

Optimization and kinetic study of non-catalytic transesterification of palm oil under subcritical condition using microwave technology

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ABSTRACT

The main transesterification used in industries involves the reaction with basic catalysts that caused unwanted soap formation, and time-consuming as post-treatment is needed. This creates the need for the utilization of a non-catalytic transesterification reaction under subcritical condition for the transformation of palm oil into biodiesel. This study evaluates the potential of using microwave technology to implement the non-catalytic transesterification for the efficient production of biodiesel. Response surface methodology (RSM) was implemented to maximise the non-catalytic biodiesel yield based on three variables: Dimethyl carbonate (DMC) to oil molar ratio, reaction temperature and reaction time. A maximum biodiesel yield of 86% was obtained with DMC to oil molar ratio of 9.5:1 at 167 °C after 2.5 hr of reaction. Also, its activation energy and pre-exponential factor were 44.88 kJ/mol and $7.88 \times 10^3 \text{ min}^{-1}$, respectively. Biodiesel quality that satisfies the EN14214 biodiesel standard was successfully produced under subcritical condition in the absence of catalysts via this microwave processing technology. This new processing method will enhance the biodiesel production and feasibility in terms of simplicity and less production step. Besides, it needs lower power consumption compared to non-catalytic supercritical method, which brings slight enhancement in cost reduction.

1. Introduction

As the natural resources of the earth are limited, society nowadays has more concerns towards sustainability. Biodiesel production needs to be developed as it contributes significantly to sustainability as it is a biodegradable fuel which can replace the petroleum-based diesel and reduce greenhouse emissions [1,2]. Among the available renewable energy, biodiesel offers the superior advantages as it is available in liquid form which can be easily replace the conventional petroleum-based diesel. In the recent years, the implementation of biodiesel and petroleum-based diesel blends in commercial fuels have led to the increase of biodiesel production, as guided by the government policies of many countries [3]. However, one of the major challenges encountered during biodiesel production is the production cost in term of raw material cost and oil-to-biodiesel conversion rate.

Transesterification has been proven as one of the widely-used method in producing biodiesel, but the current technologies shows inefficiencies in the conversion and energy consumption, which eventually leads to the higher production cost. Moreover, 75–85% of the biodiesel production cost is attributed by the feedstock cost [4]. Hence,

the selection of a suitable sustainable feedstock, like waste cooking oil [5,6], microalgae [7], and renewable non-edible oil [8,9], is essential to ensure the production of low cost biodiesel and reduce conflict of interest with food crops. Nevertheless, the conventional transesterification process has low adaptability to the cheaper feedstock due to their high free fatty acid (FFA) and water content, which will react with the catalysts used during the production process and eventually result in the formation of unwanted soap formation, instead of biodiesel. Hence, pre-treatments, such as esterification [10,11], are essential but this will result in higher overall production time and cost. In order to overcome the problems associated with conventional transesterification, the non-catalytic transesterification is introduced [12,13]. In this method, no catalyst is needed but supercritical condition needs to be achieved, thus, resulting in higher energy input and higher production cost. Non-catalytic biodiesel conversion with the conditions under subcritical condition must be developed, although there is only little information about the non-catalytic transesterification at subcritical conditions [14,15].

The development of a non-catalytic transesterification process under subcritical condition using microwave technology then becomes

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promising. The potential of microwave technology to accomplish superior outcomes over the conventional methods in biodiesel production is apparent as significant reduction of reaction time, rapid and energy-efficient volumetric heating, and cleaner product yield can be achieved [16,17]. Microwave processing has reported to be a better heating method due to its unique thermal effect or non-thermal effect, as suggested by Xu et al. [18] and Zhou et al. [19]. The reaction rate could be increased by a factor of 5–1000 under microwave irradiation in comparison to conventional methods [20,21]. Microwave processing technology has also generated interest within the scientific and industrial community due to its ability to revolutionize the chemical reaction process and produce unexplainable outcomes, such as distortion of water structure after microwave irradiation.

In biodiesel production, methanol is usually used as a solvent and at the same time, as a reactant which is required for biodiesel formation [22–24]. The selection of reactant plays an important role that can affect the economic viability of biodiesel production. Dimethyl carbonate (DMC) which is an environmentally benign chemical that has been classified as one of the greenest solvents based on the safety, health and environment evaluation shows great potential in replacing the conventional methanol used during transesterification. DMC is biodegradable, non-toxic and also a non-polar aprotic solvent with better miscibility properties [25]. With the replacement of less advantageous reactant with DMC, the transesterification of triglyceride is expected to produce higher value-added by-products, glycerol carbonate and glycerol dicarbonate production, instead of the waste glycerol. Glycerol carbonate is a cyclic carbonate with wide reactivity ability that has attracted interest of the scientific and industrial fields as it consists of excellent physical and chemical properties, such as low toxicity and flammability, biodegradable, water soluble, high boiling point and flash point. Besides, the wide reactivity of glycerol carbonate has initiated some emerging applications in various domains from solvents to polymers.

In this research, non-catalytic biodiesel production from palm oil under subcritical condition by using dimethyl carbonate (DMC) and microwave-assisted method was investigated. Response Surface Methodology (RSM) was implemented to determine the optimal condition for biodiesel yield based on variations of DMC-to-oil molar ratio, reaction temperature and reaction time. The kinetic parameters was also determined by conducting the kinetic study under optimized condition.

2. Materials and methods

2.1. Materials and equipment

The palm oil used in this project was purchased from a local supermarket in Selangor, Malaysia (Buruh, Lam Soon Edible Oils Sdn Bhd). The characteristics of the palm oil can be found in Table 1. Dimethyl carbonate (DMC) was purchased from Friendemann Schmidt (Parkwood, Western Australia). The equipment used was a 1 kW, 2.45 GHz multi-mode microwave reactor with continuous power supply and a reflux system, which was designed for carrying out chemical reaction and performing the non-catalytic biodiesel production. The microwave reactor was also installed with a temperature probe and pressure gauge to allow continuous monitoring. This functionality of the microwave reactor is adapted from [26].

2.2. Non-catalytic biodiesel production

The palm oil and DMC at certain molar ratio was firstly prepared. Then, the mixture was poured into the beaker inside the microwave reactor. Next, the microwave reactor and the magnetic stirrer were switched on to heat the mixture to the desired reaction temperature. The distillation column was connected to cool down the vaporized DMC when the reaction temperature exceeds the desired setting condition

Table 1
Characteristics and fatty acid composition of palm oil.

Characteristics/Composition of palm oil	Value
Fatty acid composition (% by weight)	
C 14:0 (Myristic)	0.8
C 16:0 (Palmitic)	42.0
C 18:0 (Stearic)	5.1
C 18:1 (Oleic)	42.0
C18:2 (Linoleic)	10.0
Total	99.9
Peroxide value (meq/kg)	2
Density (kg/m ³)	897.2
Melting point (°C)	40
Viscosity at 40 °C (cSt)	37.3
Free fatty acid as palmitic (%)	0.1
Moisture and impurities (%)	0.1
Vitamin E (ppm)	561
Phytosterols (ppm)	109–170

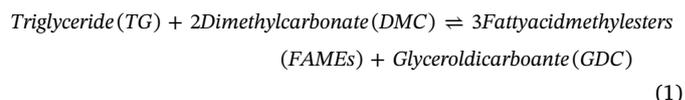
(± 10 °C temperature allowance is acceptable). Once the reaction was completed, the product was collected and allowed to cool for 24 hr. The top portion of the products, which is biodiesel, was collected and analyzed by using Gas Chromatography (GC) and Fourier Transform Infrared Spectrophotometer (FTIR). The biodiesel yield was then determined based on the FTIR results and the calibration equation created. The optimization study was performed by modelling and analyzing the yield using Box-Behnken design method into the Design Expert software.

2.3. Optimization study

The determination of the optimal condition for non-catalytic biodiesel production under subcritical condition using microwave technology was done by considering three parameters, namely: DMC to oil molar ratio, reaction temperature and reaction time (Table 2). The center point was repeated three times to evaluate the experimental errors. Based on the Design Expert 10.0.3.0 software (Stat-Ease, Minneapolis, USA), the setting conditions for 15 experimental runs were generated (Table 2). Then, the biodiesel was produced according to that particular setting condition. Next, the Design Expert was used to conduct the Analysis of Variance (ANOVA) in order to produce a mathematical model for the studied result, in this case the non-catalytic biodiesel yield. After that, the mathematical model was optimized and the optimal condition was obtained, which was then verified by conducting another set of experiment.

2.4. Kinetic parameters determination

The dimethyl carbonate (DMC)-mediated biodiesel production involves the reversible reaction between triglyceride with DMC, and finally produces fatty acid methyl esters (FAMES) and glycerol dicarbonate as by-product (Eq. (1)).



Usually, the reaction equilibrium is shifted toward the formation of FAMES by using huge excess amount of DMC with respect to palm oil. Hence, the reverse reaction was ignored and its concentration was taken as constant during the reaction. By assuming the whole reaction as a pseudo first-order reaction, the following rate equations were considered:

$$r = -\frac{d[TG]}{dt} = k[TG] \quad (2)$$

After integration, it becomes:

Table 2
Level of variables chosen for the optimization of non-catalytic biodiesel production.

	DMC to oil molar ratio, X_1	Reaction temperature, X_2 (°C)	Reaction time, X_3 (hr)
Low level, L (-1)	2:1	80	1
Medium level, M (0)	6:1	130	2
High level, H (+1)	10:1	180	3

$$\ln[TG, 0] - \ln[TG, t] = kt \quad (3)$$

and

$$[TG, t] = [TG, 0] - \frac{[FAME, t]}{3} \quad (4)$$

where k is a reaction rate constant, while $[TG, 0]$ and $[TG, t]$ is the concentration of TG at time 0 and t respectively. $[FAME, t]$, however, is the concentration of FAME at time t . By plotting a linear fit of Eq (3) through origin, the rate constant, k , was determined.

The apparent activation energy, E_a was calculated by using Arrhenius equation (Eq. (5)), once the rate constant, k at various reaction temperatures were obtained.

$$k = K_A \times e^{\frac{-E_a}{RT}} \quad (5)$$

By taking the logarithm, it gives:

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln K_A \quad (6)$$

where k is the reaction rate, K_A is a pre-exponential factor, E_a represents the activation energy, R is the gas constant, and T is the temperature.

The kinetic experiment of this non-catalytic transesterification of palm oil and DMC was conducted at the optimized condition. The procedures were repeated but the variables were the optimized parameters at varying reaction temperature. Besides, the product of the reaction was collected and analysed for every 20 min. After that, the kinetic parameters, such as rate constant and activation energy were determined using the kinetic model developed.

2.5. Gas chromatography (GC) analysis

Gas chromatographic analysis was performed in accordance with EN 14103 by using a GC-FID apparatus (Agilent Technologies 7890A) that is equipped with an auto-sampler (Agilent Technologies 7683B series injector). A 30 m long DB-WAX capillary column, with 320 μm diameter and 0.25 μm film thickness, was used for the separations of the samples in this study with a constant hydrogen flow of 3 ml/min. In every analysis, 1 μl of sample was injected in a split ratio of 1:50 with an injection temperature of 250 °C. The temperature program of the oven was started with an initial temperature of 50 °C for 2 min, and was followed by an increase in temperature up to 200 °C at a rate of 10 °C/min for 10 min. Lastly, the oven temperature was increased to 220 °C with a heating rate of 5 °C/min for 7 min.

2.6. Fourier transform infrared spectroscopy (FTIR) analysis

Shimadzu IRPrestige-21 Fourier Transform Infrared Spectrophotometer (FTIR) (Shimadzu Corporation Japan) was used to investigate the structure of the product obtained. The FTIR spectrometer used is equipped with temperature controlled DLATGS (deuterated, L-alanine doped triglycerine sulfate) detector and the FTIR analysis of the samples was performed with the scan settings as follow: (a) resolution: 4 cm^{-1} , (b) accumulation: 20 scans, (c) measurement mode: transmittance (%T), and (d) wave number: 4000–650 cm^{-1} . To conduct the FTIR analysis, the Attenuated Total Reflectance (ATR) crystal disc (Diamond Type II crystal) was firstly wiped with acetone and a background analysis of air spectrum was run. Then, the sample was dropped onto the ATR crystal disc at ambient temperature (23 ± 1 °C) and the

FTIR spectra of that particular sample, which was referenced against the background spectrum, was obtained. All the spectra obtained was analysed using IR resolution software (IR solution-window based version 1.4-Shimadzu). After analysis of each sample, the ATR crystal disc was cleaned with acetone.

2.7. Calibration curve determination

The Calibration Curve Method implements the quantitation of an unknown sample by obtaining a regression equation based on the Lambert-Beer's law. The regression equation obtained illustrates the relationship between the peak intensity of a target element and the concentration from the spectra of standard samples with known concentration.

In this study, palm oil was used in mixtures with the biodiesel (produced through conventional transesterification [27]) at different percentage. Then, the spectra with wavenumber range of 1430 cm^{-1} –1440 cm^{-1} was selected in order to create the calibration curve for the determination of biodiesel yield [28]. This is because there is strong absorption of fatty acid methyl esters (biodiesel) within this range. As shown in Fig. 1, the peak height increases along with the biodiesel concentration at wavenumber of 1436 cm^{-1} . In addition, a best-fit line, with a correlation coefficient (R) of 0.9933, was added using IRsolution software and the following equation was obtained:

$$\text{Abs} = 3.569 \times 10^{-2} + 4.723 \times 10^{-4} \times C \quad (7)$$

This equation was then used extensively in determining the biodiesel yield in the later experiment. As reported by Mahamuni et al. [28], this method gives high accuracy, 98.11%, in monitoring the biodiesel content. Besides, similar method was implemented by Rabelo et al. for quantification of FAMES in biodiesel produced by microwave-assisted transesterification reaction [29]. In their work, the quantitation method using FTIR was compared with the conventional Gas Chromatography (GC) method. Their results concluded that the FTIR quantitation method is a promising and fast analytical method without the need of sample preparation. Hence, similar method was implemented in this paper.

2.8. Biodiesel quality determination

The quality of biodiesel obtained was determined by using a rapid Kittiwake's biodiesel test kit (FG-K16897-KW). The test kit was able to determine the key factors required for biodiesel and meet the EN14214 standard accurately. The key parameters determined includes the density, water content, viscosity and total acid number of the biodiesel sample. Other than these parameters mentioned, the flash point of the biodiesel sample was also determined using the Kittiwake's flash point tester (FG-K16909-KW). Then, the high heating value (HHV) and cetane number (CN) were calculated using equations below [30]:

$$\text{HHV} = -0.0259\rho + 63.776 \quad (8)$$

$$\text{CN} = 152.43\rho + 0.3423FP + 0.108HHV - 0.021\nu + 152.43 \quad (9)$$

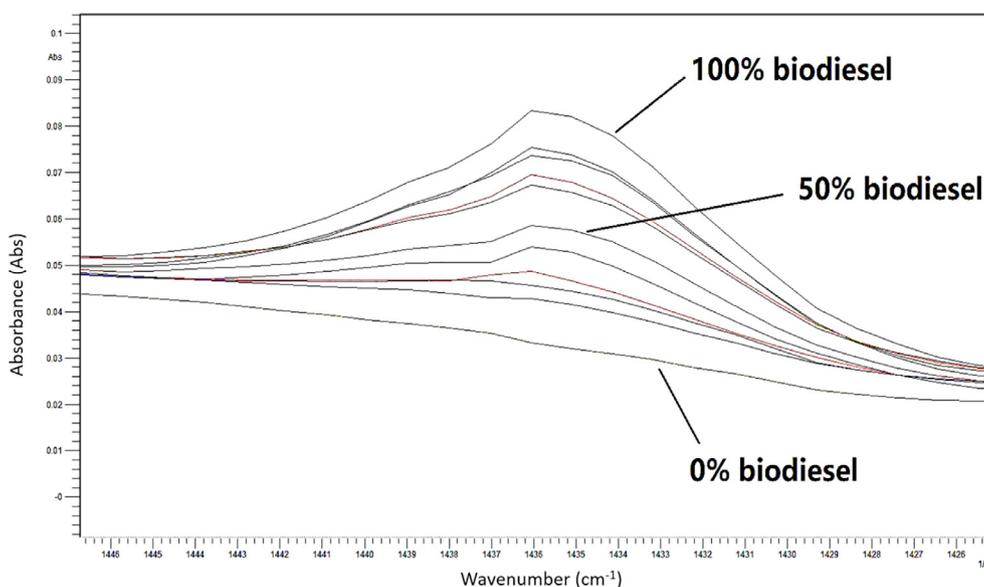


Fig. 1. FTIR analysis of standard samples in the wavenumber range of 1425–1447 cm^{-1} .

3. Results

3.1. Optimization of non-catalytic biodiesel production under subcritical condition

In this paper, the optimization study, based on variables reaction temperature, DMC to oil molar ratio and reaction time under microwave irradiation, was performed to locate the maximum non-catalytic biodiesel yield. Reaction temperature and reaction time was selected as the studied parameters because they play important roles in determining the reaction kinetics of the non-catalytic oil conversion to biodiesel under supercritical condition [31]. In all of the reports that involves supercritical methanol and ethanol, the authors concluded that the oil conversion to biodiesel mainly increased with reaction temperature and time [32]. These were due to the increase in the reaction rate constant according to Arrhenius equation. Besides, under supercritical condition, a slight change of temperature will cause a huge difference in the properties of the alkyl group donor (ethanol, methanol, DMC and etc.) [31]. Although this study involves only subcritical condition, however, it is interesting to study and compare the results with the supercritical condition. Hence, in this project, reaction temperature and time was chosen to investigate their effect on the non-catalytic oil conversion to biodiesel under subcritical condition.

On the other hand, the DMC-to-oil molar ratio was also chosen as one of the studied variables because transesterification is a reversible reaction and thus, excess amount of DMC is needed practically to achieve a complete conversion of oil to biodiesel [33]. Nevertheless, in term of economic viability, excess amount of DMC will increase the overall production cost. Therefore, this parameter should be optimized. Table 3 presented the experimental biodiesel yield results obtained. These data were then used for the further analysis using Design Expert software.

Based on these results, a fit summary table (Table 4) was provided by Design Expert to determine which model to select for further study. The findings show that the quadratic model was recommended because it is the highest order polynomial model that was suggested by the software. By adding the cubic model terms, the model would not be significantly improved, however, it would be aliased and was useless for the modeling purposes. Quadratic model has small sequential p-value, 0.0448 (< 0.05), which indicates that this quadratic model had high probability to help in explaining the response (biodiesel yield) instead of modeling the noise.

The ANOVA analysis plays a significant role to test the hypothesis on the parameters of the model (Table 5). The F value for a term shows the test in order to compare the variance of that particular term with the residual variance. The larger the F value, the more likely that the variance contributed by the model is significantly larger than random error.

As for the “Model” term, its F-value was 81.70 which implies that the model developed is significant. Moreover, there is only 0.01% chance that this “F-value” occurs due to noise. Besides, the “p-value” for every model term is suggested to be < 0.05 . In this case, A, B, C, AB and B^2 are the significant model terms. On the other hand, AC, BC, A^2 and C^2 terms are the insignificant model terms as their “p-value” are greater than 0.05. Hence, these model terms are excluded in order to further improve the selected model. Lastly, the “Lack of Fit” of the model is non-significant with a “p-value” of 0.62. A model with non-significant lack of fit and a “p-value” that is greater than 0.1 is good as the model is fit to be used for further analysis.

Two diagnostics plots were checked before entering the optimization stage in order to ensure that all the data points can be analyzed well by the selected model. The first diagnostics plot, as shown in Fig. 2(a), indicates the relationship between the residual and the experimental run order, which is useful in identifying of lurking variables that may have affected the outputs during the experiment. Residual is defined as the difference between the actual response (experimental biodiesel yield) and the predicted response (predicted biodiesel yield). This plot shows a random scatter without any trend pattern, signifying that the analysis is reasonable. The second diagnostic plot, Fig. 2(b), is the normal probability plot of residuals. This plot shows whether the residuals follow a normal distribution. In this study, all the data points are scattered evenly with the normal data. In short, the modified model selected is capable of predicting and analyzing all of the data points. Hence, no experimental run was needed to be re-conducted.

After examining the above modelling results, it is proven that the modified quadratic model is sufficient to describe this experiment using the following equation:

$$\begin{aligned} \text{Predicted biodiesel yield} \\ = -49.84302 + 0.26076A + 0.95055B + 3.6685C + 0.035924A \\ B - 0.00326845 \times B^2 \end{aligned} \quad (10)$$

where A is DMC to oil molar ratio, B is reaction temperature, and C is reaction time. Using Eq. (10), the predicted biodiesel yield is computed and recorded (Table 3).

Table 3
Optimization of non-catalytic biodiesel yield using RSM-box behnken design.

Experimental run	DMC to oil molar ratio	Reaction temperature (°C)	Reaction time (hr)	Experimental biodiesel yield (%)	Predicted biodiesel yield (%)
1	6	180	1	63.414	55.3892
2	10	80	2	43.200	43.9667
3	10	180	2	85.922	89.966
4	2	180	2	34.143	36.1494
5	10	130	3	78.819	78.806
6	6	80	3	38.823	35.0965
7	2	80	2	20.160	18.8893
8	6	180	3	68.752	66.7262
9*	6	130	2	51.826	55.4140
10	6	80	1	23.529	27.7595
11	2	130	1	32.977	32.0219
12	10	130	1	72.377	71.4690
13	2	130	3	35.251	39.3589
14*	6	130	2	59.317	55.4140
15*	6	130	2	57.331	55.4140

* The center point of this experiment was replicated three times.

In this optimization study, predicted biodiesel yield was then used as the response during the software optimization analysis. The predicted biodiesel yield is fully based on the equation generated and hence, it has a higher degree of accuracy as compared to the experimental data. From the 100 solutions proposed by the software, the combination of DMC to oil molar ratio of 9.5:1, reaction temperature at 167 °C and reaction time of 2.5 hr was selected as the final optimal condition to obtain maximum predicted biodiesel yield. This setting condition allows the optimal condition to be achieved with the lowest average reaction temperature and time, hence saving the overall operating cost.

In order to compare the effect of all variables on the non-catalytic biodiesel yield at the optimal condition in the same design space, the perturbation plot is drawn (Fig. 3(a)). Each line represents an effect on the predicted biodiesel yield. A, B and C represent the effect of DMC to oil molar ratio, reaction temperature and reaction time, respectively. As shown in Fig. 3(a), DMC to oil molar ratio and reaction temperature are the most significant factors among these three parameters. This is because a slight change in the DMC to oil molar ratio and reaction temperature will cause a major difference in the response of the experiment. As the reaction temperature increases, the predicted biodiesel yield increases parabolically. Meanwhile, the predicted biodiesel yield increases linearly with the DMC to oil molar ratio and reaction time. However, Line A (DMC to oil molar ratio) has a steeper slope, showing the biodiesel yield is more sensitive to the DMC to oil molar ratio as compared to reaction time.

Perturbation plot is a “one-factor-at-a-time” investigation and is useful in determining the individual effect of several factors on the response of the experiment. However, the effect of the interaction term, AB, on the biodiesel yield could not be demonstrated by this perturbation plot. Hence, Fig. 3(b) is plotted. Furthermore, two-dimensional contour plot and three-dimensional response for the optimization of non-catalytic biodiesel yield are illustrated as shown in Fig. 3(c) and (d). Both these graphical representations show how the reaction temperature and DMC to oil molar ratio affect the biodiesel yield. Reaction time in these two graphs were kept constant as it has the minimum effect on the biodiesel yield among the three chosen parameters.

Table 4
Fit summary table.

Source	Sequential p-value	Lack of fit p-value	Adjusted R-Squared	Predicted R-Squared	Remarks
Linear	< 0.0001	0.2131	0.8726	0.8041	
2 Factors Interaction	0.2215	0.2396	0.8959	0.7610	
Quadratic	0.0448	0.5211	0.9625	0.8572	Suggested
Cubic	0.5211		0.9637		Aliased

In conclusion, through the optimization study using RSM Box-Behnken Design, Design Expert software predicted that the non-catalytic biodiesel production with 9.5:1 DMC to oil molar ratio at 167 °C for 2.5 hr will give a maximized biodiesel yield of 86.02%. This predicted yield was then verified by conducting another set of experiments. As a result, an experimental biodiesel yield of 86% was obtained under the optimized operating condition. Even though this experimental value was slightly lower than the predicted biodiesel yield calculated by the software, however, it was higher than the highest experimental value obtained (85.92%) during the optimization study with the operating condition of 10:1 DMC-to-oil molar ratio, 180 °C and 2 hr of reaction time. In short, a comparable biodiesel yield was obtained, with a lesser amount of DMC and at a lower reaction temperature, by only increasing 30 min of the reaction time. This eventually validates the effectiveness of the optimization study using Box-Behnken Design.

In the catalytic DMC-mediated transesterification studied by Yogesh et al. [34], 99% of refined canola oil was converted into biodiesel for 3:1 DMC-to-oil molar ratio, 2.5 wt% of catalyst (Triazabicyclodecene) concentration, and at a temperature of 60 °C after 6 hr of reaction. Similar yield was gained by Dian et al. [35] with 6:1 DMC-to-oil molar ratio, 2 wt% of catalyst (potassium methoxide) concentration, and at 80 °C after 15 min of reaction. Although these studies gave a higher yield with a lower reaction temperature in comparison with the present work, but, both cases required complicated catalyst preparation and downstream purification process.

For the non-catalytic DMC-mediated transesterification, the first complete transesterification was performed by Ilham and Saka by using a batch type reactor at supercritical condition [36]. They reported that 94% (w/w) of biodiesel yield was obtained at 350 °C and 200 bar with oil-to-DMC molar ratio of 1:42 after 12 min. As compared to their work, the proposed method in this study was able to achieve a comparable biodiesel yield at a much milder operating condition. Besides using a lower amount of DMC, the milder operating condition will reduce the operating cost, despite having a slightly longer reaction time, as shown in Table 7.

The conversion of coconut oil into biodiesel using DMC via a non-catalytic transesterification reaction via continuous flow system was

Table 5
ANOVA analysis for optimization of non-catalytic biodiesel yield.

Source	Sum of squares	DoF ^a	Mean square	F Value	p-value (Prob > F) ^{**}	Remarks
Model	5676.38	5	1135.28	81.70	< 0.0001	Significant
A ^a	3112.09	1	3112.09	223.96	< 0.0001	
B ^b	2000.88	1	2000.88	143.99	< 0.0001	
C ^c	107.66	1	107.66	7.75	0.0213	
AB	206.48	1	206.48	14.86	0.0039	
B ²	249.26	1	249.26	17.94	0.0022	
Residual	125.06	9	13.90			
Lack of fit	94.94	7	13.56	0.90	0.6188	Not significant
Pure error	30.12	2	15.06			

^a A represents the DMC to oil molar ratio.

^b B indicates the reaction temperature.

^c C symbolizes the reaction time.

* DoF is the abbreviation of degree of freedom.

** Probability > F (Prob > F) shows the probability of the null hypothesis for the full model is true.

also investigated by Kwon et al. [15]. They reported a biodiesel yield of 98% within 1–2 min at a temperature of 360–450 °C under ambient pressure. Their work involved a heterogeneous reaction between the liquid coconut oil and gas phase DMC. The reaction was enhanced by the porous material, which act as the micro reaction chambers, and provided sufficient contact time between the reactants to reach the completion of transesterification. This addition of porous materials was considered as an inert support for the reaction, though it might be activated to become catalysts at high temperature. In comparison with Kwon's work, the current study has the advantages over the reaction temperature. The current work and its comparison with other previous studies can be found in Table 6.

Moreover, Table 7 compares the energy required between the proposed method with the non-catalytic supercritical reaction. Based on the table, the proposed solution needs lower energy consumption. In the other words, the cost to produce 1 L of biodiesel with the proposed method is lower (~60%) in comparison to the non-catalytic supercritical method. Nevertheless, the energy cost stands about 2% only of the overall biodiesel production cost [4]. Hence, this reduction energy consumption might only bring small impact on the cost improvement, but this is still a small step towards the cost reduction.

In overall, the proposed method, which is microwave-assisted non-catalytic reaction under subcritical condition, has slightly more economic benefit in term of time and cost if compared with the

conventional catalytic transesterification reaction (NaOH/KOH as catalyst, 60–80 °C and ambient pressure). This is because the non-catalytic reaction requires less operational steps as no catalysts is used and hence, the complicated downstream process can be eliminated.

3.2. Kinetic study of non-catalytic biodiesel production

To gain more understanding about the non-catalytic transesterification for biodiesel production under subcritical condition, its kinetic study needs to be conducted. Kinetic study is usually performed to obtain the kinetic parameters (reaction rate) for the ease of comparison with other works. Typically, kinetic analysis includes the investigation of the effect of different factors on reaction rate which is essential for the system design and the optimization of chemical reaction [38]. Besides, more information regarding the characteristics of a reaction mechanism can be obtained [39]. This will allow the construction of a mathematical model that can represent specific chemical reactions. In determining the unknown parameters for a mathematical model, a series of experiments with high accuracy should be conducted.

The kinetics of non-catalytic transesterification reaction of palm oil and DMC under microwave irradiation was performed at different temperatures of 100, 135, and 170 °C with the optimized DMC-to-oil molar ratio of 9.5:1. The maximum temperature studied was 170 °C (at ~8 bar) because it was near to the optimized reaction temperature

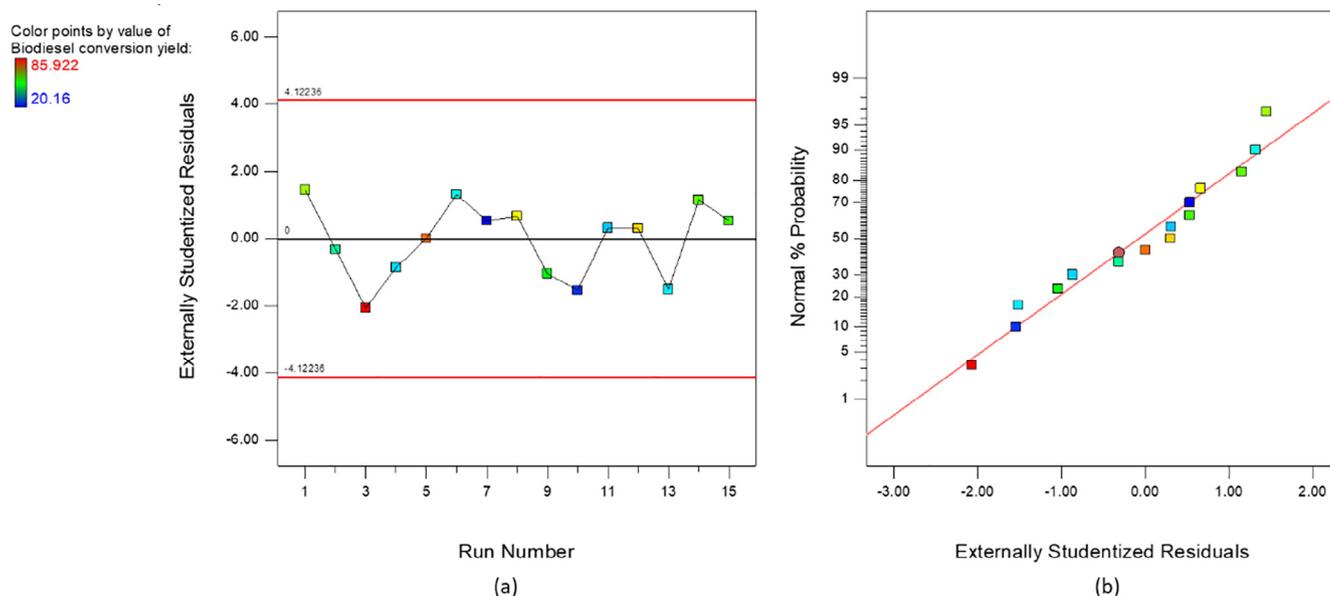


Fig. 2. (a) Residual plot and (b) normal probability plot of modified quadratic model for the optimization of non-catalytic biodiesel yield.

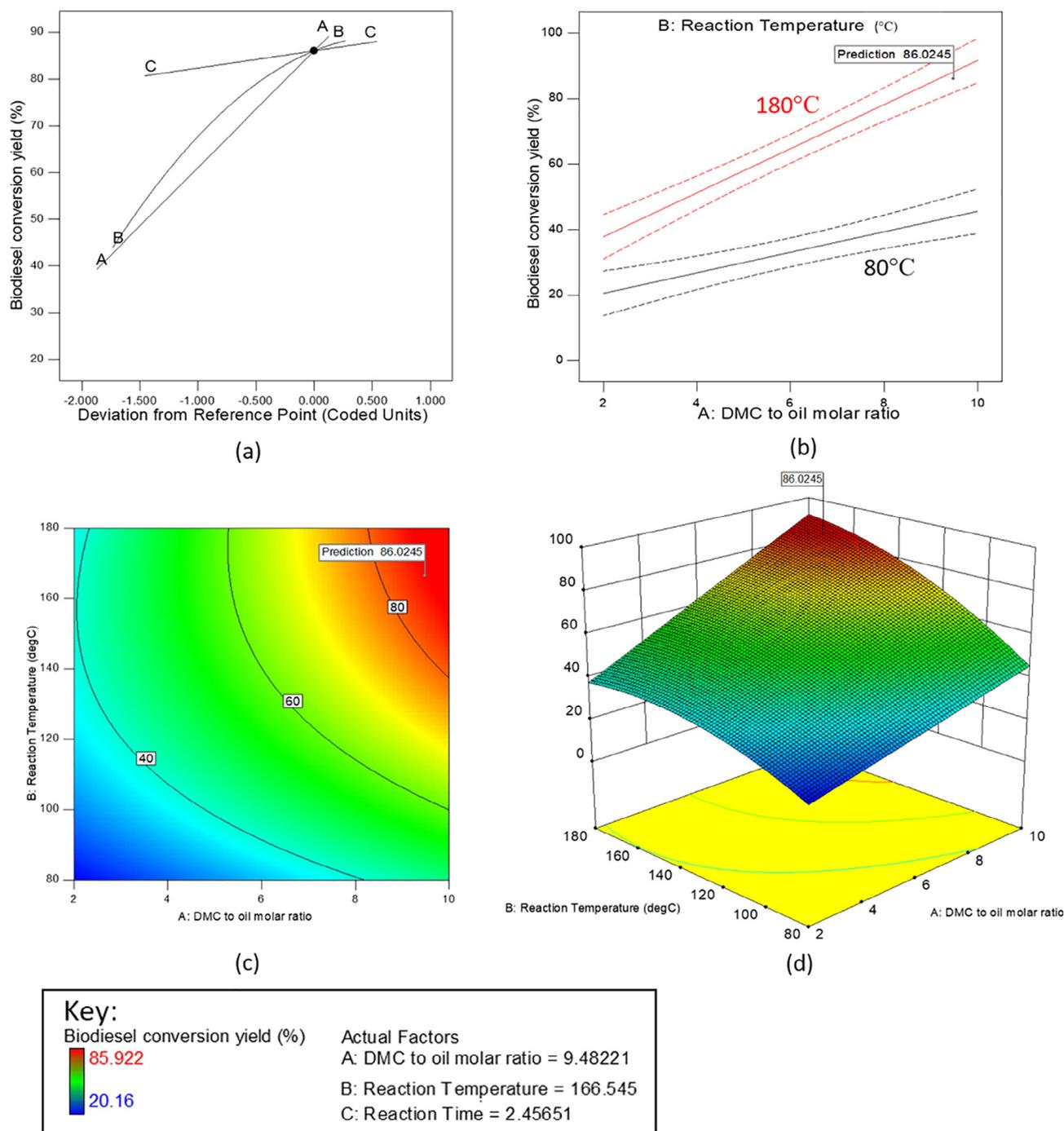


Fig. 3. (a) Perturbation plot for the studied parameters, (b) Interaction plot between DMC to oil molar ratio and reaction temperature, (c) Two-dimensional contour plot, and (d) Three-dimensional response for the non-catalytic biodiesel yield.

predicted from the previous optimization study. A typical biodiesel yield versus time profile was plotted and shown in Fig. 4. The conversion of oil into FAMES was fast at the initial stage, and slowly the conversion rate decreased and finally reached the equilibrium stage (with little change in the yield of FAMES) in about 60 min and 120 min at the reaction temperature of 170 °C and 100 °C, respectively. The kinetic study mainly focused on the initial stage of the reaction, where the formation of FAMES significantly increase over the time. Hence, Eq. (3) was plotted for the initial stage of every kinetic experiments, and then a best fit line through the origin was drawn (Fig. 5). A good linear relationship between the $\ln[\text{TG}, 0] - \ln[\text{TG}, t]$ and reaction time, t , was achieved. This validates the hypothesis that the transesterification reaction was a pseudo first-order reaction. As shown in Fig. 5(a), the

reaction rate constant for the non-catalytic transesterification increased along with the reaction temperature, from 0.004 min^{-1} to 0.039 min^{-1} , which obeyed the pseudo-first order rate law. The phenomenon observed was consistent with the previous study report and showed that the transesterification of palm oil was an endothermic reaction [40]. Besides that, the maximum reaction rate constant obtained (0.039 min^{-1}) at 170 °C of reaction temperature in this kinetic study was comparable to the reaction rate constant of non-catalytic transesterification of palm oil with methanol at 250 °C (0.004 min^{-1}), as reported by by Asri et al. [14]. It was shown that almost similar reaction rate constant can be obtained at much lower operating temperature with the assistance of microwave energy and high miscibility of DMC with palm oil.

Table 6
Summary of current work and its comparison with the previous studies.

DMC-to-oil molar ratio	Reaction temperature (°C)	Reaction time	Reaction pressure	Biodiesel yield (%)	Remarks	References
6:1	80	15 min	Ambient	99	- Conventional heating - 2.0 wt% of recrystallized potassium methoxide in methanol	[35]
3:1	60	6 hr	Ambient	99	- Conventional heating - 2.5 wt% Triazabi-cyclodecene	[34]
42:1	350	12 min	200 bar	94	- Conventional heating - Supercritical condition	[36]
10:1	360–450	1–2 min	Ambient	98	- Activated alumina was used - Continuous flow system	[15]
9.5:1	167	2.5 hr	~5 bar	86	Under microwave irradiation	Current work

Next, the apparent activation energy, E_a was calculated by using Arrhenius equation (Eq. (6)), once the rate constant, k at various reaction temperatures were obtained. As shown in Fig. 5(b), it is observed that there is a good linearity between $\ln k$ and the reciprocal of absolute temperature ($1/T$) over the temperature range of 100–170 °C with a correlation coefficient, R^2 value of 0.9979. Hence, the Arrhenius equation for the studied non-catalytic transesterification could be expressed as:

$$\ln k = -5397.9 \times \frac{1}{T} + 8.9718 \quad (11)$$

By multiplying the slope with the gas constant (8.314 J/mol·K), the activation energy, E_a was determined. Moreover, the pre-exponential, K_A was also calculated from the y-intercept of the Arrhenius equation above. The pre-exponential, K_A , is also known as collision frequency factor which describes the number of times two molecules collide. In short, the activation energy and pre-exponential factor obtained are 44.88 kJ/mol and $7.88 \times 10^3 \text{ min}^{-1}$ correspondingly. The activation energy calculated was lower than those reported by Permsuwan et al. [41] with $E_a = 105 \text{ kJ/mol}$ at 150–200 °C, and by Asri et al. with $E_a = 79.05 \text{ kJ/mol}$ at 210–290 °C for palm oil transesterification [14]. Nevertheless, it was comparable with the E_a value (48.3 kJ/mol) reported by Roschat in her study related to the transesterification of palm oil and methanol using rice-husk derived sodium silicate as catalyst [42]. The lower activation energy observed in this study showed that microwave irradiation can affect the pre-exponential factor or activation energy in the Arrhenius equation, due to the orientation effects of dipolar molecules in the presence of an electric field. In polar reaction mechanisms, the polarity is increased under microwave irradiation, from the ground state to the transition state. This eventually causes the activation energy to be decreased and results in an enhancement of reactivity. This statement has also been supported by the work of Xu et al. (2016). Normally, the activation energy of oil transesterification with the base-catalyst lies in the range of 33.6–84 kJ/mol [43]. In addition, other researchers have reported that the activation energy of other transesterification reactions was also within this range [44,45]. In this work, the activation energy obtained with DMC as the methyl group donor to replace the conventional methanol was in agreement with the reported range. Farobie and Matsumura concluded that the activation energy of transesterification using methanol is lower or similar to the reaction using DMC under same operating condition [46].

Table 7
Comparison of energy consumption between supercritical and subcritical reaction.

Condition	Reactant volume ¹ (L)	Energy consumption for 1 L of biodiesel (kWh)	Reference
Non-catalytic supercritical reaction with 1400 W microwave power for 30 min	0.64	1.09	[37]
Non-catalytic subcritical reaction with 600 W microwave power for 2.5 h	5	0.40	Current work

¹ Maximum volume for the respective reactor.

Hence, DMC has little effect on the reduction of activation energy observed in this study. Therefore, the reduction of activation energy observed can be explained by the specific effect of electromagnetic microwave energy.

The phenomenon of activation energy reduction can be explained by the model of interactions between the electromagnetic waves and molecules. It was reported that the microwave irradiation is partially transformed to alter the molecular vibration and hence, reducing the activation energy, E_a , thus exhibiting a microwave catalytic effect [19]. The microwave electromagnetic field and microwave energy (for reaction under microwave irradiation) cause a change in the molecular rotational energy level of the molecules. This will lead to the decrease in the E_a for reactions involving a polar transition state, where the polarity of the polar molecules is increased, and thus increasing the energy level of the molecules (going from the ground state to the transition state). At the same time, this effect will result in a change in the electron cloud distribution and/or bond length and/or bond angle due to the compatibility between the molecular vibration frequency and the microwave frequency. Therefore, these two factors causes molecules in the chemical reaction systems to become activated, resulting in enhanced reaction rate. The activation degrees are different for different molecules depend on their polarity. Similarly, in this work, it can be observed that the interaction between the microwave and the reactant medium (triglycerides and DMC in this case) will cause the polar molecules to move to higher energy state (transition state) and hence, reduce the activation energy value.

3.3. Fourier transform infrared spectrophotometer (FTIR) and gas chromatographic analysis of the sample

The FTIR spectrum of FTIR analysis is shown in Fig. 6. As shown in the spectrum of biodiesel sample, there is a peak at 3007.15 cm^{-1} due to the stretching vibration of =C–H (alkene) functional groups. The asymmetric and symmetric stretching vibrations of C–H (alkane) functional groups were also observed at peaks 2852.84 cm^{-1} and 2924.21 cm^{-1} respectively. The alkane groups here might be referred to the methyl (CH_3) or the methylene groups in the esters chains of biodiesel. The characteristics peak at wavenumber of 1753.37 cm^{-1} , however, indicates the stretching of C=O functional groups. Note that it is the strongest peak identified in the spectrum of biodiesel sample. These groups symbolize the presence of carbonyl functional groups in

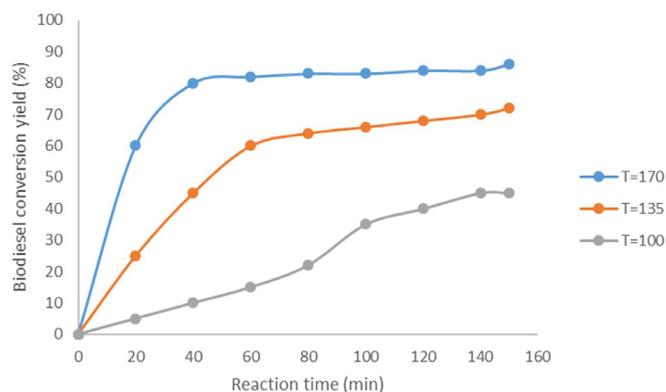
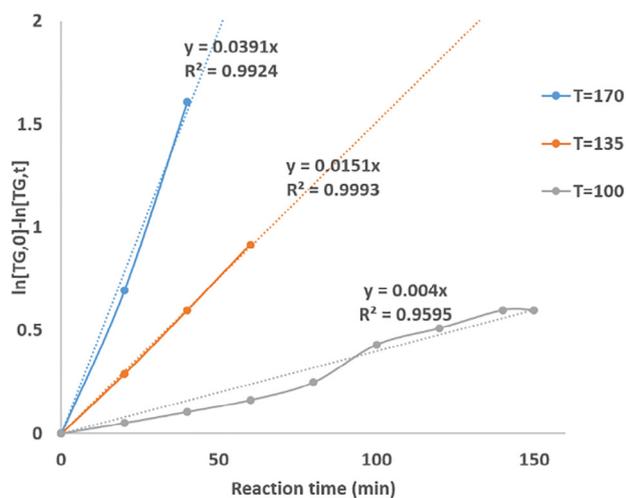


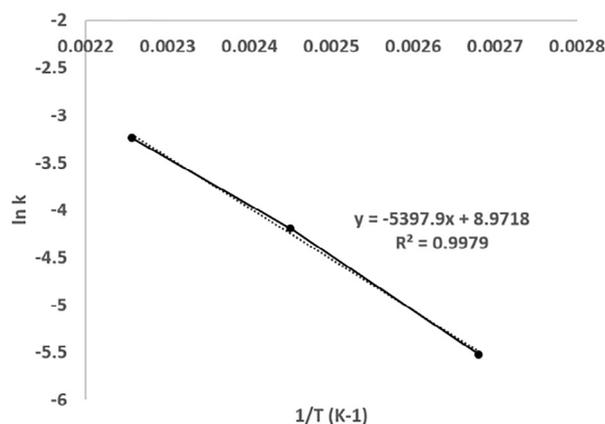
Fig. 4. Biodiesel yield profile over time at various reaction temperature.

biodiesel (FAMES). In the other words, the presence of these groups specify that the conversion of triglycerides in the oil to methyl esters was done successfully [47,48]. The peaks detected in the region of $1455\text{--}1400\text{ cm}^{-1}$ can be explained by the bending vibration of C–H methyl groups in the sample. As compared to the stretching vibration of C–H groups observed at high energy and frequency range, they require lower energy to cause bending vibration [47]. Next, the peaks in the region of $1300\text{--}1000\text{ cm}^{-1}$ are attributed to the stretching vibrations of C–O and C–O–C, or due to the bending vibration of O–CH₃ functional groups. Lastly, the band region of $1000\text{--}700\text{ cm}^{-1}$ shows the presence of =C–H alkene groups. These groups are double bonded and involve bending type of vibrations at low energy and frequency region in the spectrum. They might be identified as the olefinic functional groups (unsaturated hydrocarbon) in the biodiesel, such as methyl oleate and methyl linoleate [47,48]. Also, there is a peak overlapping by –C–H groups at 721.41 cm^{-1} , which possess rocking type of vibration. This peak indicates the presence of methylene functional group $(-\text{CH}_2)_n$ in the biodiesel. This rocking vibration of methylene is an indication that the biodiesel consists of long chain aliphatic structure, the basic structure of FAME component in biodiesel [48].

To corroborate the FTIR results obtained, GC analysis was conducted on the biodiesel sample produced. Besides, methyl palmitate, methyl oleate and methyl linoleate were analyzed using the similar GC procedures in order to identify the respective characteristic peaks. They act as the standard substances in this study as palm oil has high concentration of saturated palmitic acid and monounsaturated oleic acid.



(a)



(b)

Fig. 5. (a) First-order reaction rate constant plot, and (b) First order reaction rate constant in Arrhenius plot of palm oil in DMC during non-catalytic transesterification.

Moreover, the concentration of polyunsaturated linoleic acid is slightly higher when compared to other types of fatty acid. By comparing the GC chromatogram of biodiesel produced with these standard substances, the major FAME peaks can be identified. As shown in Table 8, the major FAME peaks are in the range of 15–25 min. Hence, a GC chromatogram of biodiesel produced was plotted within this retention time range, as displayed in Fig. 7. The presence of these FAME peaks indicates that the non-catalytic transesterification of palm oil with DMC was successful under subcritical condition via microwave heating.

The highest peak identified at 17.986 min represents the presence of methyl palmitate, followed by the peaks at 21.161 min and 21.949 min that indicate the presence of methyl oleate and methyl linoleate respectively. These results were also consistent with the concentration of fatty acid found in palm oil (palmitic acid > oleic acid > linoleic acid). Moreover, the conversion of palmitic acid of palm oil into methyl palmitate of biodiesel was further supported by the peaks at 15.893 min, 16.872 min and 18.202 min. The peaks observed in 20.676 min and 23.343 min, however, might be ascribed to the methyl stearate or the intermediate product of the reaction.

3.4. Biodiesel quality determination

The quality of the biodiesel produced was determined using the Kittiwake's biodiesel test kit, cloud point detector and flash point tester. By the rapid test kit, the water content, density, total acid number and water content of the biodiesel produced were obtained. The flash point tester, however, gave the flash point of the biodiesel sample. The parameters measured were reported in Table 9 and compared with EN14214 biodiesel standard.

4. Conclusion

In this study, RSM-Box-Behnken design was implemented to locate the optimal conditions for non-catalytic biodiesel yield based on the variables, such as dimethyl carbonate (DMC)-to-oil molar ratio, reaction temperature and reaction time, under microwave heating at sub-critical condition. Eventually, the optimal conditions were achieved and the responses were expressed in a mathematical equation. It was predicted that 86.04% will be obtained for DMC to oil molar ratio of 9.5:1 at $167\text{ }^\circ\text{C}$ after 2.5 hr of reaction. This prediction was verified by another set of experiment. In addition, the parameters of DMC to oil molar ratio and reaction temperature showed a larger effect on the non-catalytic biodiesel yield when compared to the reaction time. The

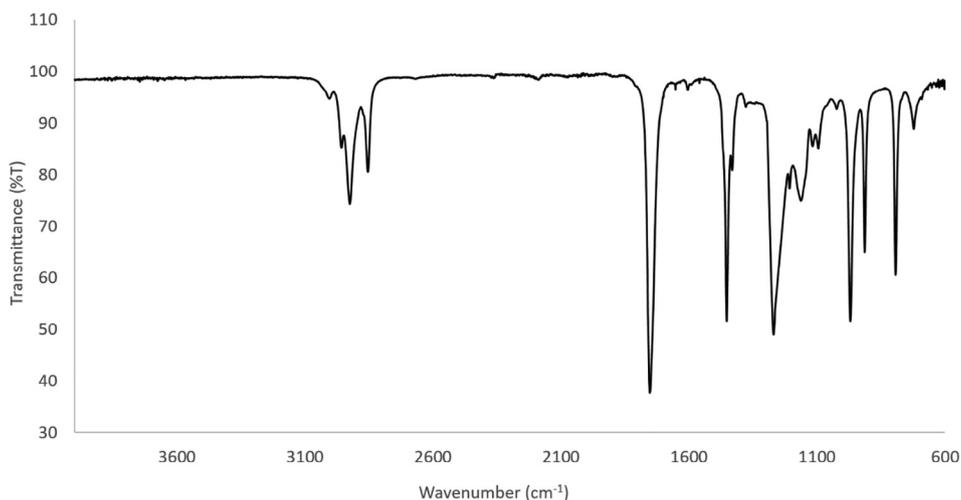


Fig. 6. FTIR spectrum of biodiesel produced.

Table 8
The major FAME peaks observed from the standard substances.

Standard substances	Retention time (min)	Peak height (pA)
Methyl palmitate	15.883	2.37057
	16.859	1.44923
	17.924	1291.87805
	18.181	1.19105
	18.897	5.57697
Methyl oleate	19.841	22.84579
	17.867	1.58817
	18.849	62.71737
	19.829	319.21646
	21.094	950.26593
Methyl linoleate	22.903	3.00086
	18.897	7.67058
	19.842	29.12728
	20.966	3.03491
	21.986	695.84717

Table 9
The properties of biodiesel produced and its comparison with EN14214.

	Unit	Biodiesel sample produced	EN14214
Density, ρ	kg/m ³	885	860–900
Viscosity, ν	cSt @ 40 °C	4	3.5–5
Flash point, FP	°C	110	> 101
Total acid number	TAN	0.35	< 0.5
Water content	%	0.02	< 0.05
High Heating Value, HHV ¹	MJ/kg	40.85	–
Cetane number ²	–	57.5	> 51

¹ High heating value was calculated using the equation: $HHV = -0.0259\rho + 63.776$ [30].

² Cetane number was calculated based on the equation: $CN = 152.43\rho + 0.3423FP + 0.108HHV - 0.021\nu + 152.43$ [30].

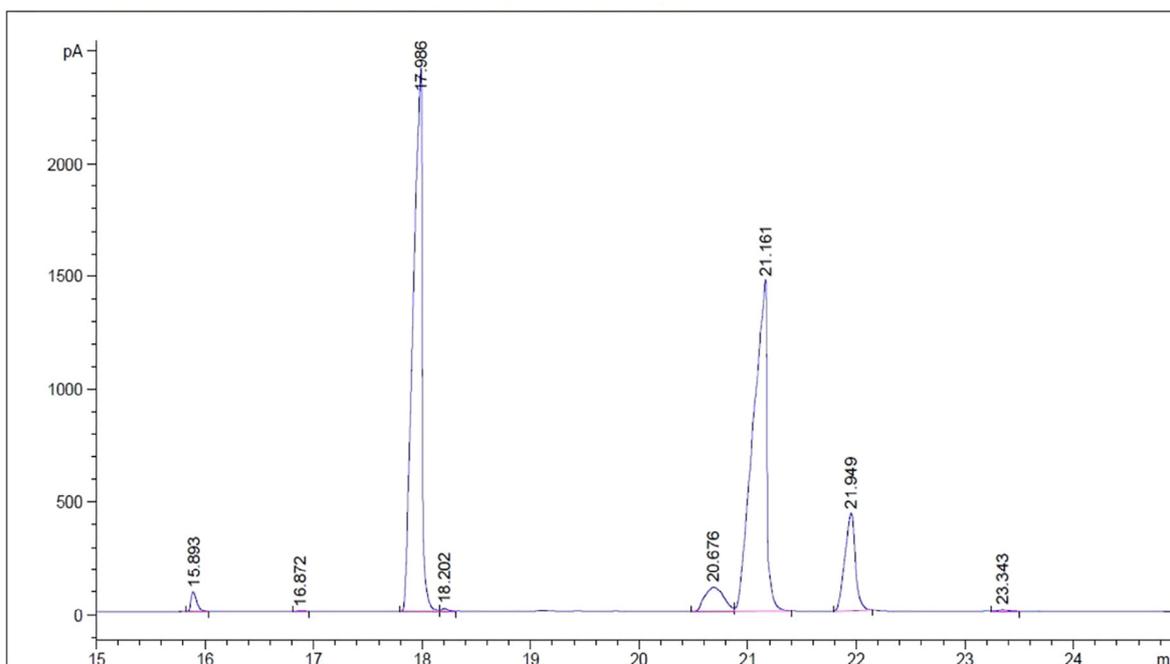


Fig. 7. GC chromatogram of biodiesel produced.

activation energy and pre-exponential factor obtained were found to be 44.88 kJ/mol and $7.88 \times 10^3 \text{ min}^{-1}$, respectively. The biodiesel produced meets the EN14214 biodiesel standard and this method shows prospects to solve the problems associated with conventional catalytic and non-catalytic transesterification, such as low adaptability of low-cost feedstocks, the requirement of complicated catalyst preparation process, and the requirement of higher energy input.

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Declaration of Competing Interest

The authors declare no conflict of interest.

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