94.6% volumetric biodiesel yield at 65°C with reaction time of 30 min, which is comparably lower than the energy requirements of conventional heating. Biodiesel yield of 97% was obtained by Elkady et al. (2015) using transesterification supplemented with micromixer.

The gas chromatogram (GC) for the transesterified cooking oil is shown in Fig. 3. The percentage of various fatty acid methyl esters (FAMES) at different retention time are shown in Table 6. The biodiesel obtained showed the presence of methyl myristate (9.41%), methyl palmitoleate (5.08%), methyl palmitate (32.94%), methyl cis-vaccenate (13.68), and methyl stearate (6.13%). A total of 71.12% FAMES were obtained mainly dominated by methyl palmitate, with 28.88% of other compounds. Similar FAME peaks were also detected in the GC chromatogram for the transesterified WCO by Sodhi et al. (2017). Peaks against C16:1, C18:2, C18:1, and C18:0 fatty acid methyl esters were also reported in the biodiesel from transesterified WVO using a micromixer by Elkady et al. (2015). The presence of single FAME in major quantity ensures the appropriateness of the transesterified oil for engine (Knothe 2012). The quality of the biodiesel was good since it contained appropriate ratios of the esters of C16:1, C18:1, and C14:0 as reported by Schenk et al. (2008). The biodiesel must possess an optimal amount of saturated and unsaturated FAMES to be recognized as suitable engine fuel (Islam et al. 2013). The presence of significant amount of saturated fatty

acids indicates appropriate fuel quality for engine. Further, appreciable percentage of unsaturated fatty acids also indicated desirable density and viscosity of the oil to be considered for engine applications.

Conclusion

A two-step acid-alkali-catalyzed microwave transesterification of waste cooking oil (WCO) was done to obtain a low-cost biodiesel from the waste resources. Optimization of process variables during the first step of acid-catalyzed esterification was carried out to reduce the FFA content, thereby preventing the deactivation of catalyst, soap formation that adds up to the downstream processing costs. Under the optimal combination of methanol:oil molar ratio of 19.57:1 (volume ratio of oil:methanol being 1.31 [expressed as decimal]), microwave power of 250 W, and reaction time of 35 s, lowest FFA of 0.082% was obtained. All the factors were found to influence the FFA content. Interactive effect of volume ratio of oil:methanol and microwave power and that of the reaction time and microwave power were found to significantly influence the FFA conversion. Alkali-catalyzed transesterification of the esterified oil with methanol:oil ratio of 5:1 and 2% NaOH at 65°C produced a volumetric biodiesel yield of 94.6% with reaction time of 30 min. Biodiesel produced had significant amount of FAMES with appropriate proportions of C16:1, C18:1, and C14:0 indicating its suitability as engine fuel. The physicochemical properties of the biodiesel were also comparable to the different standards. The present study signified that the WCO could be used as an alternative feedstock for biodiesel production with the two-step acid-alkali-based microwave-assisted transesterification.

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