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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Optimisation and Kinetic Studies of Acid Esterification of High Free Fatty Acid Rubber Seed Oil

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Abstract Pretreatment of the high free fatty acid (FFA) rubber seed oil from Malaysia (RSOM) and Vietnam (RSOV) via esterification reaction has been investigated. Response surface methodology analysis using central composite design was used to optimise important parameters, including reaction temperature, catalyst loading, methanol-to-oil molar ratio and reaction time on FFA reduction. Optimal esterification conversion was achieved at 50 °C, 1.38 wt%, 15.98:1 molar ratio and 2 h for RSOM with 99.3 % FFA reduction, whereas 65 °C, 10.74 wt%, 10:1 molar ratio and 1 h for RSOV with 98.6 % FFA reduction. Catalyst loading had been found to have the most effect on the FFA reduction followed by methanol-to-oil molar ratio while increasing temperature and reaction time had nominal effect. The frequency factor and activation energy of RSOV were about 1.8- and 1.2-fold higher than RSOM.

Keywords Rubber seed oil · Esterification · Free fatty acid · Response surface methodology · Kinetics

1 Introduction

Energy demand is accelerated around the world along with the growth of population and industrialisation. The fluctuating prices and uncertain supply of fuel due to political disturbances have inspired researchers to look for renewable and sustainable fuel. One possible solution to this problem is the prolonged utilisation of biodiesel as an alternative fuel. Biodiesel is more environmentally friendly compared to diesel fuel-based petroleum as it emits lower greenhouse gas emissions, i.e. sulphur oxides (SOx) and carbon monoxide (CO) into the atmosphere [1]. It can be directly utilised without any engine modifications due to its viscosity and heating value, which are close to diesel fuel [2].

Malaysia has sixteen registered biodiesel companies currently operating in Malaysia, and eight more companies have been approved to increase biodiesel production from 2.12 up to 3 Mt/y. However, this production value is still lower than the government's projected 10 Mt/y [3]. Highest demand of biodiesel comes from Europe at around 12 Mt/y. This is followed by the USA which is around half of that. Biodiesel can be produced from various sources, e.g. edible oil, non-edible oil [4], animal fat and algae [5]. About 95 % of world biodiesel production is derived from edible oil, such as palm, rapeseed and canola oils [6]. Malaysia is the second largest producer of palm oil in the world [7]. Consumption of this edible oil in biodiesel production has caused the edible oil and biodiesel prices to increase to 1.5-fold to twofold higher than diesel fuel [8]. In addition, an extensive consumption of edible oils for biodiesel production could result in food crisis, which creates disparity between food and fuel market

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[9]. In order to prevent food controversy, the local non-edible plant oils, e.g. nyamplung, jatropha, castor, rubber, kapok and karanja, have drawn the attention of the Malaysia government and researchers to consider them as biodiesel feedstock, which can be supplied at a viable quantity based on the large scale of cropped lands [10].

Rubber tree (*Hevea brasiliensis*), belonging to the family of euphorbiaceous, provides non-edible seed with 40–50 wt% of oil yield [11]. Malaysia's tropical weather is favourable for rubber tree plantation, and currently, it is one of the rubber producers in worldwide [9]. Association of Natural Rubber estimated that about 1.2 million hectares of unutilised rubber seed is cultivated in Malaysia. Rubber seed oil (RSO) can successfully contribute as a potential non-edible feedstock for biodiesel production. Generally, biodiesel is produced by transesterification reaction in the presence of alkali catalysts if the FFA content in feedstock oil is <2 wt% [12]. Since that alkali catalysed does not tolerate high FFA concentration in the feedstock, the acid-catalysed reaction is proposed to solve the drawbacks. Single-step process of homogeneous acid-catalysed transesterification is better than alkali-catalysed transesterification [13], which required an extra step to covert FFA to product. It could also reduce the consumption of energy, chemical and processing time. However, acid-catalysed transesterification is not commonly adopted worldwide at industrial scale for biodiesel production. It could be due to low reaction rate, difficulty in separation of catalyst from product, high reaction temperature, alcohol and acid quantities, which could contribute to corrosion and serious environmental problems.

Higher FFA content in RSO is a major hindrance of direct conversion of triglycerides to alkyl esters via transesterification reaction due to FFA can react with alkali catalyst and results in saponification. FFA content in RSO could be reduced with several pretreatment techniques, e.g. distillation, acid esterification with methanol and sulphuric acid, esterification with ion exchange resins, neutralisation with alkali followed by soap separation in a decanter and extraction with polar liquids along with acid esterification [14]. Among them, acid esterification is the most efficient method in reducing the FFA content in RSO. Esterification is a reversible reaction adopted for FFA reduction in the presence of acid catalyst (e.g. sulphuric acid) and alcohol. It occurs in a relatively straightforward way, in which one mole of free fatty acid reacts with one mole of alcohol to produce one mole of biodiesel and one mole of water [15].

The current study introduces the acid esterification process for pretreatment of high FFA content in RSOM and RSOV, which contain 23.2 and 42.5 %. The paper focuses on the optimisation of esterification conversion from RSOM and RSOV via acid esterification, based on response surface methodology (RSM). RSM was used to model the multiple parameter process and to design the optimum operating conditions for the esterification process. The relationship between reaction variables, e.g. methanol-to-oil molar ratio, catalyst amount, reaction time and temperature, was investigated. Besides, kinetics of acid esterification process for RSOM and RSOV were also investigated.

2 Materials and Methods

RSOM was purchased from the Benua Sains Sdn. Bhd., Malaysia, whereas the RSOV was provided by Kinetics Chemical (M) Sdn. Bhd., Malaysia. The chemicals used for this work were anhydrous methanol, sulphuric acid, anhydrous sodium sulphate, toluene, 2-propanol, phenolphthalein, acetic acid (glacial), cyclo hexane, Wijs solution, potassium iodide, sodium thiosulphate pentahydrate, starch, chloroform, ethanol, hydrochloric acid and acetone. A standard mixture of 37 fatty acid methyl ester is purchased from Sigma- Aldrich, Malaysia. All other chemicals were purchased from Merck Germany and are of analytical grade.

The characteristics of RSOM and RSOV were analysed according to the ASTM, EN, DIN and AOCS standards [16]. The FFA, iodine and saponification values were determined by using a titration method, which included AOCS-Cd 3d-63, AOCS-Cd 1d-92 and AOCS-Cd 3b-76. The heating value of the oil was determined using a C5000 IKA (Werke, Germany), following ASTM D 4568, whereas the kinematic viscosity was measured using Lovis 2000 M of Anton Paar following DIN 12058. The C30 Coulometric KF Titrino (Mettler Toledo) was used to determine the moisture content of the oil and biodiesel following ASTM D 2709. The fatty acid compositions of the oils were determined by converting the fatty acid of the glycerides into methyl esters of the corresponding fatty acid by using GC–FID [17]. Methyl ester

Table 1 Experimental design variables with ranges for rubber seed oil

Process parameters	Rubber seed oil Malaysia		Rubber seed oil Vietnam	
	Low	High	Low	High
Methanol-to-oil molar ratio	10	20	10	20
Catalyst loading (wt%)	0.5	1.5	6	12
Reaction temperature (°C)	45	65	45	65
Reaction time (h)	1	3	1	3

Table 2 Physicochemical properties of the rubber seed oils

Properties	Rubber seed oil Malaysia	Rubber seed oil Vietnam	Rubber Seed Oil Ahmad et al. [15]
Colour	Yellowish brown	Dark brown	Brown
FFA (wt%)	23.2	42.5	45
Moisture content (wt%)	0.90	1.5	0.93–0.98
Calorific value (MJ/kg)	37.9	37.9	37.5
Iodine value, ($g\,I_2/100\,g$)	134.5	131.8	132.6
Saponification value (mg KOH/g)	194.7	201.5	192
Kinematic viscosity at 40 °C (mm^2/s)	41	36	33
Fatty acid composition (wt%)			
Palmitic acid	9.6	8.9	10.3
Stearic acid	8.8	7.5	8.8
Oleic acid	25.3	27.0	24.7
Linoleic acid	41.0	41.4	39.8
Linolenic acid	15.3	15.2	16.4

peaks were identified by comparison with the retention time of the reference external standard. All of the experiments were conducted in three replicates, the reported values were the averages of the individual runs, and the inaccuracy percentages were <2 % of the average value.

2.1 Fatty Acid Composition Analysis

Fatty acid composition of the feedstock oil was calculated using a gas chromatograph (GC) equipped with FID (flame ionisation detector), following EN 14103. The GC system was equipped with a variable split flow injector, a temperature programmable oven, a flame ionisation detector and capillary column coated with methylpolysiloxane (DB-23) (60 m × 0.25 mm × 0.25 µm). Temperature program starts at 100 °C holding for 2 min, heating at 10 °C/min until 200 °C, heating at 5 °C/min until 240 °C and holding for 7 min. Helium was used as a carrier gas at a flow rate of 4 mL/min. The hydrogen and air were used at flow rate of 50 and 400 mL/min for flame [18].

2.2 Acid Esterification Experimental Setup and Procedure

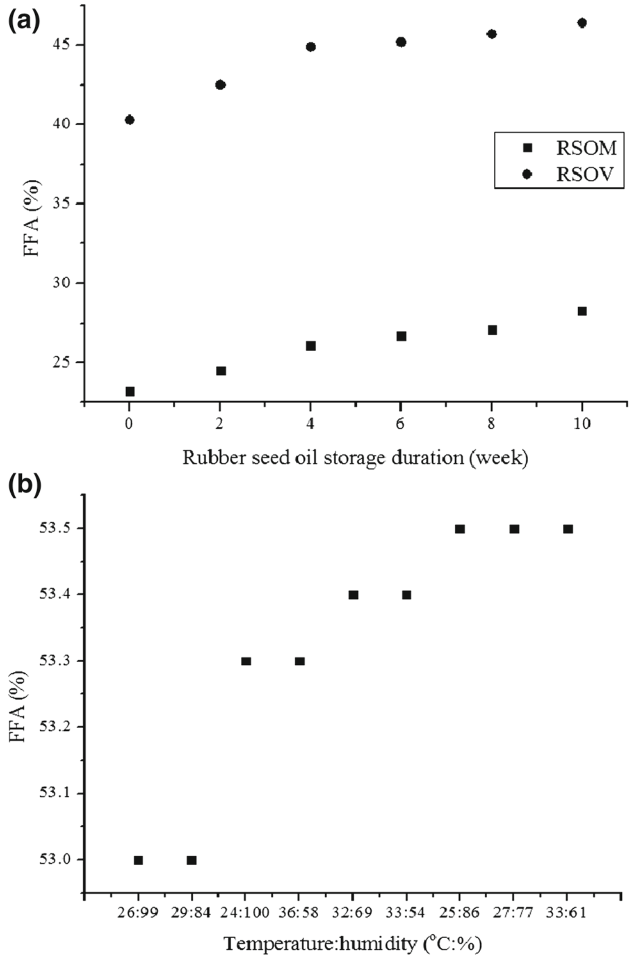


Fig. 1 **a** Storage duration effect on free fatty acid. **b** Comparative effect of temperature and humidity on free fatty acid in rubber seed oil Vietnam

The system used for acid esterification reaction consisted of 250 mL of two-necked glass reactor equipped with a condenser, thermometer and water bath. The assembled equipment was placed on a heating plate with magnetic stirrer. The RSO, methanol and potassium hydroxide were used in amounts established for each experiment. For each run, 100 g of RSO was placed in the reactor and preheated to reach the desired temperature. The mixture of methanol and catalyst (sulphuric acid) was added to the oil. The mixture in reactor was stirred at a constant speed of 400 rpm for all test runs. After a specific reaction time, the heating and stirring was stopped. The mixture was poured into the separating funnel and immersed in ice- cold water to arrest the further progress of the reaction. The mixture was poured into the separating funnel and hung out for sufficiently long time (2 h) to separate due to gravity difference. The by-product and catalyst were discharged, and the products were washed with deionised warm water at 40 °C to remove impurities in the product. The remaining methanol and water in the product were evaporated using a rotary evaporator under vacuum. A 10 g of anhydrous sodium sulphate was added to product sample to ensure complete removal of water and filtered by using filter paper (541 Whatman). FFA content of the product was analysed by following AOCS-Cd 3d-63 method. All the experiments were performed in three replicates to ensure data reproducibility.

2.3 Experimental Design

Parametric studies on the optimised orifice plate were done by employing central composite design (CCD) using Design Expert 8.0 software. Further optimisation of operating parameters was analysed by numerical optimisation technique in RSM. The experimental arrays were designed by CCD. The reaction variables and its respective ranges are shown in Table 1. The independent input process variables were primarily classified in terms of low and high levels. The factors were distributed into versatile points called axial, centre and factorial points. The axial points were coded by CCD with −2 and +2. Low- and high-level factor points were designated as −1 and +1, whereas centre points were coded with 0 and repeated experimental arrays designed on centre points.

2.4 Kinetics of RSO Esterification Process

The kinetic model for homogenous acid esterification reaction was developed using the data obtained from the optimised reaction conditions by RSM. Under optimised conditions, FFA content was frequently measured at specific intervals of time. The calculated FFA with respect to time was transformed into derivative using finite difference method. The stoichiometry of homogenous acid esterification reaction with excess of methanol is shown in Eq. (1).

$$\text{Free fatty acid} + \text{Methanol} \longleftrightarrow \text{Methyl ester} + \text{Water} \tag{1}$$

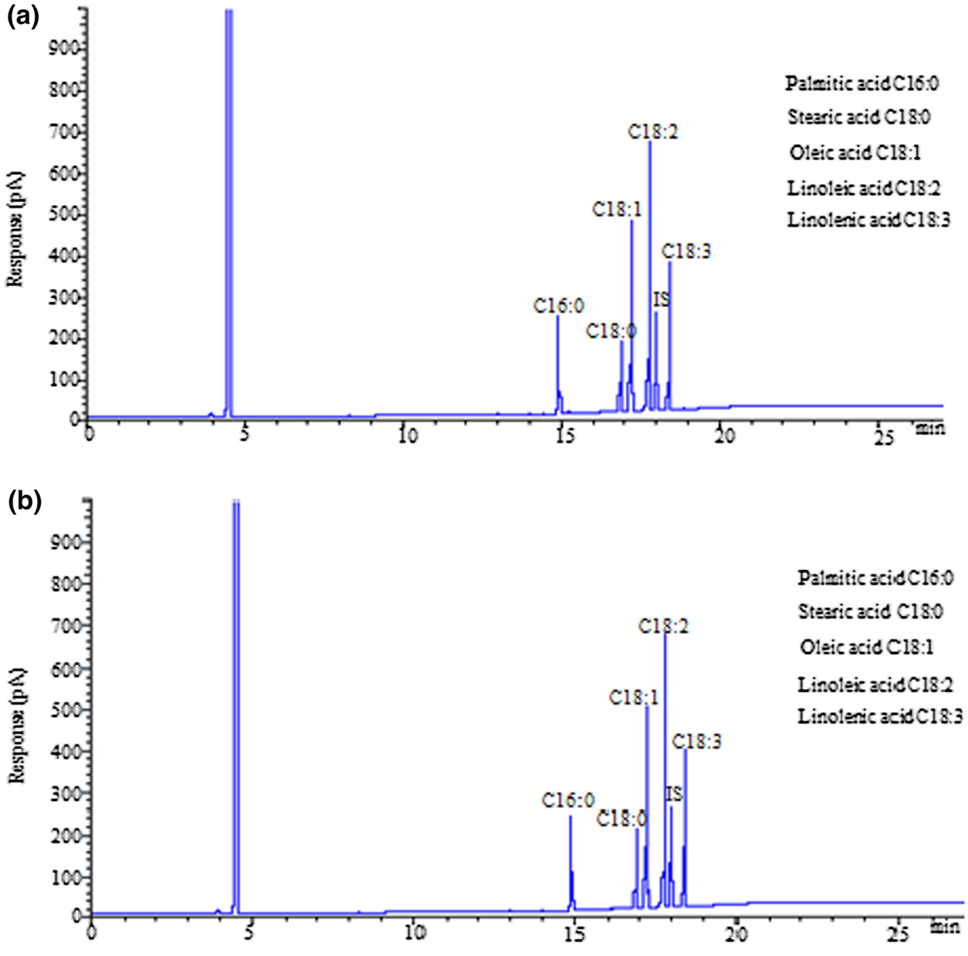


Fig. 2 The chromatogram of fatty acid composition for **a** Rubber seed oil Malaysia and **b** Rubber seed oil Vietnam

The reaction rate with respect to time (r) was determined using Eq. (2).

$$r = \frac{dC_{\mathrm{FFA}}}{dt} = k(T)\, f(C_{\mathrm{FFA}})^{\alpha} \tag{2}$$

where k is the reaction rate constant, which is dependent on temperature (T) and can be further manipulated by Arrhenius Eq. (3).

$$k(T) = k = \mathrm{A}e^{\frac{-E_{\mathrm{A}}}{RT}} \tag{3}$$

where activation energy (E_{A}), frequency factor (A) and universal molar gas constant (R). Concentration with respect to time at different temperatures was transformed to respective derivatives term by finite difference method to calculate $\frac{dC_{\mathrm{FFA}}}{d}t$ at each time interval. Taking the natural log of Eq. (2) gives Eq. (4).

$$\ln\left(\frac{dC_{\mathrm{FFA}}}{dt}\right) = \ln k + \alpha \ln C_{\mathrm{FFA}} \tag{4}$$

where α is the order of the reaction and it can be determined by taking the slope of $\ln C_{\mathrm{FFA}}$ versus $\ln\left(\frac{dC_{\mathrm{FFA}}}{d}t\right)$ plots on different reaction temperatures. Reaction rate constants at each reaction temperature can be determined by Eq. (4). Activation energy and frequency factor for acid esterification reaction were calculated by using Eq. (3) and by taking natural log of Eq. (3).

$$\ln k = \ln A + \frac{-E_{\mathrm{A}}}{RT} \tag{5}$$

Activation energy and frequency factor was determined by plotting $\ln k$ against reciprocal of $\frac{1}{T}$. The activation energy of the process is slope of the plot $(-\frac{E_{\mathrm{A}}}{R})$, and frequency factor was determined by plot intercept on $\ln A$. Experimental concentration data were fitted with predicted concentrations in order to compare the deviation of the results. The error between experimental and predicted concentrations was minimised by least square method represented by Eq. (6).

$$R_{\mathrm{i}} = \sum \left\{ \frac{y_{\mathrm{i}}^{\mathrm{exp}} - y_{\mathrm{i}}^{\mathrm{m}}}{y_{\mathrm{i}}^{\mathrm{exp}}} \right\}^{2} \tag{6}$$

where $y_{\mathrm{i}}^{\mathrm{exp}}$ is experimental concentration terms and $y_{\mathrm{i}}^{\mathrm{m}} =$ model concentration terms

3 Results and Discussion

Physicochemical of RSOM and RSOV was compared to the literature values as shown in Table 2. The results revealed that the FFA content in RSOV was 1.8-fold higher than RSOM. It could be due to longer transportation and storage duration, which resulted in an increase in FFA content. Similar observations have been reported by Zhu et al. [19]. The verification of these results is shown in Fig. 1a, which indicates FFA content in both of RSOV and RSOM increased with an increase in storage duration. The high amounts of unsaturated fatty acids present in the RSO are accountable for the increase in FFA value with respect to storage time. Figure 1b shows the combined effect of atmospheric temperature and humidity on FFA content. The results revealed that the FFA is considerably affected by an increase in humidity and fluctuation of temperature due to exposure to open atmosphere and light. The kinematic viscosity of oil decreases with an increase in temperature, and low viscosity induces the oil to flow easily. The kinematic viscosity of RSOM—41 mm^2/s was slightly higher than RSOV—36 mm^2/s at 40 °C. Saponification is a process by which the fatty acids in the glycerides of oil are hydrolysed by an alkali [20]. The saponification value is the amount of alkali (mg) required to saponify one gram of oil. This value is useful for a comparative study of fatty acid chain

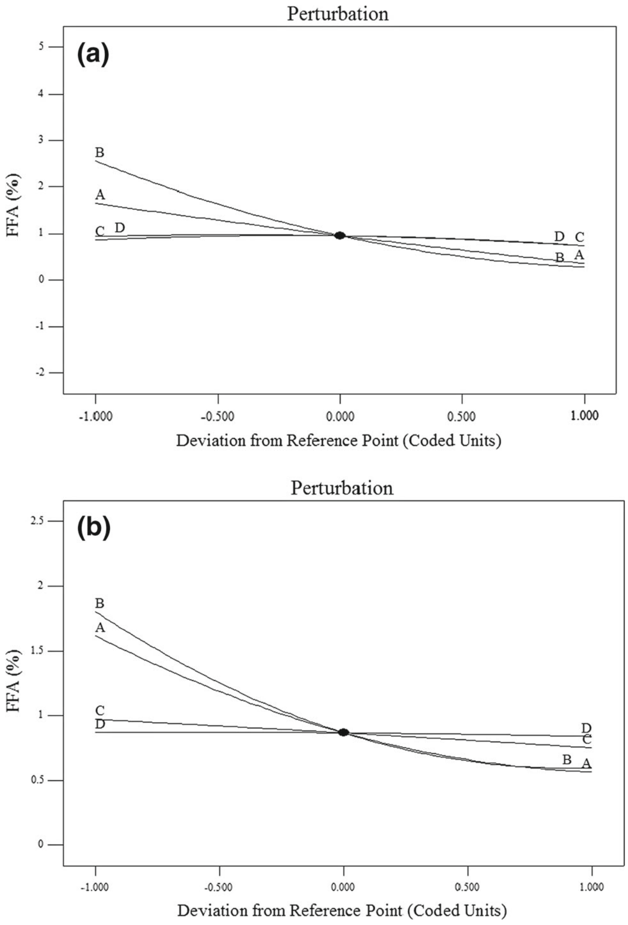


Fig. 3 Perturbation plot for **a** Rubber seed oil Malaysia and **b** Rubber seed oil Vietnam

lengths (saturated) in oil [21]. The saponification value of RSOV was 201.5 mg KOH/g, which was slightly higher than RSOM which was 194.7 mg KOH/g. The results revealed that the higher the saturated fatty acid, the higher the chain length and the higher the saponification. The moisture content and iodine value of RSOM were 0.9 wt% and 134.5 $g\,I_2/100\,g$, whereas RSOV were 1.5 wt% and 131.8 $g\,I_2/100\,g$. Higher heating value of 37.9 MJ/kg was obtained for both RSOM and RSOV using IKA C5000 bomb calorimeter. The fatty acid composition of RSOM and RSOV is presented in Table 2. The chromatogram of the RSOM and RSOV's fatty acids is illustrated in Figure 2. Results revealed that unsaturated fatty acids of oleic and linoleic acids were the most abundant fatty acids in RSO. With increased storage duration, a higher amount of unsaturated fatty acid is oxidised and contributed to an increase in FFA value [22].

The details of experimental runs associated with the independent process variables, designed by the CCD, are shown in Supplementary 1 and Supplementary 2 along with experimentally determined output responses.

3.1 Anova Analysis

ANOVA (analysis of variance) was employed to statistically analyse the output response (FFA content). The ANOVA results for RSOM and RSOV are presented in Supplementary 3 and Supplementary 4. The model *p* value determined the percentage of error in the model along with individual and combined effects of the input variables. The obtained model *p* values were <0.05, which implied that the model was significant for both RSOM and RSOV designed variables with respect to the response. The F-value describes the reliability of the fitted model with the output response. The highest F-value for the methanol-to-oil ratio and catalyst loading indicate a higher influence of these two variables on the output response. Reaction temperature and time were less significant input variables as compared to the others. Most of the combined manipulative variables show the least significant behaviour based on their *p* values. The output response (FFA content) was fitted to the input process variables through regression analysis (R^2). The regression analysis produced response surface equations for the output response model in

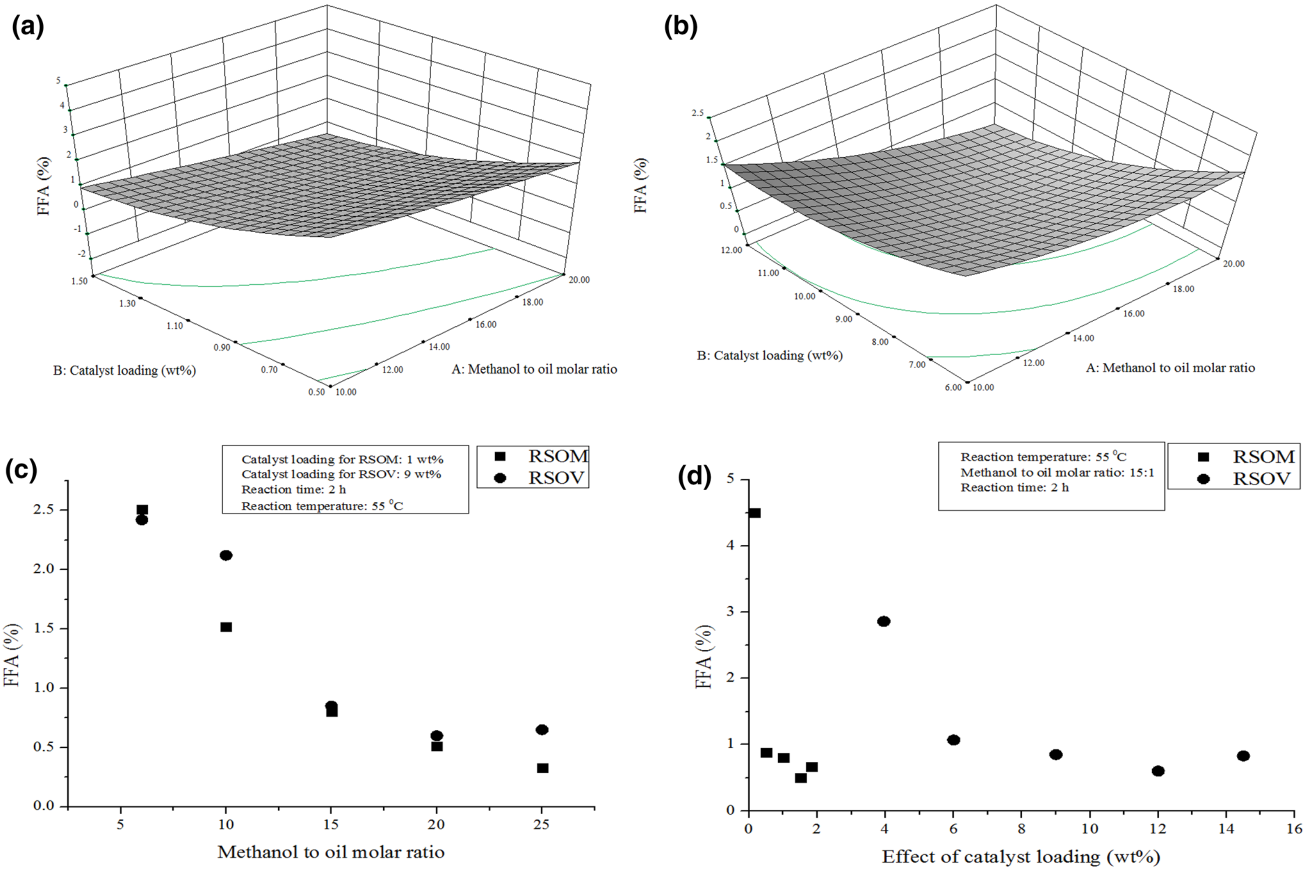


Fig. 4 Effect of methanol-to-oil molar ratio and catalyst loading on free fatty acid for **a** Rubber seed oil Malaysia, **b** Rubber seed oil Vietnam, **c** Comparative effect of methanol-to-oil ratio on rubber seed oil Malaysia and rubber seed oil Vietnam, **d** Comparative effect of catalyst loading on rubber seed oil Malaysia and rubber seed oil Vietnam

terms of actual and coded terms. Equations (7) and (8) for RSOM and RSOV represent a second-order polynomial regression model as shown below.

$$\begin{aligned}\mathrm{FFA}_{\mathrm{RSOM}}\,(\%) = {} & +0.96 - 0.65 \times \mathrm{A} - 1.14 \times \mathrm{B} - 0.06 \\ & \times \mathrm{C} - 0.10 \times \mathrm{D} - 0.06\mathrm{AB} + 0.05\mathrm{AC} \\ & - 1.04\mathrm{AD} - 0.05\mathrm{BC} - 0.14\mathrm{BD} \\ & - 0.05\mathrm{CD} + 0.05\mathrm{A}^2 + 0.46\mathrm{B}^2 \\ & - 0.16\mathrm{C}^2 - 0.12\mathrm{D}^2 \end{aligned} \quad (7)$$

$$\begin{aligned}\mathrm{FFA}_{\mathrm{RSOv}}\,(\%) = {} & +0.87 - 0.53 \times \mathrm{A} - 0.60 \times \mathrm{B} - 0.11 \\ & \times \mathrm{C} - 0.01 \times \mathrm{D} - 0.23\mathrm{AB} + 0.14\mathrm{AC} \\ & - 0.63\mathrm{AD} + 0.15\mathrm{BC} + 0.05\mathrm{BD} \\ & + 0.15\mathrm{CD} + 0.22\mathrm{A}^2 + 0.33\mathrm{B}^2 \\ & - 0.01\mathrm{C}^2 - 0.01\mathrm{D}^2 \end{aligned} \quad (8)$$

The model fitting was assessed by the R^2 for RSOM and RSOV, which show that the models can be used for the prediction of output response with reasonable precision. The value of the adjusted R^2 evaluated is in a good agreement with R^2. An adequate precision determines the signal-to-noise ratio; a ratio >4 is desirable. Indeed, ratios >4 were obtained for both the RSOM and RSOV models, indicating adequate signal.

The perturbation plots show the effect of all the parameters on one curve (Fig. 3). Perturbation curves verify the ANOVA results that factor A (methanol-to-oil molar ratio) and factor B (catalyst loading) show the maximum influence on the output response. However, factor C (reaction temperature) and factor D (reaction time) for both cases did not contribute greatly to the variation of the response value obtained.

3.2 Effect of Methanol-to-Oil Molar Ratio

The methanol-to-oil molar ratio is the second significant process variable that contributes to the FFA reduction. From an economic point of view, the minimum amount of methanol should be used to achieve maximum conversion. Theoretically, one mole of methanol is required to react with FFA to produce one mole fatty acid methyl ester and one mole water. However, an excess methanol is needed to shift the reaction equilibrium towards product and it also helps to dissolve the water during the reaction in order to avoid hydrolysis. Fig-

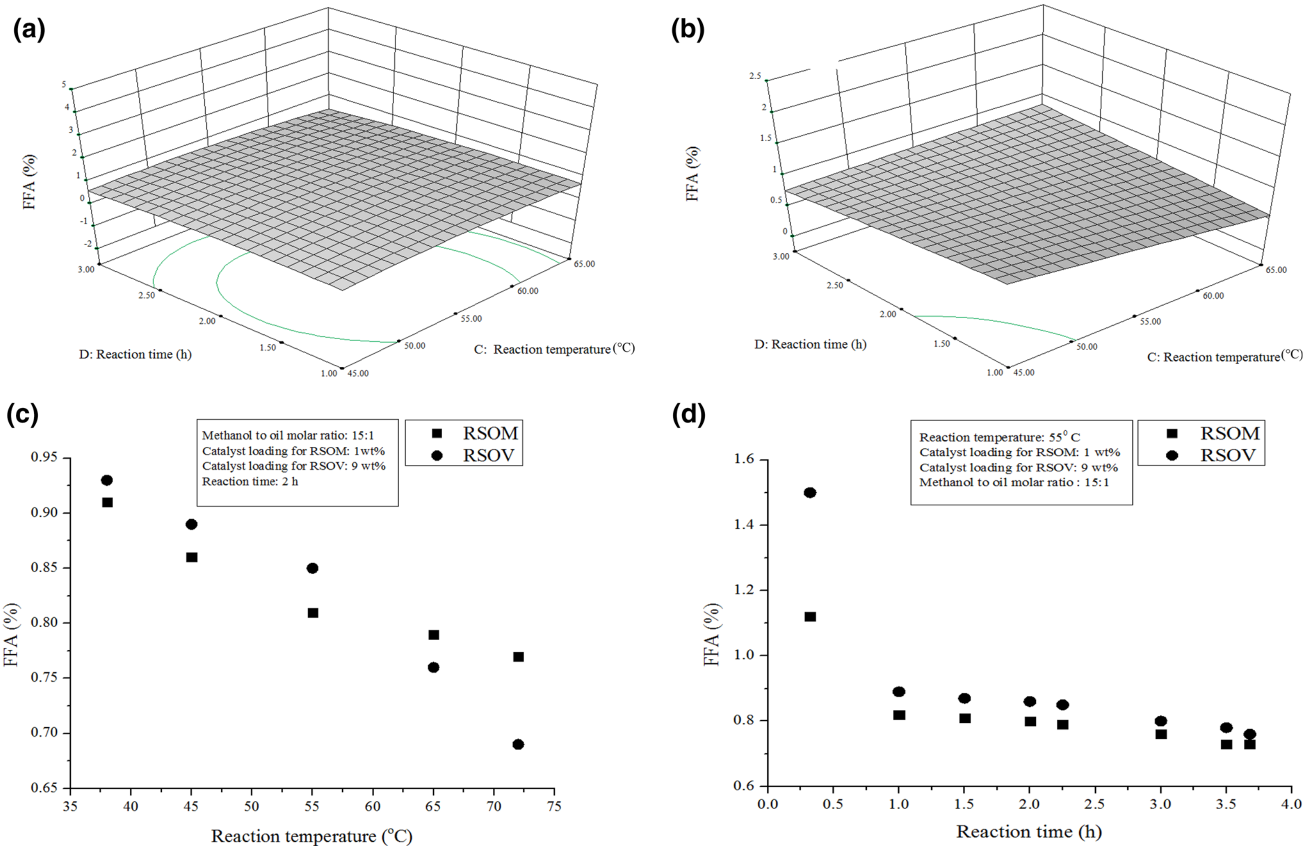


Fig. 5 Effect of reaction temperature and time on free fatty acid for **a** Rubber seed oil Malaysia, **b** Rubber seed oil Vietnam, **c** Comparative effect of reaction temperature on rubber seed oil Malaysia and rubber seed oil Vietnam, **d** Comparative effect of reaction time on rubber seed oil Malaysia and rubber seed oil Vietnam

ure 4a, b demonstrates the 3D effect of methanol-to-oil molar ratio and catalyst loading on FFA reduction. The FFA value decreased with an increase in methanol. Figure 4c shows the comparative effect of the methanol amount on RSOM and RSOV. Results revealed maximum FFA reduction at the methanol-to-oil ratio of 20:1. Further increased in methanol-to-oil ratio resulted in slightly decreased in FFA in RSOM, but FFA content in RSOV increased due to the poor separation and longer separation time. It was observed that FFA content decreased by increasing the methanol amount for both oils. A similar result was reported by Khan et al. [23].

3.3 Effect of Catalyst Loading

Catalyst loading was identified as the most important variable which affects FFA reduction. Figure 4a, b illustrates the FFA content in RSOM and RSOV decreased by increasing the catalyst loading. The FFA content in both oils was decreased by increasing catalyst loading up to certain limit at constant methanol-to-oil molar ratio of 10.

Figure 4d presents the comparative effects of catalyst on the FFA reduction. The RSOM at 0.5 % of catalyst showed maximum FFA reduction. Ramadhas et al. [24] reported a similar result for acid esterification of RSO. However, the RSOV required an excess amount of catalyst to reduce its FFA content. The maximum FFA reduction in RSOV was achieved by increasing the catalyst amount up to 12 wt%. Further increasing the catalyst concentration beyond 12 wt% did not have a significant effect on reducing the FFA. Catalyst provides the initial active ions for acid esterification process. At lower catalyst loading of 2–6 wt%, FFA content in RSOV could not be reduced to an acceptable limit. Morshed et al. [25] also reported that a higher percentage of catalyst loading (5–7 wt%) is needed for FFA reduction in RSO from Bangladesh.

3.4 Effect of Reaction Temperature

Reaction temperature is also the driven force to increase the esterification reaction rate. Figure 5a, b shows the effect of reaction temperature with respect to FFA content. The com-

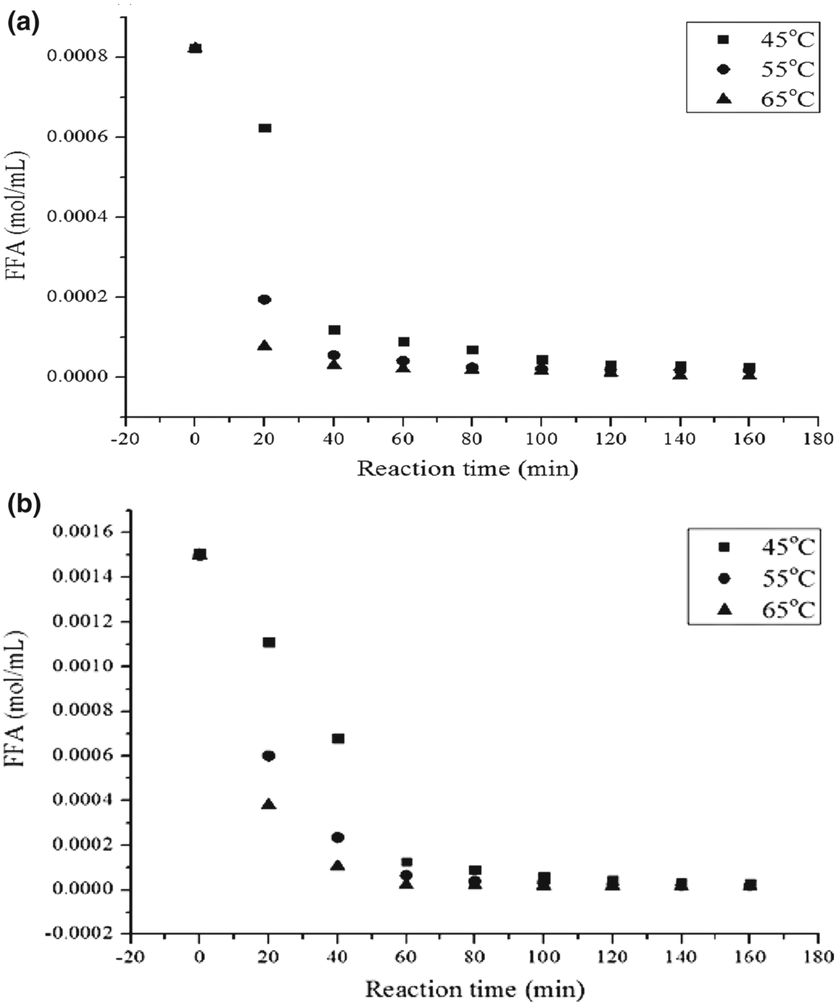


Fig. 6 Free fatty acid concentration versus reaction time plots for **a** Rubber seed oil Malaysia and **b** Rubber seed oil Vietnam

Table 3 Reaction rate constants at different temperatures

Temperature (°C)	k (min^{-1})	
	Rubber seed oil Malaysia	Rubber seed oil Vietnam
45	25.84	5.92
55	26.70	7.38
65	32.90	10.90

parative effect of reaction temperature is presented in Fig. 5c. The FFA reduction in RSOM and RSOV steadily increased with the increase in reaction temperature from 37 to 72 °C. However, it was observed that temperature above 65 °C resulted in methanol losses and dark product was formed. Lower reaction temperature is advantageous from an economic point of view; thus, 50 and 65 °C were determined as optimal conditions for RSOM and RSOV.

3.5 Effect of Reaction Time

Figure 5a, b illustrates the effect of reaction time on FFA reduction. A comparative effect of reaction time on FFA reduction is described in Fig. 5d for RSOM and RSOV. At 0.5 and 1 h, the differences in FFA reduction were still observ-

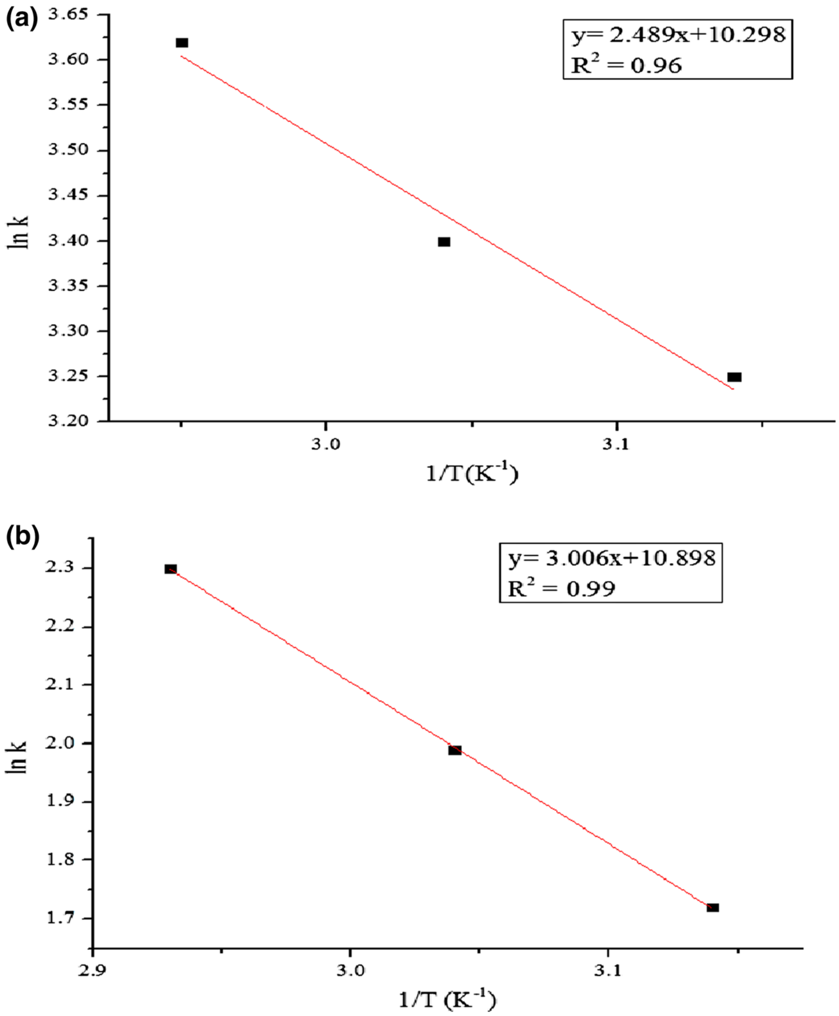


Fig. 7 ln k versus 1/T plots for **a** Rubber seed oil Malaysia and **b** Rubber seed oil Vietnam

Table 4 Activation energy and frequency factor

Kinetic parameters	This study		Marchetti et al. [27]	Rattanaphra et al. [26]
	Rubber seed oil Malaysia	Rubber seed oil Vietnam	Acid oil	Rapeseed oil
Activation energy (kJ/mol)	20.7	25	23.14	22.51
Frequency factor, 10^3 (min^{-1})	29.7	54.1	–	17.78

able (i.e. 0.3–0.6 %), but with further increase in reaction time these differences gradually diminished. Mass transfer between oil and alcohol is enhanced when specified residence time is given for reactants to interact. Ahmad et al. [11] reported that the first hour of the reaction is sufficient to reduce the FFA to a desired level.

3.6 Kinetic Modelling

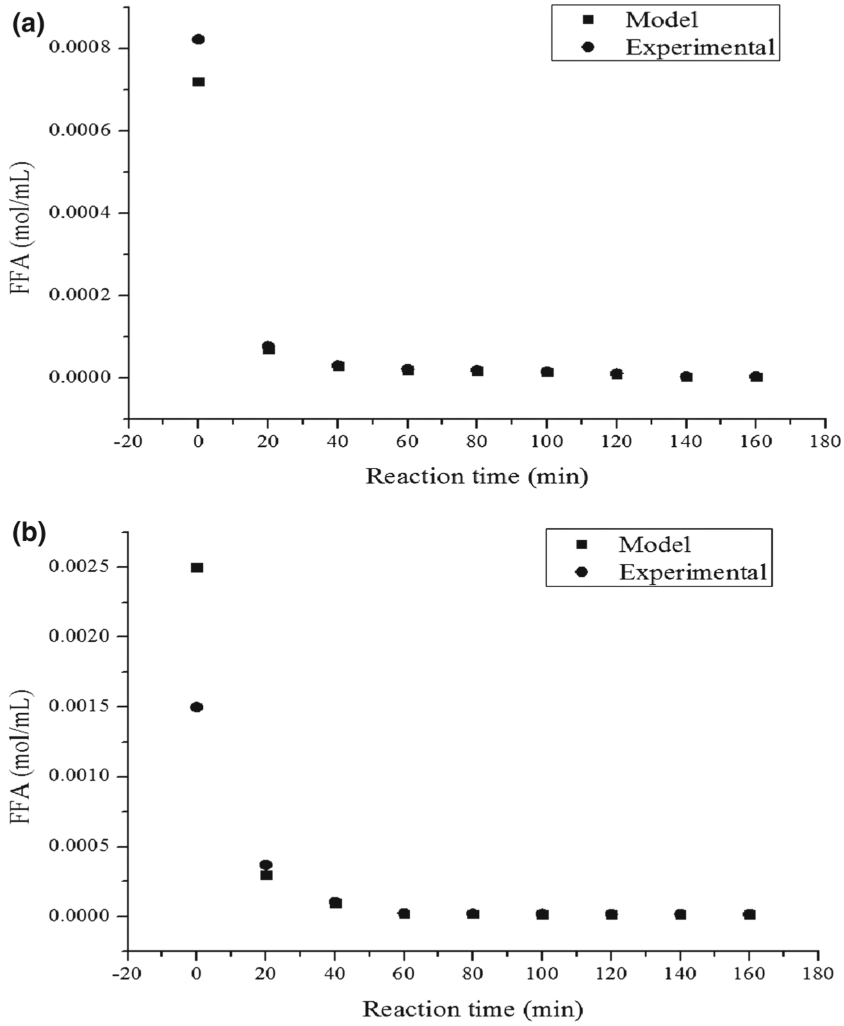
3.6.1 FFA Concentration Versus Time Plot

The FFA concentration has been determined at temperature interval of 10 °C with respect to the reaction time interval of 20 min for homogenous acid esterification process. Figure 6a, b shows that the influence of temperature reaction on conversion of the acid esterification experiments for RSOM and RSOV was conducted with various reaction temperatures in the range of 45–65 °C under the optimal conditions achieved in the above sections were adopted. Results revealed that the FFA concentration in acid esterification reaction was decreased from 45 to 65 °C. Higher reaction temperature could drive the reaction equilibrium towards product and consequently increase the esterification reaction rate. It was found that the rate constants for acid esterification reaction by utilising RSOM were 25.84 (45 °C), 26.7 (55 °C) and 32.9 min^{-1} (65 °C), whereas 5.92 (45 °C), 7.38 (55 °C) and 10.9 min^{-1} (65 °C) for RSOV as presented in Table 3. The mean reaction order for RSOM and RSOV was 1.32 and 1.52.

3.6.2 Activation Energy and Frequency Factor

Figure 7a, b shows the logarithm plot of reaction rate constant with respect to the reciprocal of temperature. The straight decline line verified that the reaction rate constant is in excellent agreement with the Arrhenius law. Following observations can be made for frequency factor and activation energy parameters listed in Table 4: (1) the frequency factor for RSOV was about 1.8-fold higher (of the order of $\sim 10^3\ \text{min}^{-1}$) than RSOM; (2) the activation energy for RSOM and RSOV was 20.7 and 25.0 kJ/mol. The obtained

Fig. 8 Comparative of model and experimental for **a** Rubber seed oil Malaysia and **b** Rubber seed oil Vietnam



activation energies are in a good agreement reported by Rattanaphra et al. [26] and Marchetti et al. [27]. They reported that acid esterification process has low activation energy.

The mathematical model equations proposed for homogenous acid esterification process using the predetermined kinetics data are shown in Eqs. (9) and (10).

$$r_{\text{RSOM}} = \frac{\mathrm{d}C_{\text{FFA}}}{\mathrm{d}t} = 29.7 \times 10^3\, \mathrm{e}^{\frac{-20.7\,\text{kJ/mol}}{RT}} (C_{\text{FFA}})^{1.32} \tag{9}$$

$$r_{\text{RSOV}} = \frac{\mathrm{d}C_{\text{FFA}}}{\mathrm{d}t} = 54.1 \times 10^3\, \mathrm{e}^{\frac{-25.0\,\text{kJ/mol}}{RT}} (C_{\text{FFA}})^{1.52} \tag{10}$$

Figure 8a, b exhibits the verification of model predicted and experimental terms by using excel solver, and the error was minimised by least square method. Results revealed that there is less error between experimental and model predicted terms, and thus, the proposed model equations are reliable to represent the experimental data.

4 Conclusion

FFA content in RSOM and RSOV has been significantly reduced by acid esterification pretreatment method, and the influence of operating parameters has been investigated. Due to high level of unsaturated fatty acids presents in RSO, the FFA content was affected by storage duration. Higher FFA was found in RSOV as compared to RSOM. Therefore, RSOV required higher catalyst loading for FFA reduction compared to RSOM. According to the ANOVA results, catalyst loading and methanol-to-oil molar ratio were the most significant factor among the other parameters examined. Second-order quadratic equation models for RSOM and RSOV, relating FFA content to input process variables, have been derived using RSM. Optimised conditions to obtain maximum FFA reduction in RSOM include a temperature of 50 °C, the catalyst loading of 1.38 wt%, the methanol-to-oil molar ratio of 15.98:1 and the reaction time of 2 h. With regard to RSOV, the optimal operating conditions for acid esterification reaction were 10:1 molar ratio of methanol to oil, 10.74 wt% of catalyst, 65 °C of reaction temperature and 1 h of reaction time. Kinetic model equations were developed for acid esterification process of RSOM and RSOV. The frequency factor and activation energy of RSOV were about 1.8- and 1.2-fold higher than RSOM.

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