



# A combination of $2^k$ factorial with Box-Behnken designs for FAME production via methanolysis of waste cooking palm oil over low-cost catalyst

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## ABSTRACT

In this work, a synthesis of fatty acid methyl ester (FAME) or biodiesel was systematically investigated via transesterification of waste cooking palm oil in the presence of methanol and KOH/activated carbon catalyst. The support was prepared via physical and chemical activation processes using an inedible/waste fruit (*Terminalia catappa*) as a carbon source. The KOH/activated carbon catalyst was easily prepared via impregnation method. The physicochemical properties of catalysts, palm oil and FAME were studied in details.  $2^k$  factorial design exhibited three significant factors which were in the order of catalyst loading > molar ratio of oil to methanol > reaction time. A maximum yield of FAME (91.05%) was successfully obtained from the actual experiment with Box-Behnken design ( $R^2 > 0.9$  and 1.1% error), providing the optimum conditions: catalyst loading (3 wt.% of oil), molar ratio of oil to methanol (1:15), reaction time (120 min) and reaction temperature (80 °C). The density, viscosity, flash point, acid value and iodine value in obtained FAME were 866 Kg/m<sup>3</sup>, 3.61 cSt, 167 °C, 0.46 mg of KOH/g and 2.08 g of I<sub>2</sub>/100 g of oil, respectively, which could be applied for diesel engine, complying with ASTM specifications.

## 1. Introduction

Nowadays, the demand of energy increases to some extent due to ever-increasing worldwide population, industrialization, rapidly economic growth and sustainable development. This increasing demand possibly results in depleting of petroleum derived fossil fuels in the future [1]. Therefore, it is necessary to search the renewable resources for solving the problem as mentioned above. Biofuels are very interesting choice to outdo the energy crisis since biomass/waste feedstocks are obtainable independently for the production of biodiesel or fatty acid methyl ester (FAME), bioethanol and biogas by different technologies [2]. Among of them, FAME production has been identified as a renewable energy since it presents similarity to petroleum-based diesel properties [3]. It has become an eco-friendly and alternative fuel for diesel engines due to its environmental benefits, biodegradability and low emissions of CO, hydrocarbons and particulates. The FAME product can be produced together with glycerol by-product from vegetable oil via transesterification reaction in the existence of methanol and catalysts [4]. This should be noted that vegetable oil consisting of triglyceride cannot be directly utilized to replace diesel due to its incomplete combustion, too high viscosity, leading to disadvantages to fuel

injection and cylinder block system of engine. As well known that oils are rich in triglycerides which add to its viscosity due to the high molecular weight of the triglycerides. Hence, transesterification reaction with an alcohol helps in breaking the bonds, providing rise to alkyl esters which have lower viscosity and better atomization properties when sprayed as a fuel in a combustion engine. The alkyl esters also have improved cold flow properties (such as pour point, cloud point, cold filter plugging point) which can be tested and reported [5].

In general, homogeneous base catalysts such as NaOH and KOH have been used in industrial practices or commercial process to produce FAME product. These base catalysts are able to catalyze in transesterification faster than acid catalysts [6,7]. Unfortunately, several drawbacks during production process are also occurred such as facile formation of soap, large amount of sewage, a low-grade glycerol with high impurities. It can lead to difficulties on separation and purification procedures of FAME, associating to high production cost [8]. On the other hand, heterogeneous base catalysts exhibit more eco-friendly and safer, which can be easily separated and recovered from mixture FAME solution. Also, unlikeable aqueous emulsion occurred from saponification can be avoided, leading to the decrease of production cost without separation process [9]. Recently, several types of heterogeneous

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catalysts applied for FAME production have been reported such as  $K_2CO_3/\gamma-Al_2O_3$  [10], KOH-loaded zeolite [11], sulfonated-multiwalled carbon nanotubes [12] and  $La_2O_3/ZrO_2$  [13]. Malins 2018 [14] reported that the application of heterogeneous alkaline catalysts such as  $K_3PO_4$ ,  $K_2CO_3$ ,  $Na_3PO_4$  and  $Na_2CO_3$  for conversion of rapeseed oil to FAME.  $Na_3PO_4$  and  $Na_2CO_3$  were found to be the most promising catalysts for practical application in FAME production since it could be recovered up to > 87% after transesterification process. Unfortunately, some disadvantages of these catalysts have been found such as low surface area and high production cost. Also, their preparation method are quite complication, which might be resulted for further application in industrial scale operation. To solve above problems, it is necessary to develop the low cost catalyst, which presents high catalytic performance for transesterification process [15]. Other essential consideration is the feasibility for KOH reclamation from economical point of view. Activated carbon derived from waste biomass feedstock can be directly applied as environmental/efficient/low-cost catalyst and catalyst support due its high surface area, porosity and abundant surface functional group such as carboxylic, phenolic and lactone [16,17].

With these backgrounds, we attempted to use the environmentally low cost/waste cooking oil and catalyst as feedstock for FAME production, which makes the process economical. For food industrial process, the recycling of waste cooking oil might be deleterious for human life due to the presence of risky compounds can be produced, which impair the food and oil quality. In this work, the KOH/activated carbons that having basic character, was tested in the transesterification of waste cooking palm oil. Activated carbon was prepared using an inedible fruit (*Terminalia catappa*) as a carbon source by chemical activation with 50%w/w  $H_2SO_4$ . The experimental designs by contribution of  $2^k$  factorial and Box-Behnken model for FAME production were utilized to investigate the significant factor and optimum conditions, respectively. Advantages of these designs are as follows: (I) the erroneousness of each factor and their interactions could be significantly decreased, and (II) lower number of experiments were conducted, resulting in a reduction of the FAME production cost [18,19]. A systematic study on the process factors such effects of catalyst loading, molar ratio of oil to methanol, reaction time and reaction temperature were performed to optimize FAME yield. The physicochemical properties of waste cooking palm oil and FAME were also measured and compared with the standard range of product specifications. This research provided the details based on cheap process which was expected to further apply for industrial FAME production.

## 2. Experimental

### 2.1. Materials and reagents

An inedible fruit (*Terminalia catappa*) was collected from Bangkok, Thailand, and used as carbon feedstocks for production of activated carbon. Proximate analysis was performed to determine the moisture (17.25%), ash (3.46%), volatile matter (59.65%) and fixed carbon (19.64%) of *Terminalia catappa* using ASTM D2867-95, D2866-94. The Waste cooking palm oil was obtained from local restaurant at Rangsit University, and its physiochemical properties are shown in Table 1. All

**Table 1**

The physicochemical properties of refined palm oil and waste cooking palm oil used in this work for FAME production.

Properties	Refined palm oil	Waste cooking palm oil
Density (kg/m <sup>3</sup> )	921–925	933.4
Viscosity (cSt) (25 °C)	80–90	102.5
Acid value (mgKOH/g)	< 11	4.85
Free fatty acids (%)	< 5	2.22
Saponification (mg of KOH/g)	190–209	199.34
Iodine value (g of I <sub>2</sub> /oil 100 g)	< 200	1.93

chemical reagents used were of analytical grade and purchased from Merck and Sigma Aldrich Companies.

### 2.2. Catalyst preparation

An inedible fruit (*Terminalia catappa*) was converted into carbon via pyrolysis at 500 °C for 2 h under the atmosphere. It should be mentioned that this pyrolysis temperature was selected based on DTG curve in thermal decomposition range of 200–500 °C (Fig. S1). Then, the obtained carbon were crushed and sieved through a 400 mesh sieve before activation procedure. Thereafter, it was mixed with 50%w/w of  $H_2SO_4$  solution at weight ratio of carbon to  $H_2SO_4$  (1:3), and then activated at 500 °C for 1 h. Finally, the obtained activated carbon were washed with distilled water until neutral pH. The KOH loading onto as-prepared activated carbon was carried out by impregnation method at weight ratio of KOH to activated carbon (1:1). 10 g of activated carbon was mixed with 100 ml of 10% w/v KOH solution, and stirred for 2 h and then dried at 105 °C in order to obtain a dry mass. To escape about the moisture matter, the obtained catalyst was collected in the desiccator before application for transesterification process. The details of catalyst characterization by XRD and SEM-EDS are provided in supporting information (SI).

### 2.3. Transesterification of waste cooking palm oil

The transesterification reaction was carried out using a 500 ml round bottom flask equipped with a condenser, a magnetic stirrer and a thermometer which was placed in an oil bath. In a typical run, certain amounts of methanol and catalyst were mixed together at the beginning. Afterward, transesterification was started by adding waste cooking palm oil preheated at 60 °C into the mixture solution under a stirring rate of 500 rpm. For DOE, the effects of catalyst loading based on KOH amount on activated carbon (1–6 wt% of oil), molar ratio of oil to methanol (1:10 to 10:20), reaction time (2–14 min) and reaction temperature (80–120 °C) were studied. After finishing procedure, the reaction was ceased by quenching in an ice bath. The mixture products were separated into two layers using a separation funnel. Here, upper layer or FAME + methanol phase was obtained while glycerol phase was in the bottom layer. The FAME product was washed with distilled water until neutral pH and dried at 105 °C.

### 2.4. Designs of experiment and optimization of response

The effects of independent input factors such as catalyst loading ( $X_1$ ), molar ratio of oil to methanol ( $X_2$ ), reaction time ( $X_3$ ) and reaction temperature ( $X_4$ ) on response of FAME yield were studied to investigate the significant levels by using  $2^k$  factorial design at confidence level of 95%. The factorial design consisting of sixteen experiments with low (-1) and high (1) values are presented in Table 2. The linear regression model for assigning the effect of each factor was given as follows in Eq. (1):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i < j} \beta_{ij} X_i X_j \quad (1)$$

Where  $Y$  is the percentage of FAME yield,  $\beta_0$  is the intercept/constant coefficient,  $\beta_i$  is the linear coefficients,  $\beta_{ij}$  is the interaction coefficient of each parameter and  $X_i$  and  $X_j$  are the codes of independent input parameters.

The optimization of transesterification for FAME production was determined using Box-Behnken model at three levels based on response surface methodology (RSM). This model was assigned from contribution of factorial design with an incomplete block, providing in the shape of a box. In addition, the internal structure of box was fixed by a wire frame which composed under edges of the box [20]. The experimental number for this model were defined as follows:  $N_{exp} = 2N_p(N_p-1) + N_{cp}$

**Table 2**  
Experimental conditions and FAME yields derived from 2<sup>4</sup> factorial design.<sup>a</sup>

Run	X <sub>1</sub> (wt.%)	X <sub>2</sub> (mol/mol)	X <sub>3</sub> (min)	X <sub>4</sub> (°C)	FAME yield (%)
1	1.0 (-1)	1:10 (-1)	60 (-1)	80 (-1)	35.3
2	6.0 (1)	1:10 (-1)	60 (-1)	80 (-1)	60.8
3	1.0 (-1)	1:20 (1)	60 (-1)	80 (-1)	54.3
4	6.0 (1)	1:20 (1)	60 (-1)	80 (-1)	70.5
5	1.0 (-1)	1:10 (-1)	300 (1)	80 (-1)	46.7
6	6.0 (1)	1:10 (-1)	300 (1)	80 (-1)	68.5
7	1.0 (-1)	1:20 (1)	300 (1)	80 (-1)	61.1
8	6.0 (1)	1:20 (1)	300 (1)	80 (-1)	86.3
9	1.0 (-1)	1:10 (-1)	60 (-1)	120 (1)	35.5
10	6.0 (1)	1:10 (-1)	60 (-1)	120 (1)	60.2
11	1.0 (-1)	1:20 (1)	60 (-1)	120 (1)	50.1
12	6.0 (1)	1:20 (1)	60 (-1)	120 (1)	69.3
13	1.0 (-1)	1:10 (-1)	300 (1)	120 (1)	48.2
14	6.0 (1)	1:10 (-1)	300 (1)	120 (1)	68.1
15	1.0 (-1)	1:20 (1)	300 (1)	120 (1)	61.8
16	6.0 (1)	1:20 (1)	300 (1)	120 (1)	89.3

<sup>a</sup> The factors are coded as follows: X<sub>1</sub> = Catalyst loading (wt.%), X<sub>2</sub> = Molar ratio of oil to methanol (mol/mol), X<sub>3</sub> = Reaction time (min) and X<sub>4</sub> = Reaction temperature (°C).

**Table 3**  
Experimental conditions and FAME yields derived from Box-Behnken design.<sup>a</sup>

Run	X <sub>1</sub> (wt.%)	X <sub>2</sub> (mol/mol)	X <sub>3</sub> (min)	FAME yield (%)	
				Observed	Predicted
1	1.0 (-1)	1:10 (-1)	180 (0)	73.4	74.1
2	6.0 (1)	1:10 (-1)	180 (0)	69.6	69.9
3	1.0 (-1)	1:20 (1)	180 (0)	74.3	74.0
4	6.0 (1)	1:20 (1)	180 (0)	70.0	69.2
5	1.0 (-1)	1:15 (0)	60 (-1)	74.6	77.7
6	6.0 (1)	1:15 (0)	60 (-1)	72.7	76.3
7	1.0 (-1)	1:15 (0)	300 (1)	74.7	71.1
8	6.0 (1)	1:15 (0)	300 (1)	66.6	63.5
9	3.5 (0)	1:10 (-1)	60 (-1)	85.1	81.2
10	3.5 (0)	1:10 (-1)	60 (-1)	88.7	85.9
11	3.5 (0)	1:20 (1)	300 (1)	73.8	76.6
12	3.5 (0)	1:20 (1)	300 (1)	67.2	71.1
13	3.5 (0)	1:15 (0)	180 (0)	89.2	89.4
14	3.5 (0)	1:15 (0)	180 (0)	89.8	89.4
15	3.5 (0)	1:15 (0)	180 (0)	89.3	89.4

<sup>a</sup> The factors are coded as follows: X<sub>1</sub> = Catalyst loading (wt.%), X<sub>2</sub> = Molar ratio of oil to methanol (mol/mol) and X<sub>3</sub> = Reaction time (min).

where N<sub>exp</sub> is the number of experiment, N<sub>p</sub> is the number of input parameter and N<sub>cp</sub> is the number of central point. The Box-Behnken design consisting of fifteen experiments with low (-1), medium (0) and high (1) values are presented in Table 3. The Box-Behnken experiment was done using Minitab 17 + Microsoft Excel. The quadratic regression model for optimizing the FAME yield was given as follows in Eq. (2):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (2)$$

Where Y is the percentage of FAME yield,  $\beta_0$  is the intercept/constant coefficient,  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  are the linear coefficients,  $\beta_{11}$ ,  $\beta_{22}$  and  $\beta_{33}$  are the quadratic coefficients,  $\beta_{12}$ ,  $\beta_{13}$  and  $\beta_{23}$  are the interaction coefficient of each parameter and X<sub>1</sub>, X<sub>2</sub> and X<sub>3</sub> are the codes of independent input parameters.

## 2.5. Analysis of FAME product

The FAME yield was analyzed by gas chromatography (GC, Shimadzu GC-17A), equipped with a flame ionization detector (FID) and a capillary column (DB-WAX, 30 m long × 0.32 mm ID × 0.25 μm film thickness). The EN 14103 standard method was applied to define the FAME yield using methyl heptadecanoate (C17:0) as an internal

standard. The GC temperatures at 250 °C were used for injector and detector using helium (He) as a carried gas with a flow rate 2 mL/min. Split mode was also applied for sample injection at split rate of 27 mL/min. The initial oven temperature was 150 °C with an equilibration time of 5 min. The oven was further heated at a rate of 3 °C/min to 190 °C and held for 5 min. Thereafter, the temperature of over was increased until to 220 °C and held for 10 min. All experiments was repeated at least three times under the same conditions in order to minimize error or variability and corroborate its repeatability. The calculation of FAME yield (%) was expressed as follows in Eq. (3):

$$\text{FAME yield (\%)} = \frac{(\sum A) - A_{\text{EI}}}{A_{\text{EI}}} \times \frac{C_{\text{EI}} \times V_{\text{EI}}}{W_s} \times \frac{W_p}{W_o} \times 100 \quad (3)$$

where  $\sum A$  is the total peak areas of FAME product,  $A_{\text{EI}}$  is the peak area of internal standard,  $C_{\text{EI}}$  is the concentration of internal standard (mg/mL),  $V_{\text{EI}}$  is the volume of internal standard solution (mL) and  $W_s$  is the weight of used sample for GC (mg).  $W_p$  is the weight of FAME product (mg) and  $W_o$  is the weight of waste cooking palm oil.

## 2.6. Characterization of waste cooking palm oil and FAME product

The physicochemical properties of samples were determined according to the standard method such as specific density (ASTM D4052), kinematic viscosity (ASTM D445), flash point (ASTM D93), pour point (ASTM D97), cloud point (ASTM D2500), acid value (EN 14214), saponification (ISO 3657) and iodine value (EN 14111).

For analysis of free fatty acid amount in sample, 0.5 of sample was added into 10 ml of ethanol, and stirred at a speed of 500 rpm under ambient temperature for 30 min. The mixture solution was titrated with 0.1 N NaOH solution using phenolphthalein as an indicator. The amount of free fatty acid was calculated based g/100 g of oleic acid as follows in Eq. (4):

$$\text{Free fatty acid (\%)} = V \times N \times \frac{28.2}{W} \quad (4)$$

where V is the volume of NaOH solution used for titration, N is the concentration of NaOH solution and W is the weight of sample.

For analysis of saponification value (SV), 0.5 g of sample was added into 20 ml of 0.5 N KOH alcoholic (EtOH) solution, and refluxed at 40 °C until clear solution was obtained. After finishing and cooling processes, the mixture solution was titrated with 0.5 N HCl solution using phenolphthalein as an indicator. The calculation of SV was expressed as follows in Eq. (5):

$$\text{Saponification value} = (b - s) \times N \times \frac{56.1}{W} \quad (5)$$

Where b and s are the volume of HCl solution used for titration with blank or distilled water and sample, respectively. N is the concentration of HCl solution (N) and W is the weight of sample.

For analysis of iodine value (IV), 0.1 g of sample was added into 20 ml of carbon tetrachloride containing in Wijs reagent flask, and shaken in dark place for 30 min. Thereafter, 20 ml of 15% KI and 100 ml of distilled water were added into mixture solution. The prepared mixture solution was titrated with 0.1 N S<sub>2</sub>O<sub>3</sub><sup>2-</sup> solution using starch as an indicator. The calculation of IV was expressed as follows in Eq. (6):

$$\text{Iodine value} = (b - s) \times N \times \frac{12.69}{W} \quad (6)$$

Where b and s are the volume of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> solution used for titration with blank or distilled water and sample, respectively. N is the concentration of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> solution (N) and W is the weight of sample.

For analysis of cetane number, it was reported by Krishnangkura, 1989 [21], which could be calculated as follows in Eq. (7):

$$\text{Cetane number} = 46.3 + \left( \frac{5458}{SV} \right) - 0.225 \times IV \quad (7)$$

Where SV and IV are the saponification and iodine values, respectively.

### 3. Results and discussion

#### 3.1. Physical and chemical properties of waste cooking palm oil

As shown in Table 1, the physical properties of waste cooking palm oil had higher values of density and viscosity than refined palm oil, resulting from frying process at high temperature. Also, the leaching of water during food frying process resulted in hydrolysis reaction with triglyceride to form free fatty acid in oil. It should be mentioned here that free fatty acid was polar molecule due to the presence of carboxylic group. Thus, when a lot of free fatty acid amount existed in oil, the attraction force between molecules could be increased, leading to increasing of oil density and viscosity. In addition, free fatty acid and other properties found in waste cooking palm oil which was in pleasing criterion for direct catalysis with a basic transesterification reaction [22]. Considering on chemical properties, one can see that saponification, iodine and acidity in of waste cooking palm oil exhibited values were in the satisfactory range when compared with refined palm oil, suggesting that waste cooking palm oil selected in this work had amount of triglyceride with chemical properties that could be passably controlled for FAME production with high quality.

#### 3.2. Effect of FAME production using $2^4$ factorial design

The complete sixteen experiments with observed FAME yield under  $2^4$  factorial design is shown in Table 2. One can see that the percentage of FAME yield altered in the range of ~30 to ~80%. The minimum and maximum yields of FAME were achieved following low and high values in independent input parameters. In order to primarily screen and confirm the important parameters for FAME production from waste cooking palm oil over KOH/activated carbon catalyst, normal probability plots with estimated values were preformed, and their results are shown in Fig. 1. As observed, three parameters such as catalyst loading, molar ratio of oil to methanol and reaction time with their interactions exhibited a significant influence based on the productive order of catalyst loading > molar ratio of oil to methanol > reaction time for response of FAME yield. The reaction temperature in the range applied had no influence on promoting the FAME yield, indicating that a lowest temperature of 80 °C was adequate for FAME production in this study. In general, a basic transesterification strongly required high temperature due to its endothermic nature. However, when too high temperature was applied, the collision of three-phase reflux system consisting of

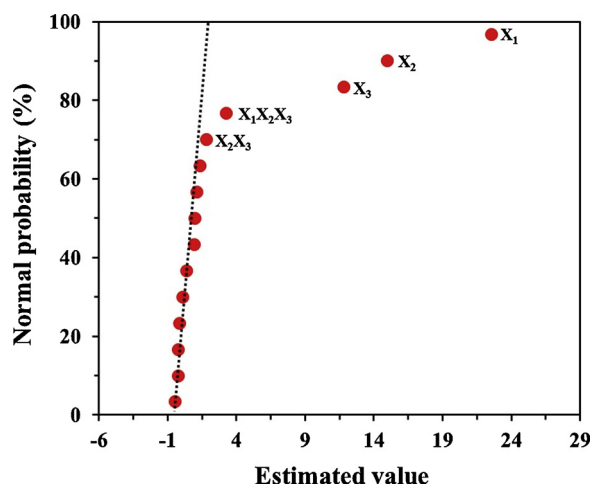


Fig. 1. Normal probability plot of estimated value determined  $2^4$  factorial design for FAME production from waste cooking palm oil over KOH/activated carbon catalyst.

Table 4

Analysis of variance (ANOVA) determined from  $2^4$  factorial design for FAME production from waste cooking palm oil over KOH/activated carbon catalyst.

Source of variation	Sum of square	Degree of freedom	Mean square	F <sub>value</sub>	F <sub>critical</sub>
X <sub>1</sub>	2034.01	1	2034.01	923.19	4.97
X <sub>2</sub>	897.00	1	897.00	407.13	
X <sub>3</sub>	556.96	1	556.96	252.79	
X <sub>2</sub> X <sub>3</sub>	13.32	1	13.32	6.05	
X <sub>1</sub> X <sub>2</sub> X <sub>3</sub>	42.90	1	42.90	19.47	
Error	22.03	10	2.20		
Total	3566.23	15			

methanol-waste cooking palm oil-KOH/activated carbon catalyst was quite difficult since methanol could be converted into vapor phase (above boiling point), resulting in a few available of methanol liquid phase under reaction system [23,24]. That is why the influence of molar ratio of oil to methanol were important for FAME production. It should be noted that in this study, methanol could possibly exist in the vapour phase by condensation under reflux system since it used at high amount (Molar ratio of oil to methanol 1:10 to 10:20). The results of analysis of variance (ANOVA) at 95% confidence level derived from experimental design are shown in Table 4. Here, the model terms were significant owing to the F-value of > 4.97. As expected, highest and lowest F-value of catalyst loading and reaction time were found to be 923.19 and 252.79, respectively, indicating to level of significant influence. The ANOVA results were in good agreement with the normal probability plots. To identify a significant coefficient based on above results, linear regression model is expressed as follows in Eq. (8):

$$Y = 60.38 + 11.275X_1 + 7.488X_2 + 5.9X_3 + 0.912X_2X_3 + 1.638X_1X_2X_3 \quad (8)$$

where Y is the FAME yield (%), X<sub>1</sub> is the catalyst loading (wt.%), X<sub>2</sub> is the molar ratio of oil to methanol (mol/mol) and X<sub>3</sub> is the reaction time (min).

The dependability of linear regression model was investigated by the normal probability plot with residual values as shown in Fig. 2. As expected, the model was well fitted with correlation coefficient (R<sup>2</sup>) value > 0.9 (R<sup>2</sup> = 0.9447), showing a good linearity. Meantime, the residue distribution on the plot of residue value versus predicted FAME yield did not meet with a respective trend, suggesting that the model applied in this study was high accuracy. From above results, a lowest temperature range was chosen for optimization of FAME production.

#### 3.3. Optimization of FAME production using Box-Behnken design

The complete fifteen experiments with observed FAME yields under Box-Behnken design is shown in Table 3. From this design consisting of low, medium and high levels, the quadratic regression model is expressed in order to define the predicted FAME yields as follows in Eq. (9):

$$Y = 89.433 - 2.263X_1 - 0.199X_2 - 4.864X_3 - 12.093X_1^2 - 5.53X_2^2 - 5.2X_3^2 - 0.13X_1X_2 - 1.555X_1X_3 - 2.548X_2X_3 \quad (9)$$

where Y is the FAME yield (%), X<sub>1</sub> is the catalyst loading (wt.%), X<sub>2</sub> is the molar ratio of oil to methanol (mol/mol) and X<sub>3</sub> is the reaction time (min).

From Eq. (9), the predicted FAME yields were calculated and the results are shown in Table 3. One can see that the predicted yields of FAME were very close to observed values derived from the experimental results. Also, the plot of observed versus predicted FAME yields is presented in Fig. 3, providing a high value of R<sup>2</sup> > 0.9 (R<sup>2</sup> = 0.9109). This indicates that the model was well fitted with 91.09% of variability for polynomial investigation. In order to provide more details on the interaction among the independent input parameters, their response



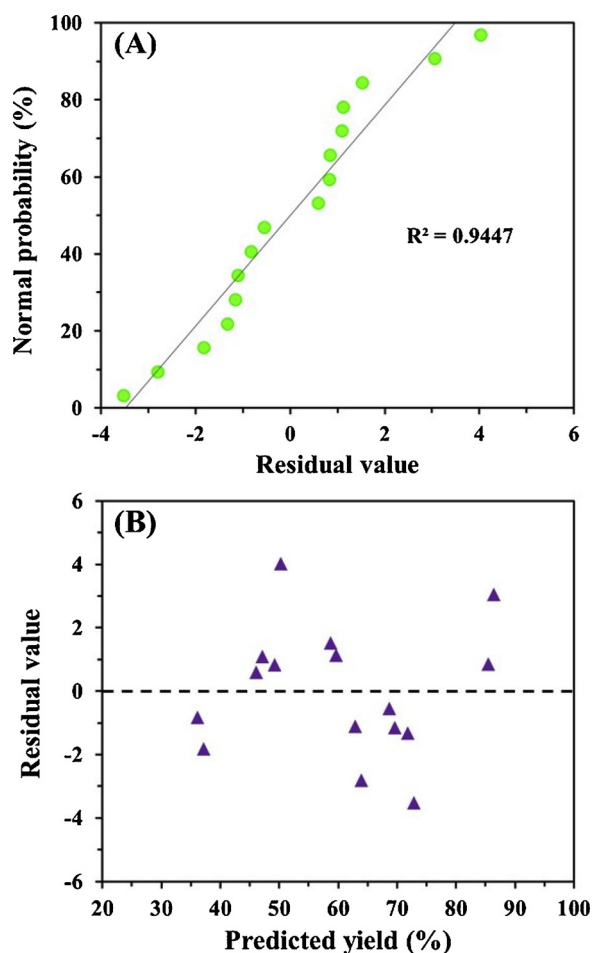


Fig. 2. (A) Normal probability plot of residual and (B) distribution plot of residual versus predicted FAME yield determined from  $2^4$  factorial design for FAME production from waste cooking palm oil over KOH/activated carbon catalyst.

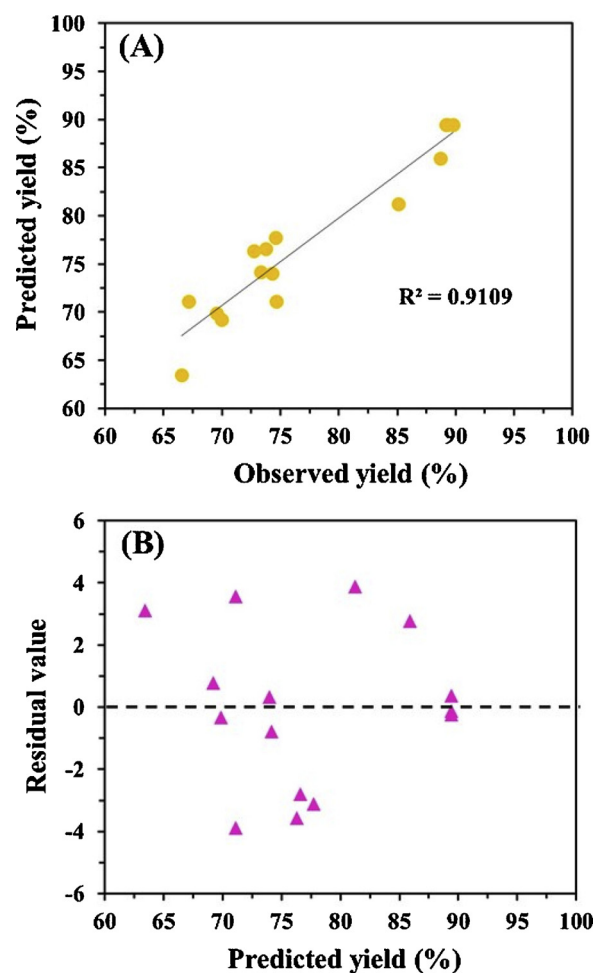


Fig. 3. (A) Plot of observed versus predicted values of FAME yield and (B) distribution plot of residual value versus predicted FAME yield determined from Box-Behnken design for FAME production from waste cooking palm oil over KOH/activated carbon catalyst.

surface and contour plots are also presented in Fig. 4. As shown in Fig. 4A and B, the influence of catalyst loading and molar ratio of oil to methanol on FAME production from waste cooking palm oil over KOH/activated carbon catalyst at a constant reaction time of 180 min (medium level) was investigated. It is found that an increase in the FAME yield from ~70 to ~89% was mainly due to an increase in the amount of catalyst loading between 1 to 3 wt.% of oil, respectively. This indicates that an increase in the number of active basic sites (KOH) in the reaction system was well promoted via transesterification. This should be also generally attributed to the increasing of the contact rate/mass transfer between the triglyceride with the catalyst active sites. Furthermore, a reduction of FAME yield was observed when higher 3 wt.% of catalyst loading was applied, resulting from a poor mixing in mixture solution (too high viscous slurries) with an resistance in mass transfer in the multi-phase system [25]. Also, saponification might be easily promoted under base catalyst loading at too high amount. This reduction trend of FAME yield was also appeared in Fig. 4C and D, with influence of catalyst loading. The possible mechanism for basic transesterification of triglyceride are also provide in Fig. 5. For the first step, an alkoxide nucleophile was formed under the mixing between alcohols with base catalysts [26]. Then, it further undergo the raiding at carbonyl carbon position of the fatty acid as a tetrahedral intermediate. For second step, molecule of tetrahedral intermediate was subtracted and rearranged in order to release the FAME product. Also, the alkoxide ion formed on the glycerol backbone was suddenly protonated to form -OH group. Finally, remained diglyceride and monoglyceride were

further converted based on the same mechanism. Considering on influence of molar ratio of oil to methanol on FAME yield, a maximum FAME yield of ~89% was obtained with a molar ratio of oil to methanol (1:15). As well known that the stoichiometry for transesterification reaction required a ratio of oil to methanol (3:1). However, since transesterification reaction was a reversible reaction, thus an excessive amount of methanol was strongly required following to Le Chatelier's principle in order to shift the equilibrium forward to FAME and glycerol sides [27]. At economic part, the remaining methanol after reaction could be economically recovered by evaporation process. Whereas, when ratio of oil to methanol was increased from 1:15 to 1:20, the FAME yield was also slightly decreased to some extent, suggesting to (I) the capricious on reaction equilibrium, (II) the existence of lower relative concentration of waste cooking palm oil, (III) the possible problem for phase separation process [28]. In addition, the catalyst surface might be covered by methanol molecules, leading to available of fewer active sites for transesterification [29]. Fig. 4E and F show the influence of molar ratio of oil to methanol and reaction time on FAME production from waste cooking palm oil over KOH/activated carbon catalyst at a constant catalyst loading of 3.5 wt.% of oil (medium level). One can see that the increasing of reaction time exhibited a positive result which optimum time was found for 120 min based on a highest FAME yield (~90%). The backward reaction might be occurred in case of too long reaction applied, leading to the reduction of FAME yield. It should be mentioned here that this reaction time parameter was still presented to be lower influence than other

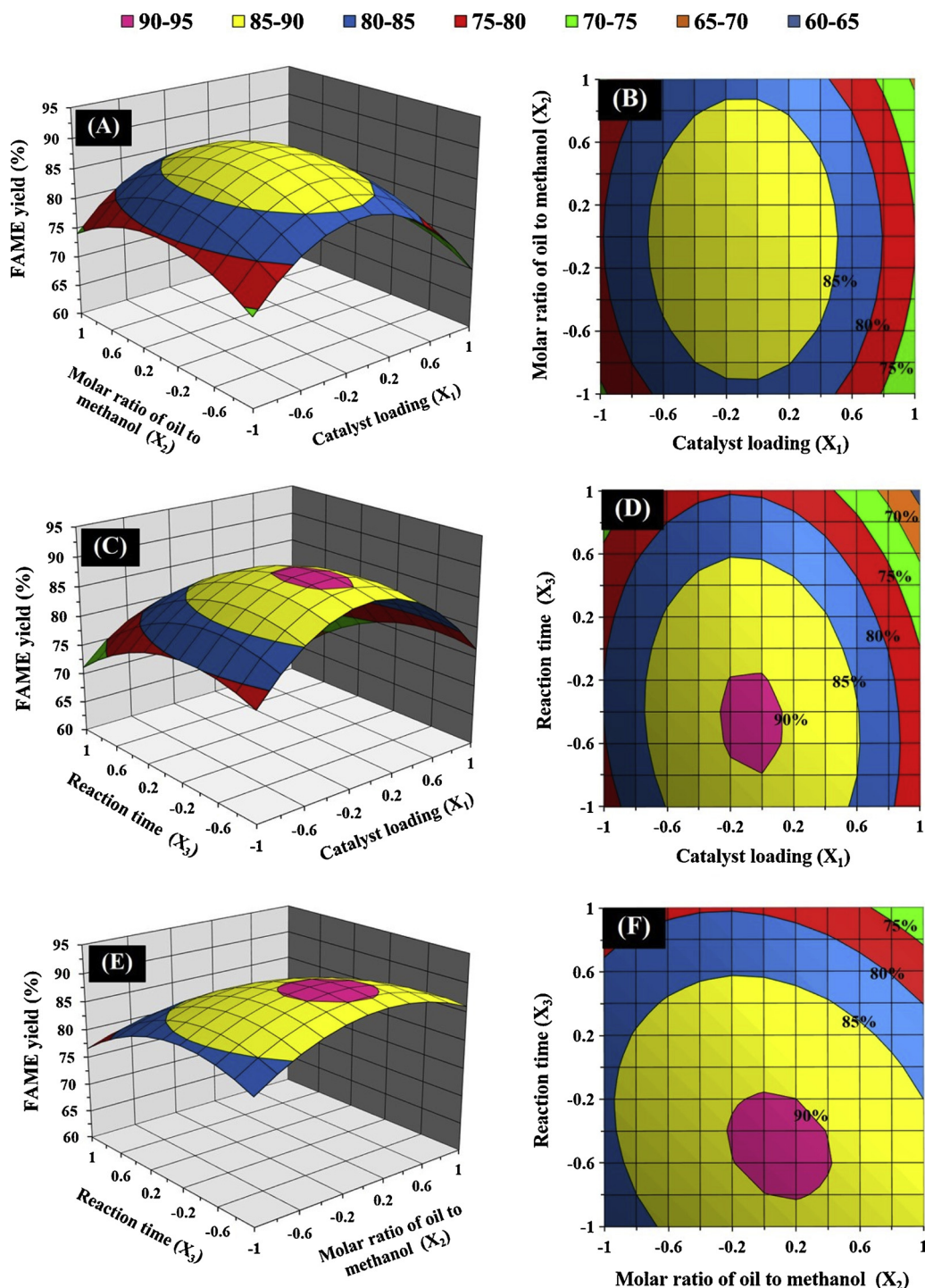


Fig. 4. Response surface and contour plots of FAME yield: (A,B) based on catalyst loading and molar ratio of oil to methanol, (C,D) based on catalyst loading and reaction time, and (E,F) based on molar ratio of oil to methanol and reaction time.

parameters such as molar ratio of oil to methanol and catalyst loading. Considering on economic process, high production cost for FAME production process occurred from the use of too high catalyst loading or methanol amount as well as separation process with duration time could be well suppressed by our experimental designs proposed in this work.

Based on above results, the equilibrium conditions with optimization could be obtained from quadratic regression model. A maximum predicted yield of FAME (90.7%) was successfully obtained under the optimum conditions: catalyst loading of 3 wt.% of oil, reaction time of 120 min, reaction temperature of 80 °C and ratio of oil to methanol of

1:15. In order to verify the accuracy and precision results of experimental designs, the FAME production based on actual experiment was also further carried out for three replicates under optimum conditions mentioned above. As expected, an average FAME yield of 91.05% was obtained, which six types of methyl esters such as lauric acid (C12:0), myristic acid (C14:0), palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2) were obviously found in this study (Fig. 6 and Table 5). Based on these designs, it was substantiated on dependable with 1.1% error. It should be noted that the reusability did not test in this study. Here, it could be predicted that the yield of FAME was slightly decreased to some extent in each cycle since low

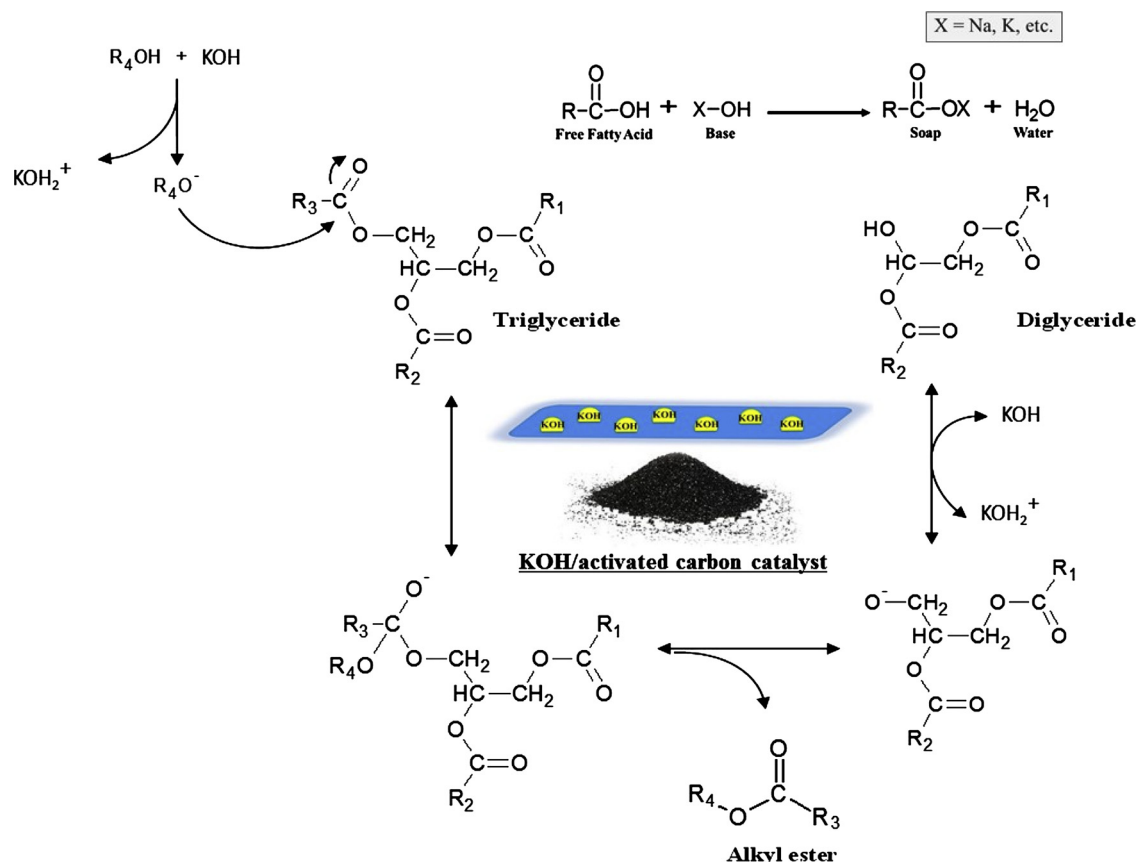


Fig. 5. The possible mechanism of base-catalyzed transesterification of triglyceride.

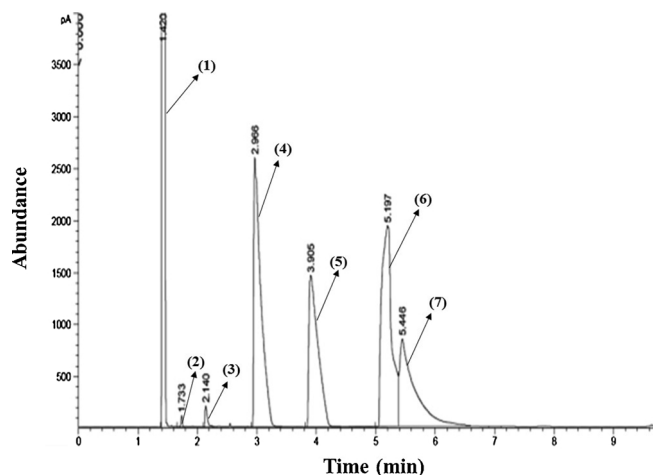


Fig. 6. GC Chromatogram of FAME sample using heptane and C17:0 as organic solvent and internal standard ((1) heptane, (2) C12:0, (3) C14:0, (4) C16:1, (5) C17:0, (6) C18:0 and (7) C18:1).

amount of free fatty acid existed in waste cooking oil could generally reacted with base catalyst via saponification reaction. Thus, the decreasing of basicity of catalyst should be resulted on FAME yield. However, KOH/activated carbon could still be considered for application in economical-practical processes since it had very low cost, strong efficiency for transesterification and environmental friendly. Narowska et al., 2019 [16] reported on advantages of KOH/activated carbon catalyst in transesterification that the produced glycerol was no necessary to purify by washing with water since a few basic pH value of  $\sim 7.5$  was found in reaction system, comparing with homogeneous KOH catalyst ( $\text{pH} > 9$ ). This phenomena could reduce the production cost of

Table 5

Example of FAME percentages derived from optimum conditions: 3 wt.% catalyst loading, 1:15 M ratio of oil to methanol, at  $80^\circ\text{C}$  for 120 min which determined from GC peak areas.

Peak NO.	Name	Retention time	Area	FAME (%)
1	Heptane	1.420	1577630	–
2	C12:0	1.733	532.70	0.81
3	C14:0	2.140	20541.5	31.33
4	C16:0	2.966	15513.0	23.66
5	C17:0 (Ref. peak)	3.905	12779.0	–
6	C18:0	5.197	9206.89	14.04
7	C18:1	5.446	13901.3	21.21
	Total			91.05

FAME as well as manufacture it more competitive advantage with conventional process. In the other words, one challenging for direct utilization of glycerol in boiler fuel was in the presence of salt content.

#### 3.4. Physical and chemical properties of produced FAME

The physicochemical properties of FAME produced from transesterification of waste cooking palm oil at optimum conditions over KOH/activated carbon catalyst are shown in Table 6. As expected, the density and viscosity of the produced FAME product were evidently lower values, when compared to the waste cooking palm oil. This phenomenon was described in the changes of chemical structure and hydrocarbon number. Chhetri et al., 2008 [30] reported that the density of FAME could lead to breaking up of fuel spray from the engine. Meanwhile, too high viscosity of FAME resulted in low combustion and cold cylinder of engine, leading to the black smoke emission [31]. Also, this should be resulted on lubrication for the oil injection pump. The pour point, flash point and cloud point of fuels were used as indicator on minimum

**Table 6**

The physicochemical properties of FAME product derived from optimum conditions: 3 wt.% catalyst loading, 1:15 M ratio of oil to methanol, at 80 °C for 120 min.

Properties	FAME standard	FAME (This study)
Density (kg/m <sup>3</sup> )	860–900	866
Viscosity (cSt) (25 °C)	3.5–5.0	3.61
Flash point (°C)	> 120	167
Pour point (°C)	–15 to 10	8
Cloud point (°C)	–3 to 12	10
Acid value (mgKOH/g)	< 0.50	0.46
Free fatty acids (%)	< 0.23	0.21
Saponification (mg of KOH/g)	280	196.73
Iodine value (g of I <sub>2</sub> /oil 100 g)	< 120	2.08
Cetane number	≥ 47	73.58

operation temperature for ignition process [32]. These also suggest to proper safety and handling of the bio-fuel. To investigate the FAME stability, the iodine value was used to determine the degree of FAME unsaturation. Over degree of FAME unsaturation promoted in polymerization reaction owing to the formation of epoxide by introduction of O<sub>2</sub> in double bonds [33]. As expected, the properties of as-synthesized FAME were found to be comparable with ASTM standard (ASTM D6751-02) specifications. It should be mentioned here that cetane number of FAME was 73.58, which was in the acceptable range for FAME standard. From these results, it indicates that high quality such ignition-combustion processes and its oil stability was obtained in FAME product produced in this study, which could be expected to truly apply as a substitute fuel for engine process.

#### 4. Conclusion

The present work disclosed the effective application of low cost KOH/activated carbon catalyst for FAME production from transesterification of waste cooking palm oil. A combination of 2<sup>k</sup> factorial and Box-Behnken design exhibited high preciseness with R<sup>2</sup> value > 0.9 as well as 1.1% error, and provided the optimum conditions: catalyst loading (3 wt.% of oil), molar ratio of oil to methanol (1:15), reaction time (120 min) and reaction temperature (80 °C). Under these optimum conditions, 91.05% of FAME yield was obtained, consisting of C12:0, C14:0, C16:0, C18:0, C18:1 and C18:2. The catalyst loading exhibited most significant influence for FAME production. The physicochemical properties of FAME were found to be in good agreement with ASTM standard requirements which could be applied for diesel engine. The uses of waste cooking palm oil and inedible fruit (*Terminalia catappa*) as feedstock for FAME and catalyst support presented economical and ecologically friendly which were useful for solving the energy crises and environmental issues.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jece.2019.103389>.

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