

# A facile noncatalytic methyl ester production from waste chicken tallow using single step subcritical methanol: Optimization study

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## Summary

In this modern era, an increase in urbanization causes the escalating trend of fuel demand as well as environmental pollution problems. Various biofuels research with the respect of climate change and emission reduction recently intensifies, particularly in biodiesel. In Indonesia, diesel oil currently in use contains 20% of biodiesel. Utilizing waste-based resources such as rendered chicken tallow as the feedstock could be the solution to both energy and environmental challenges. However, chicken tallow contains a significant amount of free fatty acid (FFA) which will obstruct the production yield of biodiesel. In this study, catalyst-free subcritical methanol has been employed to convert waste chicken tallow (WCT) with high FFA into biodiesel. Design of experiment was conducted to study the effect of temperature, time, and the molar ratio of methanol to fats on the purity and recovery of fatty acid methyl esters (FAMES). Based on the optimization study performed by response surface methodology (RSM), all three independent variables gave a significant effect on the recovery of FAME. From the experimental results, the maximum FAME yield obtained was  $98.43 \pm 0.22\%$  with the optimum condition as follows: 167°C, 36.8 minutes, and 42.7:1 (methanol/WCT, mol/mol), while the predicted FAME yield obtained using RSM was 97.76%. The methyl ester composition of WCT-based biodiesel ranges from C13 to C24.

## KEYWORDS

catalyst-free, facile transesterification, optimization study, renewable energy, subcritical methanol, waste chicken tallow, waste-derived biodiesel

## 1 | INTRODUCTION

Energy sustainability is regarded worldwide as one of the indicators of economic and infrastructure development of

a country.<sup>1</sup> To date, Indonesia uses fossil energy sources as much as 94%, and only the remaining 6% use the benefits of bioresource-based energy to meet the yearly energy requisites. Excessive use of fossil energy increases

**Abbreviation:** WCT, waste chicken tallow; FFA, free fatty acid; FAME(s), fatty acid methyl ester(s); RSM, response surface methodology; SpCM, supercritical methanol; SCM, subcritical methanol; GC-FID, gas chromatography-flame ionization detector; CCC-CCD, circumscribed central composite design

the depletion rate, and the availability of the sources of these fuels in nature will subsequently begin to decline. Another problem that arises from the use of fossil fuels is environmental pollution, caused by the emission of SO<sub>x</sub>, NO<sub>x</sub>, and CO<sub>2</sub>.<sup>2</sup>

With the depletion of petroleum reserves, various efforts have been taken to seek more sustainable and environmentally friendly alternative energy sources. In the last few decades, studies to find alternative sources of renewable energy have been widely performed with biodiesel as one of the most vastly studied renewable energy. Biodiesel derived from biological sources received extensive interest as it lowers the global reliance on petroleum products, the energy crisis, and pollution.<sup>3,4</sup> Various feedstocks including edible oils,<sup>1,5,6</sup> nonedible oils,<sup>7,8</sup> raw oils,<sup>9</sup> algae,<sup>10-12</sup> and animal fats,<sup>13,14</sup> as well as sundry of processing techniques, have been developed to produce high-quality biodiesel.

Several routes that have been studied for the conversion of lipid to biodiesel are as follows: the base-catalyzed transesterification,<sup>1,14</sup> two steps acidic esterification followed by alkaline transesterification<sup>9,13,15</sup>; enzyme-catalyzed esterification/transesterification<sup>3</sup> and noncatalytic transesterification using methanol under subcritical,<sup>5,12</sup> and supercritical conditions.<sup>10,16</sup> The selection of a suitable technique depends on the quality of fats.

Currently, Indonesia commercially produces biodiesel from edible oil, primarily from palm oil. However, the use of edible oils leads to food shortages. Thus, they are noneconomic and nonfeasible. Non-edible oil, particularly waste-based resources, is one of the best alternatives for biodiesel feedstock due to its lower cost and positive waste utilization. Waste-derived biodiesel also has the additional advantage of avoiding environmental impacts.

Indonesia produces more than 2 million tonnes of chicken annually,<sup>17</sup> where the fat content is around 13.6%.<sup>18</sup> Chicken tallow is usually discarded as waste due to a health hazard. In spite of that, waste chicken tallow (WCT) possesses a substantial amount of free fatty acids (FFA) and triglycerides which is able to be converted into biodiesel. Direct application of WCT as raw material for the production of biodiesel faces several problems since it is impossible to directly convert the tallow into biodiesel using transesterification. The presence of water in WCT induces the hydrolysis of triglycerides into FFA, and high level of FFA content (> 0.1%) in the tallow promotes the saponification reaction between FFA with base catalyst, leading to the lower conversion of WCT into biodiesel. Therefore, it requires at least one-step pretreatment to remove the water content and two-step esterification/transesterification process to achieve the commercial biodiesel conversion and yield.

Alptekin and Canakci (2010) investigated the two-step method to transform chicken oil with 15% FFA to biodiesel, with 90% of said FFA is esterified into methyl esters in the first step using 20% (wt) sulfuric acid (acting as an acidic catalyst). Subsequently, the transesterification between chicken oil, methanol, and water occurred in the second step, in the presence of caustic soda (NaOH) as a basic catalyst. The yield of biodiesel after the transesterification step is 87.4%.<sup>19</sup> Gürü et al (2010) reported a similar two-step esterification/transesterification route for the conversion of chicken oil to biodiesel and the optimum fatty acid methyl ester (FAME) recovery obtained is 89%.<sup>20</sup>

However, the use of the two-step process will certainly escalate the processing and maintenance costs, thus leading to economic inability to use chicken tallow as raw material for biodiesel. Correct modification of reaction design and operation will be able to reduce the steps of the downstream process and significantly increase savings in the cost of separation. It is important to single out a suitable, environmentally and economically friendly technique to transform this resource.

Methanol under subcritical and supercritical condition has attracted much attention since their degree of hydrogen bonding, cluster formation, ion solvation, and ion association make them widely known as novel reaction medium.<sup>21,22</sup> Ong et al (2013) reported the biodiesel production from *Ceiba pentandra* (kapok) oil via catalyst-free supercritical methanol (SpCM) transesterification with the optimum FAME yield of 95.5% at 322°C, 16.7 MPa, 476 seconds of reaction time and 30:1 of methanol to oil molar ratio.<sup>16</sup> Meanwhile, Gunawan et al (2014) evaluated the transesterification of vegetable oils wastewater sludge to biodiesel using methanol under subcritical condition, with the highest yield of FAME (92.67 ± 2.23%) obtained at 215°C, 6.5 MPa, and 5:1 of methanol to lipid mass ratio.<sup>8</sup> Huynh et al (2012) also reported that the noncatalytic subcritical methanol (SCM) method has successfully converted 90% of activated sludge to FAME.<sup>23</sup>

In this study, WCT was converted into biodiesel using methanol under subcritical condition. Compared with the conventional technique, SCM is a strategic choice in biodiesel production since it promotes the simultaneous reaction of esterification and transesterification, it does not require a catalyst, and the time needed to convert raw material to biodiesel is shorter. SCM also operates in moderate temperature and pressure, indicating higher process security and lower capital costs as compared with the SpCM technique. According to Ju et al (2013), the SCM method is tolerant of high water and high FFA content, where it still produces high yield biodiesel regardless of the raw material quality.<sup>5</sup>

To date, there is no research conducted on the conversion of WCT to biodiesel using the noncatalytic SCM technique as well as its optimization approach, even though a large amount of WCT is produced annually. This study focuses on the utilization of WCT as raw material to produce biodiesel with high purity and recovery under SCM condition. The optimum point of processing variables (temperature, reaction time, and alcohol to fats molar ratio) was determined using response surface methodology (RSM) optimization approach.

## 2 | MATERIALS AND METHODS

### 2.1 | Materials

WCT was obtained from a local market in Surabaya, Indonesia. Methanol (99.9%) and n-hexane (90%) were of technical grade and obtained from Merck, Germany, while reagents used in the gas chromatography-flame ionization detector (GC-FID) were of either HPLC grade or analytical grade. The standard of FAME mixture (37 Component FAME mix, 47885 U) was purchased from Supelco (Bellefonte, PA, USA). Ultra-high purity grade nitrogen and helium gases (99.9%) were supplied by Aneka Gas Industry Pty. Ltd., Surabaya.

### 2.2 | Experimental design and optimization

The process optimization using the design of experiments (DOE) was statistically employed using RSM, coupled with the standard design tool known as Circumscribed ( $\alpha = 1.682$ ) Central Composite Design (CCC-CCD). Three optimized variables were reaction temperature ( $^{\circ}\text{C}$ ), time (min), and the molar ratio of methanol to WCT (mol/mol). The coded variables and their correlative values were presented in Table 1. The independent variables are encoded into three levels: low ( $-1$ ), high ( $+1$ ), and center point ( $0$ ), whereas the axial values of this CCC-CCD are coded as  $\pm \alpha$  ( $\pm 1.682$ ). The choice of reaction

**TABLE 1** The coded parameters and their corresponding values in the experimental design

Reaction Parameter	Encoded Factor	Factor Level				
		$-1.682$	$-1$	$0$	$1$	$1.682$
Temperature ( $^{\circ}\text{C}$ )	$X_1$	83	100	125	150	167
Time (min)	$X_2$	3.2	10	20	30	36.8
Molar ratio of methanol to WCT (mol/mol)	$X_3$	13.7:1	28:1	49:1	70:1	84.3:1

parameters, as well as its factor level used in the experiments, was based on the direct relevance of these parameters to the process efficiency, safety concern, and its economic feasibility to be scaled up to an industrial scale.

The matrix of CCC-CCD in regards to the actual and encoded independent variable is listed along with the results in Table 2. To obtain a good reproducibility, all experiments were conducted in triplicates with their average values regarded as the final result. Six replicates of central data point ( $0,0,0$ ) were carried out and expressed as individual data for every run.

The randomized order of experiments was performed with all the responses fitted into a quadratic regression model, developed using three-way analysis of variance (ANOVA), generated by Minitab (version 18.1) with 95% confidence level. The goodness-of-fit for the mathematical regression model was statistically assessed by the coefficient of determination ( $R^2$ ) and the lack-of-fit sum of squares. Response surface plots were generated from the regression analysis of experimental results by holding one parameter constant while changing the other two parameters.

**TABLE 2** The experimental design matrix based on CCC-CCD

Run	Input Parameters			Response (FAME Yield, %)	
	$X_1$	$X_2$	$X_3$	Experimental <sup>a</sup>	Prediction <sup>a</sup>
1	0	0	0	84.21	84.80
2	0	0	0	84.74	84.80
3	$-1$	1	$-1$	66.92	66.59
4	$-1$	1	1	77.53	77.41
5	0	0	0	85.85	84.80
6	0	1.682	0	87.31	88.98
7	0	0	0	84.86	84.80
8	1	$-1$	1	80.99	81.08
9	0	0	$-1.682$	66.14	66.13
10	1.682	0	0	87.42	88.82
11	0	0	0	86.23	84.80
12	$-1.682$	0	0	66.09	65.03
13	0	0	0	82.98	84.80
14	0	$-1.682$	0	79.14	77.82
15	$-1$	$-1$	1	75.48	76.23
16	1	1	$-1$	91.04	90.04
17	1	$-1$	$-1$	78.07	77.95
18	1	1	1	88.74	87.20
19	$-1$	$-1$	$-1$	58.16	59.45
20	0	0	1.682	77.49	77.86

<sup>a</sup>The average standard error of estimate (SEE) between the experimental result and its corresponding predicted response was 1.06%.

The predicted optimization results between the yield of FAME (%) as the response parameter and the independent variables are represented by Equation (1), where  $Y$  is the predicted yield of FAME (%);  $k_0$ ,  $k_i$ ,  $k_{ii}$ , and  $k_{ij}$  are the coefficients obtained from the regression for the intercept, linear, quadratic, and interactions of the independent variables, respectively;  $X_i$  and  $X_j$  are the encoded design parameters.

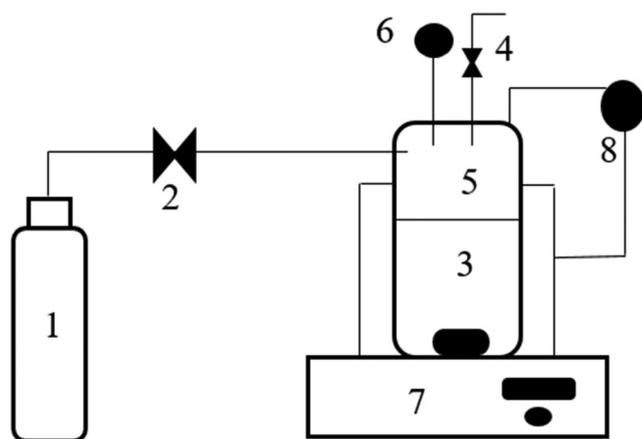
$$Y = k_0 + \sum_{i=1}^3 k_i X_i + \sum_{i=1}^3 k_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=1}^3 k_{ij} X_i X_j \quad (1)$$

### 2.3 | Biodiesel production from WCT using SCM method

The biodiesel production from WCT was conducted in a 150-cm<sup>3</sup> cylindrical reactor, made of stainless steel type 316 and is completed with a pressure gauge (0-70 kg/cm<sup>2</sup> scale), thermocouple, and heater (Figure 1). Various amounts of WCT (26.0-70.0 g) and methanol (35.1-108.0 mL) were added into the reactor vessel to attain the desired molar ratio of methanol to WCT. The average molecular weight of WCT was calculated using the following equation:

$$\begin{aligned} \text{Molecular weight of WCT} \left( M_{WCT}, \frac{\text{g}}{\text{mol}} \right) \\ = 56.1 \times 1000 \times \frac{3}{(SV - AV)} \end{aligned} \quad (2)$$

where SV is the saponification value of WCT ( $\frac{m_{KOH}}{m_{oil}}$ , mg/g), and AV is the acid value of WCT ( $\frac{m_{KOH}}{m_{oil}}$ , mg/g).<sup>24-26</sup> After the sample was put in the chamber,



**FIGURE 1** Subcritical reactor system. (a) Nitrogen cylinder; (b) safety valve; (c) magnetic-stirring bar; (d) safety valve; (e) reactor; (f) pressure gauge; (g) agitation controller; (h) thermocouple

the reactor and its cap were then properly tightened using M8 screws.

The reactor was heated with steady heat flow (the rate of temperature increment is 20°C/min) until it reached the desired temperature. To remove air and increase the pressure, nitrogen gas at the rate of 3 mL/min was purged into the system until it reached 45 bar. The reaction begins once the desired temperature and pressure are achieved. The mixture was stirred at the constant agitation speed (500 rpm) to keep the system homogenous. Throughout the process, the isobaric and isothermal condition was maintained by controlling the heating rate and nitrogen gas injection.

After the reaction had completed, the system was immediately cooled down to room temperature. The separation of FAME was carried out using liquid-liquid extraction. The liquid mixture and 100 mL of n-hexane as the extracting solvent were introduced into a separatory funnel for the extraction process. The mixture was then allowed to settle, and subsequently, two layers were formed in the separatory funnel. The upper layer contains n-hexane and FAMES, while the bottom layer was glycerol, unreacted methanol, and other byproducts. The bottom phase was rewashed for two times using the same amount of n-hexane to confirm that all FAMES had been extracted. Afterward, the FAME was obtained by evaporating n-hexane using a rotary evaporator (IKA RV 10B).

### 2.4 | FAME analysis using GC-FID analysis

The analysis of FAME purity and composition was performed using GC, completely equipped with a split-splitless injector and an FID. The incorporated silica column used was DB-WAX capillary column (30 m × 0.25 mm ID × 0.25 μm film thickness, Agilent Technology, CA). FAME sample (50 mg) was dissolved in 1 mL of 0.01 g/mL internal standard (methyl heptadecanoate, MH) solution; 1 μL of the as-prepared sample was injected with a split ratio of 1:50. The initial column temperature was 50°C and held for 15 minutes; then, the temperature was ramped to 220°C at 4°C/min. The final temperature was held constant for another 15 minutes. The total analysis time was 72.5 minutes. The temperature of injector and detector was set constant at 250°C and 260°C, respectively. The velocity of carrier gas (helium, 99.9%) was adjusted at 30 cm/s.

External FAME reference (47885 U, containing 37 components FAME standard mix) was used for the identification of methyl ester peaks in the sample; as well as for the calibration of the instrument along with methyl

heptadecanoate solution as internal standard (IS). The purity of FAME in the sample was calculated as follows:

$$\text{FAME purity } (F_p, \%) = \left( \frac{\sum A_{\text{FAME}} - A_{\text{MH}}}{A_{\text{MH}}} \times \frac{V_{\text{MH}} C_{\text{MH}}}{m} \right) \times 100\% \quad (3)$$

where  $\sum A_{\text{FAME}}$  is the area sum of FAME peaks,  $A_{\text{MH}}$  is the corresponding area of MH peak,  $V_{\text{MH}}$  is the volume of MH solution (mL),  $C_{\text{MH}}$  is the actual concentration of MH solution (g/mL), and  $m$  is the actual weight of the FAME sample (g). Meanwhile, the yield of FAME based on the lipid weight fraction was determined using the following equation:

$$\text{Yield of FAME } (\%) = \left( \frac{m_{\text{FAME}}}{m_{\text{WCT}}} \times F_p \right) \times 100\% \quad (4)$$

where  $m_{\text{FAME}}$  is the weight of FAME obtained after the reaction and separation process (g),  $m_{\text{WCT}}$  is the weight of the initial WCT sample (g), and  $F_p$  is the FAME weight fraction obtained from Equation (3).

### 3 | RESULTS AND DISCUSSIONS

#### 3.1 | Characteristics of WCT

The characteristics of WCT have been analyzed in accordance with the standard method of AOAC 950.46, AOAC 991.36, AOCS Ca 5a-40, and ISO 12966 to determine water content, crude fat content, FFA content, and fatty acid profile, respectively. According to the results, WCT possesses high FFA and moisture content, with the corresponding value of 0.91% and 17.79%. The fatty acid profile in WCT consists of 11.77% tridecanoic acid (C13:0), 5.71% myristoleic acid (C14:1), 5.82% palmitoleic acid (C16:1), 2.19% linoleic acid (C18:2), 33.43% eicosenoic acid (C20:1), 11.15% erucic acid (C22:1), 25.92% docosadienoic acid (C22:2), 1.23% docosahexaenoic acid (C22:6), 1.37% lignoceric acid (C24:0), and 1.41% nervonic acid (C24:1). WCT also contains quite a significant amount of crude fat, including triglycerides, diglycerides, monoglycerides, phospholipids, and sterols. It covers 72.04% of the total mass of WCT. Canakci and Gerpen (2001) reported that biodiesel production using fat with high FFA content, more or less 1%, through base-catalyzed transesterification leads to the formation of soap due to saponification reaction.<sup>27</sup> High water content also interferes the conventional production of biodiesel. Water is able to hydrolyze fats into FFA, which then leads to the saponification reaction. This phenomenon subsequently decreases the yield of biodiesel and causes difficulty in the separation. However, in the SCM

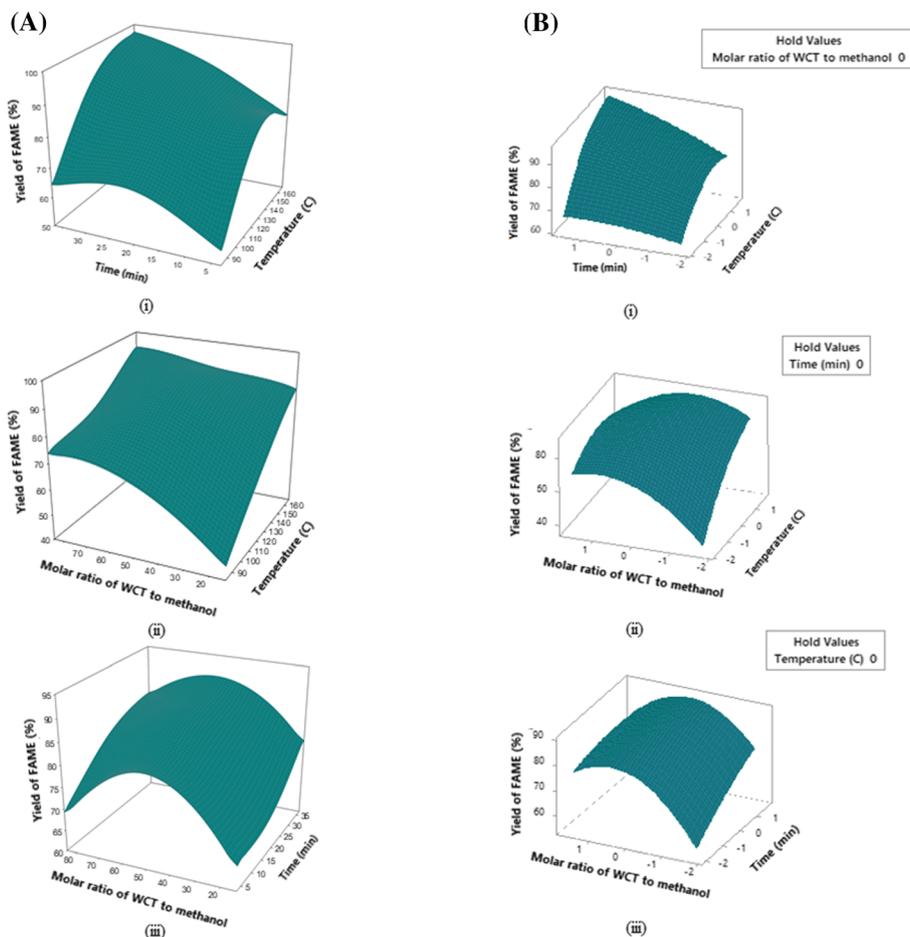
method, high water content is required to promote the simultaneous esterification/transesterification reaction, where FFA is concurrently extracted from the raw material and esterified into fatty esters.<sup>8</sup> Ju et al (2013) also described that under subcritical condition, high water, and FFA content can be tolerated and still able to yield a high amount of biodiesel.<sup>5</sup>

#### 3.2 | Reaction parameter study

The interaction effect between two reaction parameters on the yield of FAME is shown in Figure 2A(i) to (iii). The experimental results revealed that the increase of temperature from the lowest level (83°C) to level 1 (150°C) greatly improve the FAME yield regardless of the processing time. Reaction temperature played a major role in influencing the chemical reaction inside the vessel. Both esterification and transesterification reactions are known as reversible and highly endothermic. Based on the Arrhenius law, the escalating reaction temperature affects the rate constant and stimulates the reaction to shift to the product (right-hand) side.

At room temperature, both water and methanol have low miscibility with WCT. However, their dielectric constant was significantly reduced at high temperature, rendering the mixture system to be more homogenous. The elevation of temperature caused a weakening of hydrogen bonding between the water molecules as well as that of the hydroxyl group in methanol, magnifying their miscibility in the lipid phase.<sup>28</sup> Chin et al (2009) reported that that higher temperature in the reaction process causes an increase in the intrinsic reaction rate constant.<sup>29</sup> Furthermore, from the kinetic perspective, enhanced FAME yield at a higher level of temperature was likely attributed to the higher rate of mass transfer and diffusivity between the reactants, generated due to higher miscibility among them.

Another reason is the existence of the water inside the system, which hydrolyzed the lipids to form FFA. As the hydrolysis progresses, more FFA formed increased the miscibility between water and lipid phase, and certainly, the diffusion rate of reactants. FFA is also known to be highly reactive with methanol as compared with the acyl glycerides, which lead to a better yield of FAME. High water content in the WCT might as well promote the esterification/transesterification reaction between FFA/triglycerides and methanol to form biodiesel. The rate of dissociation of water into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  significantly enhances by increasing the temperature. The presence of hydronium ion acts as an acid catalyst for the esterification reaction between FFA with methanol, while the hydroxide ion acts as the base catalyst for the



**FIGURE 2** The yield of FAME (%) based on (a) the experimental results, (b) the 3D response surface plot, with the interaction between (i) temperature and time, (ii) temperature and molar ratio of methanol to WCT, and (iii) time and molar ratio of methanol to WCT [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

transesterification of WCT and methanol. Therefore, with a sufficient number of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions in the system, this simultaneous reaction can occur more intensively to produce a higher yield of FAME.<sup>8</sup>

It was observed from Figure 2A(i) that the biodiesel yield reached the plateau point near the highest level of temperature. On top of that, in some levels of reaction time (−1.682 and −1), a further escalation in temperature resulted in the slight decline of FAME yield. Wang et al (2018) also reported that a positive effect on the FAME yield was obtained by increasing the temperature from 50°C to 90°C. Further rise of reaction temperature did not increase the FAME yield significantly.<sup>30</sup> This phenomenon was likely due to the thermal decomposition caused by the carbon-chain splitting into shorter ones. The thermal decomposition product consists of smaller molecular weight of fatty esters in the range of C13 to C14. Marulanda et al (2010) and Shin et al (2011) also stated that increasing temperature might improve the chance of partial degradation to occur during the process, particularly for the unsaturated FAMES in the mixture.<sup>31,32</sup> Ortiz-Martinez et al (2019) mentioned that

although high temperature generally increases FAME yield, thermal decomposition of the product can occur above certain values.<sup>33</sup>

The effect of reaction time was investigated at five different levels of the time period from 3.2 minutes (−1.682) to 36.8 minutes (1.682). Figure 2A(i) and (iii) showed that either in the constant temperature or molar ratio of methanol to WCT, a moderate increase of FAME yield was observed by prolonging the duration of reaction time from the lowest to the highest level. Allowing longer contact between the subcritical methanol, water, and lipid phase ensures the conversion of triglycerides and FFA into FAME through the simultaneous esterification-transesterification process. However, even though the duration of reaction gave an advantageous effect on the FAME yield, its significance was incomparable to the effect of temperature.

The required stoichiometric ratio of methanol to lipid in the production of biodiesel via transesterification method to form 3 moles of fatty esters and 1 mole of glycerol is 3:1. The transesterification itself is a reversible reaction; thus, it is commonly carried out by using the

excess alcohol to purposely shift the chemical equilibrium to the right-hand side to ensure high conversion of FAME within a short time.<sup>34,35</sup> In accordance with the experimental results, the addition of excess methanol to the system from the ratio of 13.7:1 (−1.682) to 49:1 (0) greatly increases the FAME yield by 1.5 folds. It is likely due to the more frequent interaction between the lipid and methanol, triggering the formation of FAME. Gunawan et al (2014) also mentioned that excess methanol to WCT molar ratio seems to be favorable toward the biodiesel yield to a certain extent.<sup>8</sup> However, as seen in Figure 2 A(ii) and (iii), a remarkable declining trend in FAME yield was monitored by the further addition of excess methanol to the highest level of the molar ratio of methanol to WCT. Encinar et al (2005) reported that further addition of excess methanol tends to give a negative response on the product yield since the presence of excess glycerol reversed the transesterification to the reactant side. An increase in the concentration of FAME and glycerol in the system during reaction will lead to the recombination of products to monoglycerides, resulting in the lower yield.<sup>36</sup> Thoai et al (2017) also mentioned that high methanol to oil molar ratio gives a lower mono-, di-, triglycerides concentration that makes disadvantages for the reaction since both alcohol and oil are needed to promote the reaction rate.<sup>37</sup> Moreover, higher methanol content in the system would also drive the extraction of compounds with higher polarity, namely phenols and proteins which hindered the fatty esters formation.<sup>23</sup> As a matter of fact, the enhanced amount of excess methanol above the optimum value will not only decrease the product yield but also escalate the raw material and rectification processing costs.

### 3.3 | Statistical analysis and development of optimization model using response surface methodology (RSM)

Statistically, RSM depicts the relationship between several independent input variables and single or multiple responses. Its primary goal is to employ a series of designed experiments to determine the optimum value of the response variable. SCM technique provides many benefits as compared with the conventional ones, since it reduces the reaction time, eliminates the needs of catalyst as well as the pretreatment and separation cost. However, this method is an energy-intensive process which requires the use of high temperature and pressure. Therefore, the optimization process including the statistical analysis and development of the mathematical model are significant for the implementation of this technique on the industrial scale.

For this very reason, RSM was conducted to determine the optimal conditions for the production of FAME by integrating three important variables (temperature, reaction time, and methanol to WCT molar ratio) simultaneously. Circumscribed type of CCD (CCC-CCD) was used to design the experimental input parameters. Table 2 showed the correlation between the response and the sets of coded input parameters. The response of the experimental design was the yield of FAME (%), and the average standard error of estimate (SEE) between the experimental and predicted results were found to be fairly close to each other, with the value of 1.06% ( $n = 20$ ). As shown in Equation (1), the second-order polynomial equation, as a function of the independent variables, was suggested by the RSM using the least square analysis.

The result of the statistical ANOVA applied in determining the significance of the independent variable individually, quadratically as well as their interactions were presented in Table 3. Probability of error value, known as  $P$  value, is a parameter to analyze the significance of each regression coefficient. Smaller  $P$  value indicated that the term was statistically more significant. Based on the ANOVA results, the mathematical model suggested that all the terms except that of reaction time ( $(X_2)^2$ ,  $P$  value  $>0.05$ ) were significant. All linear terms were equally significant, while the similarly notable quadratic terms were temperature ( $X_1$ )<sup>2</sup> and methanol to WCT molar ratio ( $X_3$ )<sup>2</sup>. The two-way interactions were found to be prominent between ( $X_1$ )( $X_2$ ), ( $X_1$ )( $X_3$ ), and ( $X_2$ )( $X_3$ ), with the significance order of temperature/molar ratio of methanol to WCT  $>$  time/molar ratio of methanol to WCT  $>$  temperature/time. By inserting the coefficient values of the significant parameters to Equation (1), the mathematical model can be expressed by the given equation below:

**TABLE 3** The fitted values of regression coefficients and their significance for the calculation of yield of FAME

Term	Coefficient	SE Coefficient	T-Value	P Value
Constant	84.800	0.581	145.96	<0.0001
$X_1$	7.074	0.385	18.35	<0.0001
$X_2$	3.316	0.385	8.60	<0.0001
$X_3$	3.487	0.385	9.05	<0.0001
$X_1^2$	−2.784	0.375	−7.42	<0.0001
$X_2^2$	−0.495	0.375	−1.32	0.2160
$X_3^2$	−4.528	0.375	−12.07	<0.0001
$X_1X_2$	1.239	0.504	2.46	0.0340
$X_1X_3$	−3.414	0.504	−6.78	<0.0001
$X_2X_3$	−1.491	0.504	−2.96	0.0140

$$\begin{aligned}
 \text{Yield of FAME } (\%), Y = & 84.8 + 7.074(X_1) + 3.316(X_2) \\
 & + 3.487(X_3) - 2.784(X_1)^2 \\
 & - 4.528(X_3)^2 + 1.239(X_1)(X_2) \\
 & - 3.414(X_1)(X_3) \\
 & - 1.491(X_2)(X_3) \quad (5)
 \end{aligned}$$

where Y is the yield of FAME (%);  $X_1$ ,  $X_2$ , and  $X_3$  are the coded value of input variables (−1.682, −1, 0, 1, 1.682).

Equation (5) showed that the coefficients of intercept, linear variables ( $X_1$ ,  $X_2$ ,  $X_3$ ), and interaction variables of temperature and time ( $(X_1)(X_2)$ ) indicated the favorable effect to the FAME yield. On the other hand, the coefficient of quadratic variables ( $(X_1)^2$ ,  $(X_3)^2$ ) and the other two-way interaction variables of either temperature or time with the methanol to WCT molar ratio ( $(X_1)(X_3)$ ,  $(X_2)(X_3)$ ) gave the antagonistic effect to the response.

Table 4 showed the analysis of goodness of fit for the mathematical regression model using ANOVA. As presented in Table 4, the  $R$ -squared value of the coded model (Equation 5) was 0.9866, referring that 98.66% of the experimental data were able to be reasonably interpreted by the second-order polynomial equation above (Equation 5). The predicted and actual response of yield of FAME was also in a good agreement, pointed by the value of adjusted and predicted  $R$ -squared which were close to unity (0.9746 and 0.9258, respectively). Based on the lack of fit test results, the  $P$  value of the coded model is 0.235. This value indicated that the equation

derived by ANOVA was well-fitted to the experimental data. In the lack of fit test, the  $P$  value higher than 0.05 is highly desirable since  $P$  value lower than 0.05 represents that there might be the interaction of input variable and response that is not considered by the model. From the results of the statistical ANOVA, the model is deemed adequate to represent all the independent variance assumption.

The 3D response surface plots of the interactions between the two independent variables were presented by Figure 2B(i) to (iii). As shown in Figure 2B(i), the increase in the level of both temperature and time gave an overall positive influence on the yield of FAME. At the fixed molar ratio of methanol to WCT (49:1), the yield of FAME rose sharply along with the increment of temperature from 83°C (−1.682) to 150°C (1) at constant reaction time; however, further elevation in temperature to the highest level (1.682) leads to a reduction of the yield of FAME. A similar trend was monitored for the other level of reaction time at the same profile of temperature increment. The response was monitored to be rapidly escalated before it reaches a stagnant line close to the highest level of temperature. It is also evident from the figure that the temperature gives a more significant effect on the yield of FAME than reaction time.

Figure 2B(ii) depicted the correlation between temperature and methanol to WCT molar ratio to the FAME yield. Based on this response surface plot, it can be seen that the maximum yield of FAME was

**TABLE 4** The analysis of variance (ANOVA) for the fitted regression model

Source	DF	Sum of Squares	Mean Squares	F-Value	P-Value
Model	9	1498.30	166.478	82.04	<0.0001
$X_1$	1	683.49	683.493	336.81	<0.0001
$X_2$	1	150.13	150.130	73.98	<0.0001
$X_3$	1	166.07	166.074	81.84	<0.0001
$X_1^2$	1	111.73	111.734	55.06	<0.0001
$X_2^2$	1	3.54	3.535	1.74	0.2160
$X_3^2$	1	295.52	295.517	145.63	<0.0001
$X_1X_2$	1	12.28	12.284	6.05	0.0340
$X_1X_3$	1	93.27	93.265	45.96	<0.0001
$X_2X_3$	1	17.79	17.794	8.77	0.0140
Error	10	20.29	2.029		
Lack-of-fit	5	13.49	2.698	1.98	0.235
Pure error	5	6.80	1.361		
Total	19	1518.60			
$R$ -squared ( $R^2$ )	0.9866	Adjusted $R^2$	0.9746	Predicted $R^2$	0.9258

obtained at the middle level of both factors. Further increase in the molar ratio of methanol to WCT and temperature resulted in a gradual decrease and in significant increase of the FAME yield, respectively. A consistent effect of the molar ratio of methanol to WCT on the yield was also monitored in Figure 2B(iii), with the factor gave maximum response at the middle level, while prolonged reaction time caused a steady increase of the yield of FAME.

The optimization of biodiesel production was performed to find the optimum levels of combined process variables at which the maximum response is attained. The solution with these independent variables (temperature, reaction time, and methanol to WCT molar ratio) were generated by Minitab software (version 18.1) based on the model obtained and the experimental data input (Table 2). The optimal variable of the transesterification process of WCT into biodiesel are as shown in Figure 3: temperature of 167°C (1.682), the reaction time of 36.8 min (1.682), and methanol to WCT molar ratio of 42.7:1 (-0.5266). The predicted yield of FAME under this optimum condition was 97.76% with model desirability of 1.00. Three replicated experiments were conducted using these optimal variables to verify the reliability of the prediction. Based on the experimental results, the optimum yield of FAME was  $98.43 \pm 0.22\%$  with the purity of 97.17%. The result at the optimum point indicated that the experimental and predicted values were close to each other, with the error of only 0.89%. Thus, it can be concluded that the established model is highly reliable and possesses adequate accuracy in predicting the biodiesel yield using the reaction parameters within the levels. This optimization results with high temperature (167°C) and low molar ratio of methanol to WCT (42.7:1) are generally highly desirable in the industries since on the process economic viewpoint, the operating expenditures at high

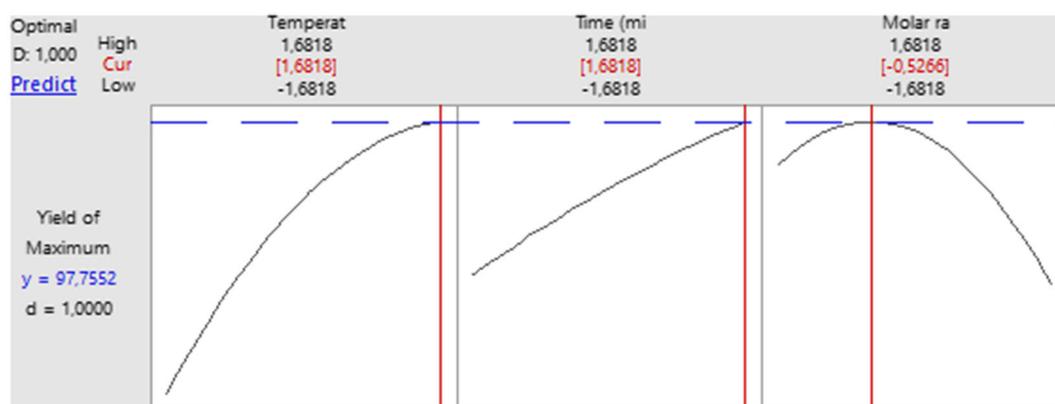
temperature are much less important than the cost of raw materials.<sup>38</sup>

### 3.4 | Chemical composition of WCT-based biodiesel

The resulting biodiesel obtained at the optimum condition (temperature of 167°C, the reaction time of 36.8 min, and the molar ratio of methanol to WCT of 42.7:1) was analyzed by using GC-FID for its purity and chemical composition. The purity of the FAME obtained from the analysis was 97.17%, higher than that required in ASTM D6751 (96.5% purity). The chemical composition of FAME was obtained by comparing the peaks of methyl esters in the chromatogram with that of the external FAME standard (47885 U, containing 37 components FAME standard mix). There are 11 identified peaks in the chromatogram, namely tridecanoic acid methyl ester (C13:0), myristoleic acid methyl ester (C14:1), palmitoleic acid methyl ester (C16:1), both cis- and trans-linoleic acid methyl ester (C16:2), eicosenoic acid methyl ester (C20:1), erucic acid methyl ester (C22:1), docosadienoic acid methyl ester (C22:2), docosahexaenoic acid methyl ester (C22:6), lignoceric acid methyl ester (C24:0), and nervonic acid methyl ester (C24:1).

### 3.5 | Properties of WCT-based biodiesel

The properties of WCT-based methyl esters are presented in Table 5. These properties are required to meet international standards such as ASTM D6751 to be defined as biodiesel. The results were also compared with the properties of biodiesel prepared from chicken fat using the conventional method<sup>19</sup> and diesel fuel specifications (ASTM D975-08). As seen in Table 5, the flashpoint of



**FIGURE 3** Response optimization plot of the three independent reaction parameters (D —composite desirability, y = predicted response, d = desirability) [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**TABLE 5** Fuel properties of WCT-based biodiesel and its comparison with ASTM D6751, diesel fuel (ASTM D975-08), and a similar study by Alptekin and Canakci (2010)<sup>19</sup>

Properties	Methods	Unit	WCT-Based Methyl Ester	Chicken Fat Methyl Ester <sup>19</sup>	ASTM D6751	Diesel Fuel (ASTM D975-08)
Density (at 15°C)	ASTM D4052	g cm <sup>-3</sup>	0.869	0.883	-	-
Kinematic viscosity (at 40°C)	ASTM D445	mm <sup>2</sup> s <sup>-1</sup>	2.13	4.94	1.9 – 6.0	1D: 1.3-2.42D: 1.9-4.1
Flash point	ASTM D93	°C	97.2	171.8	93 min	1D: 38 min2D: 52 min
Acid value	ASTM D664	mg KOH/g	0.19	0.22	0.50 max	-
Calorific value	ASTM D240	MJ kg <sup>-1</sup>	39.752	40.173	-	-

WCT-based biodiesel is close to the minimum value required by the ASTM D6751, indicating the low activation energy needed for combustion and feasibility of this fuel to be used in the diesel engine without extensive modification. This goes as well for the kinematic viscosity, which is one of the most critical properties in biodiesel that is related to the fluidity performance. According to ASTM D975-08 standards, WCT-based biodiesel possesses kinematic viscosity that is comparable to the diesel fuel, emphasizing the possibility of the product to be used widely as a petrodiesel blend. Both density and acid value are also suitable for the standards. The calorific value of WCT-based biodiesel was found to be comparable to the study conducted by Alptekin and Canakci (2010),<sup>19</sup> but slightly lower than the usual petro-diesel (42-46 MJ/kg).<sup>39</sup> Based on the summarized fuel properties (Table 5), it can be concluded that the measured properties met the requirements, indicating that the biodiesel produced from WCT can be used as an energy replacement for diesel fuel.

#### 4 | CONCLUSIONS

WCT is an appealing alternative resource to produce biodiesel using the catalyst-free subcritical methanol (SCM) method. RSM and three-way ANOVA have been well employed to design, predict, and optimize the experiments, by integrating three independent variables (temperature, reaction time, and methanol to WCT molar ratio). High biodiesel recovery of  $98.43 \pm 0.22\%$  with high purity (97.17%) was obtained as the maximum result in this optimized SCM process at 167°C, 36.8 minutes, and methanol to WCT molar ratio of 42.7:1. The predicted value of FAME yield in this optimum point is 97.76%. The actual and predicted values are in direct agreement, with an error of 0.89%. The analysis of goodness of fit showed that the second-order polynomial regression conforms with the experimental results, with the *P* value of lack-of-fit analysis higher than 0.05

and the adjusted coefficient of determination close to unity (0.9746). The properties of WCT-based biodiesel are in accordance with ASTM D6751 and ASTM D975-08. This study indicated that SCM is a prospective technique to replace the traditional process in the utilization of WCT as low-cost raw materials for biodiesel production since it is more sustainable and environmentally friendly compared with the latter. Further study on the use of the SCM method to convert WCT to FAME is still being done to determine its feasibility to be scaled up to the mass production.

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