OPTIMISATION OF FAME PRODUCTION FROM WASTE COOKING PALM OIL WITH KOH CATALYST SUPPORTED ON PALM KERNEL SHELLS ASH (PKSA) USING RESPONSE SURFACE METHODOLOGY (RSM)

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ABSTRACT

Fatty acid methyl ester (FAME) was produced from waste cooking palm oil (WCPO) using KOH catalyst supported on palm kernel shells ash (PKSA). Response surface methodology (RSM) based on Box Behnken design (BBD) was used to design the experiment and analyse three parameters: Catalyst amount, KOH loading and methanol to oil molar ratio. The result found that the catalyst activity depended on basicity of the catalysts. The statistical model predicted that the highest yield of 96.73% was achieved with an optimised parameter of 15 wt.% catalyst amount, 20 wt.% of KOH loading and 11.39:1 methanol to oil ratio at the temperature of 65ºC. Experiments performed at the predicted condition yield of 92.74% suggest that the RSM is an accurate method for biodiesel production. The Gas Chromatography Mass Spectrometry (GC-MS) was used to identify the chemical composition of biodiesel. The catalyst reusability test verified that the synthesised catalyst could be reused up to 3 times. The results demonstrated that waste cooking palm oil can be completely transformed into methyl ester. This study indicates that KOH supported on palm kernel shell ash is an effective catalyst for the conversion of waste cooking palm oil to biodiesel.

INTRODUCTION

Renewable sources of energy have become a more attractive alternative due to global warming and environmental concerns. Worldwide population growth at a rapid rate increases the global energy consumption from petroleum sources and resulting in the increase of the greenhouse gases emissions which are mainly responsible for global warming and has impact on human health (Basumatary *et al.*, 2021). The alternative energy technologies can overcome the much-exploited use of fossils fuel.

Among the various possible alternatives, biodiesel has been seen as tremendous potential for growth for a long time ago. In this regard, biodiesel from vegetable oil is an environmental-friendly fuel due to non-toxic, renewable, biodegradable, less sulphur and greenhouse gases emissions (Sharma *et al.*, 2020).

Biodiesel is derived from the transesterification of triglycerides present in vegetable oil or animal fat and alcohol with the presence of a catalyst (Sharma *et al.*, 2020). Appropriate selection of feedstock for biodiesel production is one of the crucial factors for reducing the cost of biodiesel feedstock. The use of low-price oil such as waste cooking oil will considerably reduce the cost of the final product (Putra *et al.*, 2018). This is because of the low cost of waste cooking oil (WCO), which is 2-3 times less than virgin vegetable oil.

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Bio or green catalyst is a type of catalyst derived from natural source as biomass. The advancement in the agricultural sector provides tons of waste and by-products daily and hence a potential low-cost precursor of green catalysts (Arumugam and Sankaranarayanan, 2020). The total amount of waste from oil palm plantations is approximately 13.71 million tonnes, comprising fibre, palm shells, empty fresh fruit bunches and palm oil trunks (Malithong *et al.,* 2017). Currently, the wastes are either disposed of as landfills or used in a boiler to generate electricity. For instance, palm kernel shells (PKS) do not decompose easily and require furnace modifications if there are to be used in boilers in place of firewood or fuel oil. Direct use of PKS in boiler in their raw form produces a large amount of smoke and insufficient energy (Bazargan *et al.,* 2015).

The current research goal is to produce the catalyst from agricultural biomass such as palm kernel shell, which will therefore reduce costs and improves overall efficiency. The present study aimed to improve the activity of palm kernel shells as a catalyst by impregnation method to increase the basicity through the addition of base metal onto the surface of the catalyst (Oko and Kurniawan, 2019).

Therefore, transesterification parameters were optimised using response surface methodology (RSM) based on the Box-Behnken design to establish the best condition for biodiesel production (Singh *et al.,* 2018). Dwivedi and Sharma (2015) use the Box-Behnken design to optimise Pongamia biodiesel yield of 98.4% with a methanol molar ratio of 11.06:1, 1.43 wt.% of KOH catalyst, at a reaction temperature of 56.6°C and 81.43 min of time. Latchubugata *et al.* (2018) have reported optimisation of reaction parameter at 6 wt.% calcium oxide (CaO) catalyst and methanol molar ratio of 15:1 at a reaction temperature of 65.0°C in 4 hr reaction time using Box-Behnken design, the experimentally obtained yield of biodiesel was 93.50%. Marwaha *et al.* (2019) used Box-Behnken response surface design to maximise biodiesel yield at 97.98% from *Terminalia bellerica* oil with a methanol molar ratio of 9:1, 2.25 wt.% calcium oxide (CaO) catalyst from waste eggshells and reaction temperature of 62.5°C.

The present work attempted to develop a low-cost support base catalyst using KOH impregnated onto PKS for the transesterification of Waste Cooking Palm Oil (WCPO) for biodiesel production. The influence of catalyst basicity, methanol-to-oil molar ratio and catalyst weight percent were investigated using response surface methodology (RSM) combined with a Box-Behnken design. Furthermore, the physicochemical properties of the produced biodiesel are compared with the standard requirements of Thailand.

MATERIALS AND METHODS

Material

The WCPO was collected at a cafeteria nearby King Mongkut's University of Technology, North Bangkok (Rayong Campus). The oil was filtered to remove impurities and heated to 100°C to remove moisture. To prevent oxidation, the WCPO was stored in a container with a tight seal. After that, the WCPO's acid value, iodine value, moisture and volatile matter content, and saponification value were determined.

Palm kernel shells ash (PKSA) was donated by an Indorama Petrochem (PTA) thermal power plant in the city of Rayong. The PKSA was crushed in a mortar before being sieved to a mesh size of 250 μm. To eliminate moisture and impurities, the sieved PKSA was heated in an oven at 120°C for 12 hr.

PKSA Multi-element Characterisation

In Teflon tubes, 5 g PKSA was digested with 9 mL of 65% nitric acid, 3 mL of hydrofluoric acid, and 2 mL of 37% hydrochloric acid. A microwave-heated pressure digestion apparatus was used to digest the solution (Berghof Speedwave 4). The digestion conditions used were as follows: The temperature was ramped to 210°C with a heating rate of 5°C/min at 80% power, followed by a dwell time of 30 min. After digestion, about 10% boric acid was added to a mixture to re-dissolve the insoluble fluoride compounds. Once again, the solution was transported to a microwave-heated pressure digestion system. The temperature was ramped up to 190°C using a heating rate of 5°C/min, and held for 10 min at that temperature. After that, the solution was transferred to 25 mL volumetric flasks, filled with MilliQ water to the correct volume, and stored in a refrigerator at 4°C for MP-AES analysis.

The Agilent MP-AES was utilised to determine the concentration of residual Si, Al, Fe, Ca, Mg, and K in the digested solutions. The calibration curve was linear, and quantification was based on a five-point standard calibration curve (2.0, 4.0, 6.0, 8.0 and 10.0 mg/L). For every determination, both the standard and the sample were scanned three times. The metal determination wavelengths were as follows: Si (251 nm), Al (396 nm), Fe (259 nm), Ca (393 nm), Mg (285 nm), and K (766 nm). *Figure 1* depicts the graphical representation of the standard calibration curve for each metal. The R^2 values from the standard were Si 0.9991, Al 0.9998, Fe 0.9983, Ca 0.9956, Mg 0.9979 and K 0.9976. The results demonstrated that all determination coefficients (R^2) were within the acceptable values.
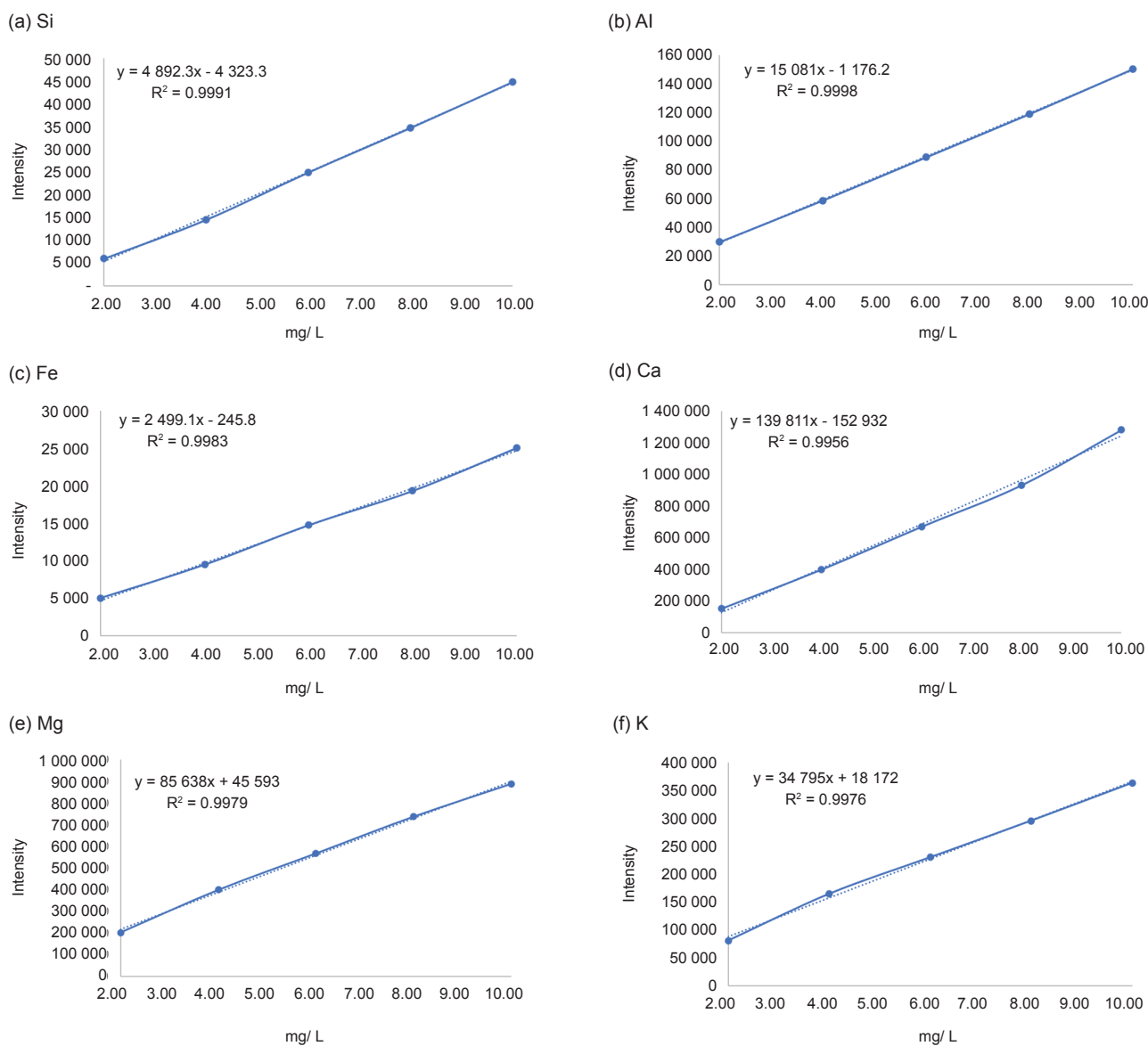
(a) Si

$y = 4\,892.3x - 4\,323.3$
$R^2 = 0.9991$

(b) Al

$y = 15\,081x - 1\,176.2$
$R^2 = 0.9998$

(c) Fe

$y = 2\,499.1x - 245.8$
$R^2 = 0.9983$

(d) Ca

$y = 139\,811x - 152\,932$
$R^2 = 0.9956$

(e) Mg

$y = 85\,638x + 45\,593$
$R^2 = 0.9979$

(f) K

$y = 34\,795x + 18\,172$
$R^2 = 0.9976$

Figure 1. Calibration curve for (a) Si, (b) Al, (c) Fe, (d) Ca, (e) Mg and (f) K using MP-AES.

Catalyst Preparation

The KOH-supported PKSA catalysts were synthesised using the incipient wetness impregnation method. Potassium hydroxide solution was introduced dropwise to PKSA at various weight percentages (10%, 15% and 20%) and agitated for 12 hr. The KOH/PKSA mixture was heated in an oven at 110°C for 6 hr, after that the dried catalysts were calcined at 600°C for 6 hr. The calcined catalyst was then placed in a desiccator.

Catalyst Characterisation

The synthesised catalysts were characterised using various techniques. By using the Hammett indicator method, the basicity of the KOH/PKSA catalyst was investigated. This method is used to indicate the catalyst's basic strength (Leung and Gua, 2006). Typically, 0.05 g of catalysts were mixed with 5 mL of methanol and 3 drops of Hammett indicator and allowed to equilibrate for 2 hr. The catalyst's alkaline abnormality was indicated by a colour change. Thermogravimetric analysis (TGA, TA Instruments Q50) was used to obtain volatile components by monitoring the weight change of PKSA from room temperature to 800°C at a heating rate of 10°C/min under a flow of nitrogen. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) techniques were used to calculate the specific surface area and pore volume of the catalyst which uses nitrogen adsorption. Before the experiment, the sample was outgassed under vacuum for 4 hr at 150°C to remove moisture from the catalyst surface.

WCPO Characterisation

To characterise the properties of WCPO, the standard method was used. The moisture content, acid value, and iodine value of the used palm cooking oil were all measured. The acid valve and FFA concentration were determined by titrating against 0.025 M KOH and phenolphthalein as an indicator. A moisture analyser was used to determine the moisture content (Mettler Toledo model HC103). The iodine value was determined by volumetric titration; 0.2 g of WCPO was mixed with 15 mL of cyclohexane and 25 mL of Wijs reagent, and the mixture was shaken for 5 min and placed in the dark for 30 min. The mixture was then added with 20 mL of 10% KI and 50 mL of boiled distilled water. Following that, the mixture was titrated with 0.1 $Na_2S_2O_3.5H_2O$ using starch as an indicator to determine the endpoint.

Experimental for Transesterification Reaction

The transesterification reaction for WCPO was performed at atmospheric pressure in a 250 mL three-necked, flat-bottom flask equipped with a reflux condenser and magnetic stirrer. The reaction flask was placed on a hotplate stirrer. About 50 g of WCPO was heated to 65°C in the reaction flask. Following that, methanol and PKSA catalyst were added to the process. The mixture was then maintained at 65°C for 60 min while being constantly stirred. After the reaction was complete, the mixture was transferred to a separation funnel and allowed to settle for 12 hr before separating the top layer (biodiesel) from the bottom layer (glycerol and solid catalyst). The biodiesel was evaporated at a temperature of 110°C to remove moisture and methanol. A Fourier transform infrared spectrum (FTIR) equipped with a diamond attenuated total reflectance (ATR) was utilised to measure the FAME content of the sample.

Box-Behnken Design of Experiment

Response surface methodology (RSM) based on Box-Behnken design was used to optimise the biodiesel conversion parameters using Minitab software. The three independent variables used in this study were ash catalysts dosage (amount of catalyst (wt.%): 5% to 15%), KOH concentration on the supported catalyst (%K: 10% to 20%), and methanol to oil molar ratio (M/O: 6 to 12 molar ratio) (*Table 1*). FAME yield (Y) was chosen as the dependent variable. The reaction time was set to 60 min and the temperature was set to 65°C. The significance of the components and their interaction was determined using analysis of variance (ANOVA) with a confidence level of 95% ($P<0.05$).

TABLE 1. LEVEL OF THE INDEPENDENT VARIABLES IN THE BOX-BEHNKEN DESIGNS (BBD)

Independent variables	Code	Level		
		-1	0	-1
PKSA	Catalyst (wt.%)	5	10	15
KOH concentration	%K	10	15	20
Methanol to oil molar ratio	M/O	6	9	12

Biodiesel Characterisation

The produced biodiesel was evaluated by functional groups and methyl esters profile analyses. Thirteen calibration solutions of biodiesel standard (Biodiesel standard donated by a biodiesel factory from the Suksomboon group located in Chonburi, Thailand) were prepared with varying concentrations of WCPO, ranging from 0% to 100%. A Fourier transform infrared spectrum (FTIR) equipped with a diamond attenuated total reflectance (ATR) was used to characterise the functional groups of standard and produce biodiesel. FTIR spectra were collected from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution and 32 scans.

A 100 mg sample was placed in a 10 mL volumetric flask and diluted to the desired volume with toluene. A gas chromatography-mass spectrometer (Agilent 7890B GC and Agilent 5977B MSD) with an HP5MS capillary column was used to analyse the prepared sample. Helium was used as the carrier gas, and the injector and detector temperatures were set to 250°C. The temperature program started at 60°C and was held for 2 min then increased to 200°C at a rate of 10°C/min and finally to 240°C at a rate of 5°C/min and held constant for 7 min.

Catalyst Regeneration and Reusability

After each reaction, the used catalyst was filtered. The catalyst was successfully treated in two steps. In the first step, the used catalyst was rinsed in n-hexane and sonication for 30 min, then dried at 110°C overnight. In the second step, the catalyst was rinsed in methanol and sonication for 30 min, then dried at 110°C overnight. The recovered catalyst was used for another transesterification process.

RESULTS AND DISCUSSION

Properties of WCPO

The results of WCPO's characterisation are shown in *Table 2*. The initial FFA value of WCPO was 0.34%. The result was below the optimal threshold limit of FFA 1 wt.%, which indicates that the WCPO could be directly converted into biodiesel with an alkali base catalyst. The moisture and volatile

content of WCPO was 1 wt.%; therefore, the oil must be heated to eliminate the moisture and volatile impurities before transesterification to prevent a saponification reaction. The iodine value of WCPO was 58.23 per 100 g of oil. It is a measure of the degree of unsaturation of WCPO and will indicate the stability of the raw material. The result of iodine value was within the suitable range for conversion into biodiesel.

TABLE 2. PROPERTY OF WCPO

Property	Unit	Value
Free fatty acid	%	0.34
Iodine value	g I_2/100 g oil	58.23
Moisture and volatile matter	wt.%	1.00

Elemental Composition of PKSA

The elemental composition of PKSA is summarised in *Table 3*. The major elements found in 100 g of PKSA were Si (30.00 wt.%), Al (3.33 wt.%), Fe (0.67 wt.%), Ca (13.33 wt.%), Mg (3.33 wt.%), and K (1.33 wt.%). Metal concentrations found in PKSA decrease in the following order: Si > Ca > Al = Mg > K > Fe. Si ion in PKSA was 30.00 wt.% in form of SiO_2, equal to 63.37 wt.%. Thus, SiO_2 is suitable for catalyst support.

TABLE 3. ELEMENTAL COMPOSITION OF PKSA

PKSA	Composition (%)					
	Si	Al	Fe	Ca	Mg	K
	30.00	3.33	0.67	13.33	3.33	1.33

Basicity of Catalyst

The Hammett indicator method was used to estimate the basicity of the catalyst. The titration was accomplished in presence of Methyl red (H _ 5.1), Neutral red (H _ 6.8), Bromothymol blue (H _ 7.0) and Phenolphthalein (H _ 9.7). *Table 4* shows the strength of distribution and total basicity of the catalyst. The alkalinity of PKSA was found to be in the range of 6.8 < H _ < 7.0, indicating that the support has a low-basicity. The overall basicity of the catalyst gradually increases in the range of 7.0

< H _ < 9.7 after being loaded with KOH from 10 to 20 wt.%. The basic strength of the catalyst increases in the order of PKSA < 10%K/PKSA = 15%K/PKSA < 20%K/PKSA respectively.

Thermogravimetric Analysis

TGA was used to investigate the PKSA's degradation patterns. *Figure 2* depicts the profile of PKSA's decomposition in the atmosphere. According to the TGA curve, there was a 99.62% weight loss between 100ºC and 230ºC due to the elimination of adsorbed moisture from the material. The significant loss of 97.63% and 96.70% in the range of 336ºC to 568ºC due to the decomposition of organic matters such as hemicellulose, cellulose and lignin (Abdullah *et al.*, 2021). The mass loss stage at 600ºC to 800ºC may possibly be due to the decomposition of residual products of CO_2, CO and tar which originated from the decomposition of residue lignin (Abdullah *et al.*, 2021; Ashok *et al.*, 2015; Yashim *et al.*, 2016).
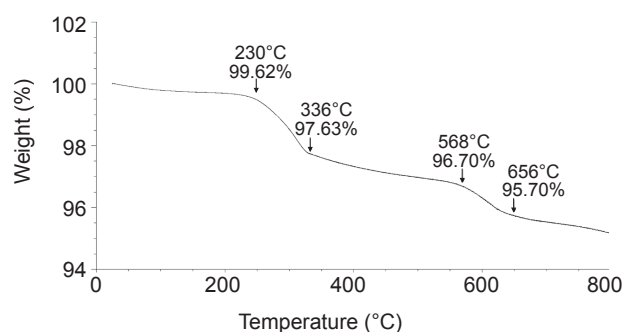

Figure 2. TGA profile.

BET Surface Area

BET surface of PKSA was observed to be 4.99 m²/g. Pore size adsorption average pore width was obtained at 12.27 nm. Single pore adsorption total pore volume was obtained at 0.02 cm³/g. The result shows that surface area of PKSA was less, the activity of PKSA catalyst needs to be improve by adding basicity site as KOH onto the surface of PKSA. However, after impregnation of KOH at 10 wt.%, 15 wt.% and 20 wt.% the result of BET surface area was observed as non-porous material with very low

TABLE 4. LIST OF HAMMETT INDICATORS USED FOR SURFACE ACIDITY MEASUREMENT

Indicator	Color		H _	Color			
	Acidic	Basic		PKSA	10%K/PKSA	15%K/PKSA	20%K/PKSA
Methyl red	Red	Yellow	5.1	Yellow	Yellow	Yellow	Yellow
Neutral red	Yellow	Red	6.8	Red	Red	Red	Red
Bromothymol blue	Yellow	Blue	7.0	Blue	Blue	Blue	Blue
Phenolphthalein	Colorless	Pink	9.7	Colorless	Light pink	Light pink	Pink

surface area for all impregnation catalysts. A similar behaviour has been reported for potassium and TiO_2 when calcined at high temperature. Salinas *et al.* (2012) found that using a high loading of potassium and a high calcination temperature resulted in the lower BET surface area of potassium supported TiO_2 catalysts. The BET areas of the catalyst calcinated at 300ºC, 500ºC and 700ºC were 18, 19 and 2 m^2/g, respectively. In addition, Soetaredjo *et al.* (2011) have reported that the BET surface area of the bentonite catalyst decreased with KOH loading. During the impregnation, the KOH molecules filled the catalyst's available pores, resulting in a decrease in the catalyst's surface area. This suggests that the KOH molecules present on the surface of the pores were probably converted to K_2O during calcination. As a result, after loading with KOH, the pore structure of mesoporous material changes to a nonporous structure. The activity of the K/PKSA catalyst was investigated using RSM to determine the optimal reaction.

Quantitative Analysis of Biodiesels by ATR-FTIR

FTIR analysis of thirteen calibration solutions of biodiesel standard with different levels of biodiesel in WCPO is presented in *Figure 3.* The overlaid peak at 1435 cm^{-1} band corresponds to the asymmetric stretching of -CH_3 present in the biodiesel spectrum and absent in the WCPO spectrum (Soria-Figueroa *et al.,* 2019). The calibration curve for the FAME concentration was made by measuring the peak at 1435 cm^{-1}. According to the data, a linear calibration model was created. The method was used to predict the concentration of biodiesel and unreacted starting WCPO, or reaction intermediates (*e.g.*, mono-, di-, and triglycerides).

For qualitative analysis, The FTIR spectra of biodiesel standard and biodiesel standard blends with WCPO were compared. The biodiesel yield was calculated using the relation shown in Equation (1).

$$\text{Yield (\%)} = \frac{\text{(Weight of biodiesel produced)} \times \text{(\%FAME from FTIR)}}{\text{Weight of waste cooking oil}} \times 100 \quad (1)$$

Optimisation of Methyl Ester using Response Surface Methodology

The relationship between FAME yield and three independent variables were analysed with RSM based on Box-Behnken design. Three variables affected such percentage of catalyst [Catalyst (wt.%)], percentage of potassium on surface of catalyst (%K) and methanol/oil ratio (M/O ratio) were studied. The fifteen experiments conducted are presented in *Table 5.* The methyl ester yield is the response variable which depended on the different variation in the three parameters. The validity of the significant model is verified by a low *p*-value ($p < 0.05$). Regression analysis of the biodiesel yield prediction was employed to fit full second-degree polynomial model, including linear, quadratic, and interaction at 5% level of significance except for %K*%K, Catalyst (wt.%)*%K and %K*M/O ratio as shown in *Table 6.* Meanwhile, a *p*-value of lack of fit greater than 0.05 indicates that when compared to error, lack of fit was found to be insignificant (Arumugam and Sankaranarayanan, 2020).
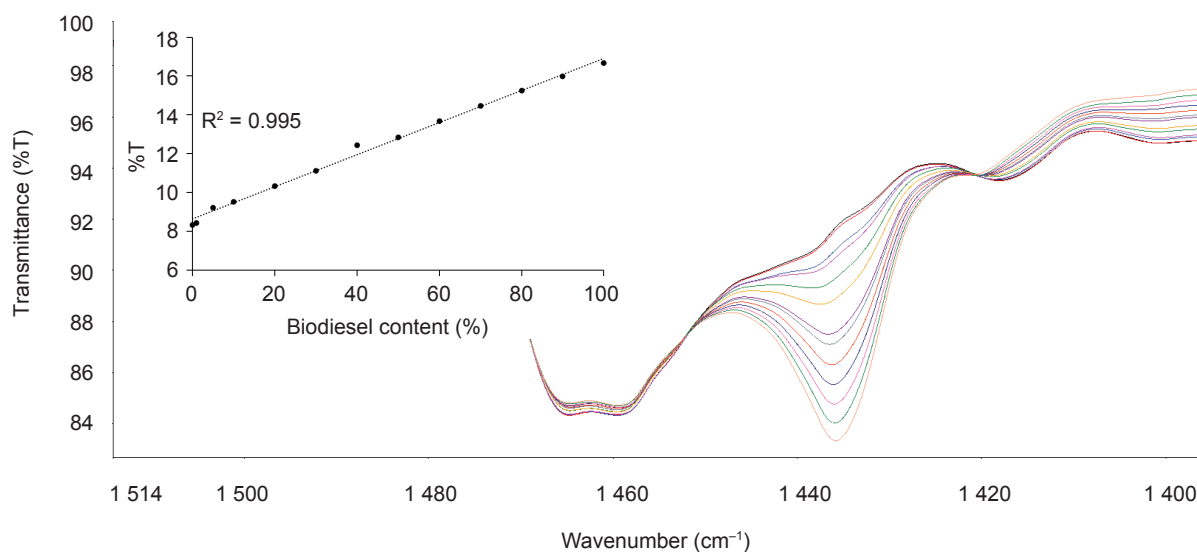

Figure 3. Infrared spectra for different percentages of biodiesel blend with WCPO.

TABLE 5. BIODIESEL YIELD RESPONSES OF BBD

Runs	Catalyst (wt.%)	%K	M/O	Biodiesel yield
1	5	10	9	9.55
2	15	10	9	43.48
3	5	20	9	65.21
4	15	20	9	84.58
5	5	15	6	34.92
6	15	15	6	2.18
7	5	15	12	2.94
8	15	15	12	80.97
9	10	10	6	3.87
10	10	20	6	49.42
11	10	10	12	38.14
12	10	20	12	72.45
13	10	15	9	69.85
14	10	15	9	65.42
15	10	15	9	67.38

TABLE 6. ANOVA STATISTICS FOR RESPONSE SURFACE QUADRATIC MODEL OF BIODIESEL YIELDS

Source	Sum of squares	df	Mean square	F-value	p-value	Remarks
Model	12 195.9	9	1 355.10	100.63	0.000	Significant
Linear	6 469.1	3	2 156.38	160.13	0.000	Significant
Catalyst (wt.%)	1 215.1	1	1 215.05	90.23	0.000	Significant
%K	3 899.3	1	3 899.29	289.55	0.000	Significant
M/O	1 354.8	1	1 354.81	100.60	0.000	Significant
Square	2 527.1	3	858.38	63.74	0.000	Significant
Catalyst (wt.%)2	701.2	1	701.18	52.07	0.001	Significant
%K2	34.7	1	34.74	2.58	0.169	
M/O2	2 042.2	1	2 042.22	181.65	0.000	Significant
2-Way interaction	3 151.6	3	1 050.54	78.01	0.000	Significant
Catalyst (wt.%) * %K	53.1	1	53.06	3.94	0.104	
Catalyst (wt.%) * %M/O	3 067.0	1	3 067.01	227.75	0.000	Significant
%K * M/O	31.6	1	31.56	2.34	0.000	Significant
Error	67.3	5	13.47			
Lack of fit	57.3	3	19.16	3.89	0.000	
Pure error	9.8	2	4.92			
Total	12 263.3	14				

$R^2 = 0.9945$, adj = 0.9846, pred = 0.9232.

The regression coefficient (R^2) indicates and measures the goodness and accuracy of fit for regression models. The R^2 value determined was 99.45%. R^2 adjusted and R^2 predicted shows a close correlation among predicted and observed values. The R^2 adjusted was determined as 98.46% and R^2 predicted was determined as 92.32% indicating that a model's accuracy is high. Regression equation for FAME yield (%) obtained by regression analysis as Equation (2).

$$\% \text{ Yield} = -237.7 - 0.94 \text{ Catalyst (wt.\%)} + 11.24 \text{ \%K} + 35.72 \text{ M/O ratio} - 0.5512 \text{ Catalyst (wt.\%)}^* \text{ Catalyst (wt.\%)} - 0.1227 \text{ \%K*\%K} - 2.613 \text{ M/O ratio*M/O ratio} - 0.1457 \text{ Catalyst (wt.\%)*\%K} + 1.846 \text{ Catalyst (wt.\%)*M/O ratio} - 0.187 \text{ \%K*M/O ratio}$$
(2)

The distribution of residuals was analysed to evaluate the adequacy of the model. The residuals plots were straight lines as shown in *Figure 4a* indicated that the residuals follow a normal distribution (Körbahti and Rauf, 2008; Noshadi *et al.*, 2012). *Figures 4b, 4d* shows the value of the residual random pattern, which suggests that the model is consistent with the experimental data with no error recorded (Hasni *et al.*, 2017). The histogram of the residual was shown in *Figure 4c*. The following histogram of residuals suggests that the residuals (and hence the error terms) are normally distributed.

Surface and contour plots illustrated in *Figure 5* depict the effect of independent parameter variables on the percent yield of biodiesel. It was observed that the parameter variables influence the processing of biodiesel. The effect of the interaction of Catalyst (wt.%) and %K on biodiesel yield was demonstrated in *Figure 5a and 5d*. The biodiesel yield of over 80% can be obtained at 12 wt.% of Catalyst and 18%K this could be attributed to the fact that at high alkalinity of the catalyst increases the rate of reaction. When the number of catalysts is increased, the reaction species also increased, thereby shifting the reaction forward, hence increase yields of biodiesel. It indicates that both %K and Catalyst (wt.%) has a positive effect on biodiesel yield. It has been shown that catalyst weight present increase over 13% shows a decrement in biodiesel yield. *Figure 5b, 5e* show the effect of Catalyst (wt.%) and M/O ratio on the yield of biodiesel. The yield of biodiesel increases to over 80% at Catalyst (wt.%) and M/O ratio to about 13% and 11 molar ratio respectively. It has been observed that biodiesel yield decreases when Catalyst (wt.%) was beyond 13 wt.%, substantiating the previous results. The surface plots and contour plots of *Figure 5c, 5f* show combined effect of %K and M/O ratio on biodiesel yield respectively. The result shows that increasing both variables increase the yield of biodiesel. The biodiesel yield increases over 80% were observed at 18%K and 10:1 molar of M/O ratio, the biodiesel yield declined beyond the M/O ratio (10:1) this could be attributed that the excess methanol deactivated the catalyst activity thereby reducing its effectiveness (Ezekannagha *et al.*, 2017).
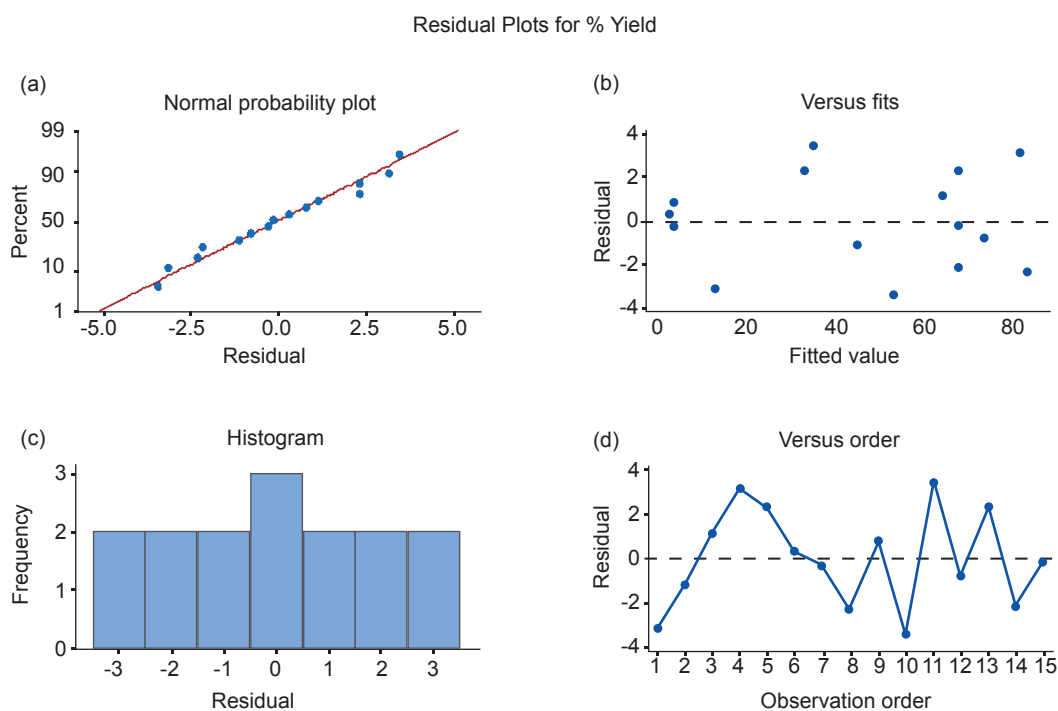

Residual Plots for % Yield

Figure 4. Residual plots for biodiesel yield.
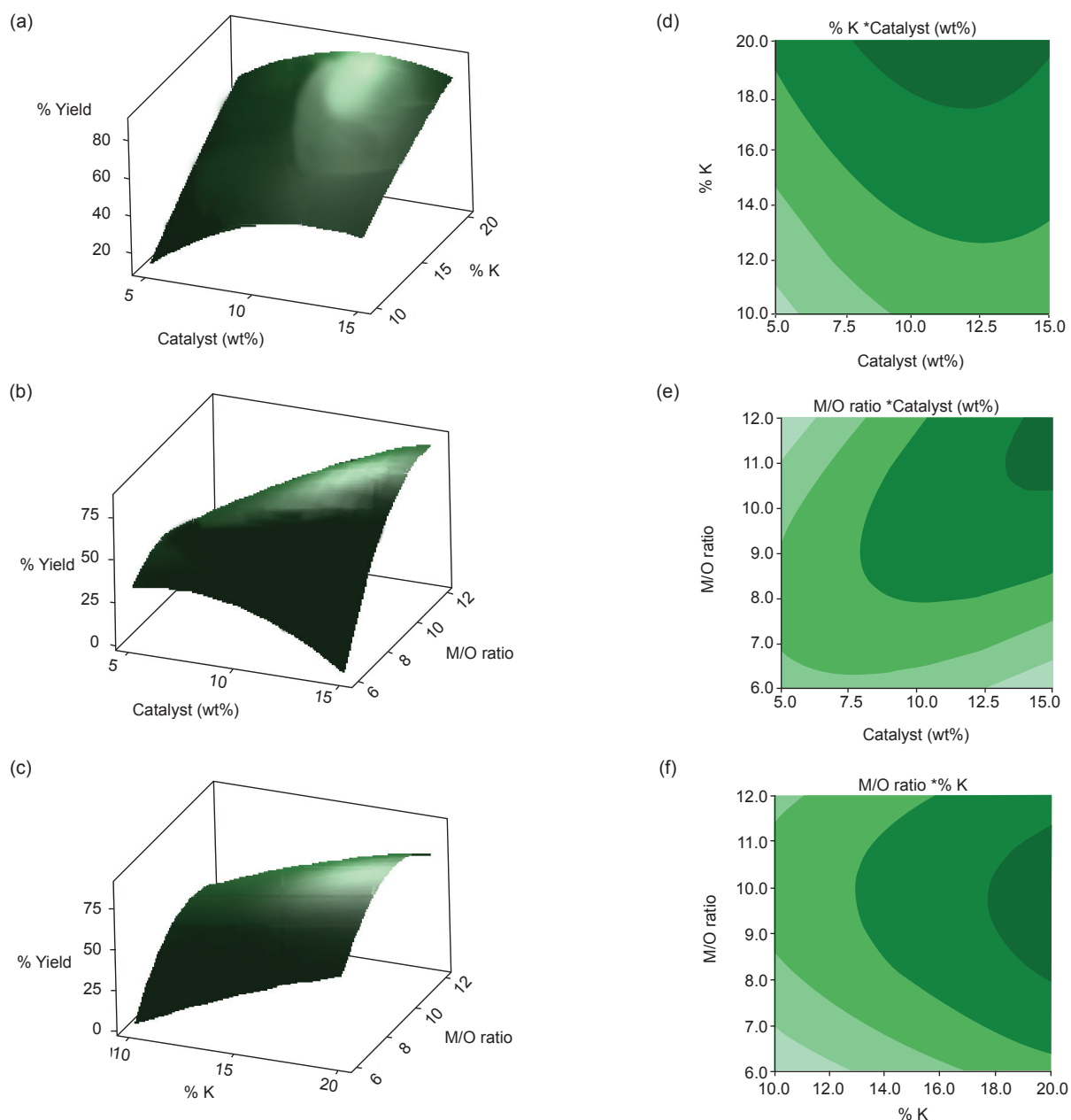
(a)

(b)

(c)

(d)

(e)

(f)

Figure 5. Contour and 3D surface.

The optimisation parameter of individual responses was 15% Catalyst (wt.%), 20% K and 11.39 M/O with the highest biodiesel yield of 96.73%. The experimental verification yielded a maximum of 92.74%, which corresponded well with the value obtained from the regression model.

Physicochemical Properties of FAME Derived from WCPO

The physicochemical properties of biodiesel were measured and compared with the fuel reference standard of Thailand. From the results, the fuel properties of the synthesised biodiesel met the established standard. The properties such as

kinematic viscosity, density, acid value, flash point and moisture content of the synthesised biodiesel were measured and listed in *Table 7*.

TABLE 7. PHYSICOCHEMICAL PROPERTIES OF BIODIESEL PRODUCED FROM WCPO WITH PKSA CATALYST

Properties	Unit	Biodiesel from WCPO	Biodiesel standard
Viscosity	mm^2/s	4.77	3.5 – 5.0
Acid value	mg KOH/g	0.27	< 0.5
Cloud point	°C	7.00	-
Pour point	°C	6.00	-
Flash point	°C	166.00	> 120.0
Iodine value	g I$_2$/100 g oil	56.00	< 120.0

The chemical composition of biodiesel was determined by using GC-MS analysis and the mass percent of fatty acid methyl ester is presented in *Table 8*. From the table, it was observed that biodiesel primarily contained methyl myristate (0.44 wt.%), methyl palmitoleate (4.43 wt.%), methyl palmitate (22.49 wt.%), methyl linoleate (20.50 wt.%), methyl oleate (41.33 wt.%), methyl elaidate (2.88 wt.%), methyl stearate (7.24 wt.%) and methyl eicosenoate (0.69 wt.%). *Figure 6* shows the fatty acid methyl ester chromatogram of biodiesel produced from WCPO.

TABLE 8. BIODIESEL COMPOSITION DETERMINED BY GAS CHROMATOGRAPHY – MASS SPECTROMETRY

RT (min)	Compound	Content (%)
15.77	Methyl myristate	0.44
17.83	Methyl palmitoleate	4.43
18.08	Methyl palmitate	22.49
20.28	Methyl linoleate	20.50
20.38	Methyl oleate	41.33
20.43	Methyl elaidate	2.88
20.68	Methyl stearate	7.24
23.14	Methyl eicosenoate	0.69
Total		100

Comparison Studies

The activity of the 20%K/PKSA was compared with previous reports as presented in *Table 9*. The effects of reaction temperature, reaction time, methanol to oil molar ratio, percentage yields, and catalyst recyclability are compared. The maximum biodiesel yield provided by the 20%K/PKSA under optimum conditions was 92.74%. It was discovered that the 20%K/PKSA catalyst has a comparable catalytic activity to the catalyst previously reported in the literature as stated in *Table 9*. In several studies, biodiesel production using various biomass base catalysts report higher percentage yields with longer reaction time and higher reaction temperature than 20%K/PKSA. It demonstrates that the 20%K/PKSA catalyst was more active than the catalysts used in this investigation.

Catalyst Regeneration and Reusability

Figure 7 shows the effect of the recycling process on the production of biodiesel. For the third successive cycle performed under the optimal conditions, the biodiesel yields were 92.74%, 73.55% and 52.23%, respectively. Subsequently, the catalytic activity of the catalyst continued to
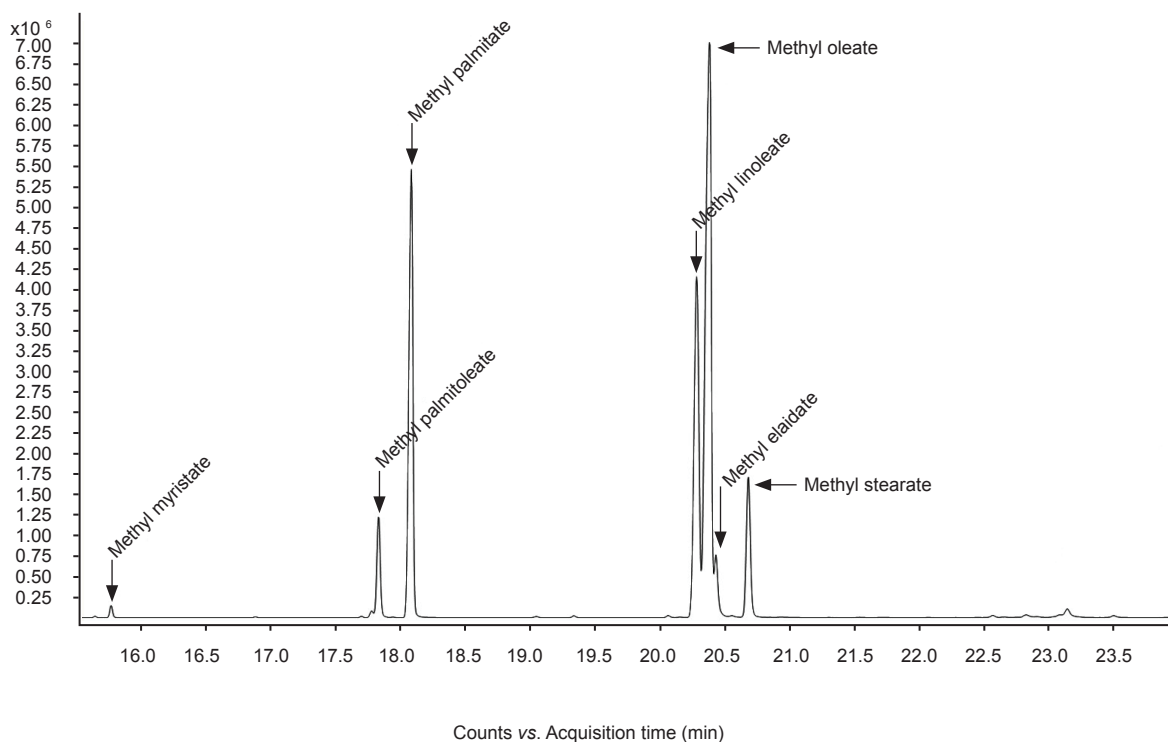

Figure 6. Chromatogram biodiesel production from WCPO.

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TABLE 9. THE COMPARISON OF BIODIESEL PRODUCTION USING ASH AS HETEROGENEOUS CATALYSIS REPORTED IN THE LITERATURE WITH THE PRESENT WORK

Catalyst	Temp. (°C)	Time (min)	Molar ratio	Yield (%)	Ref.
ZnO/Coal fly ash	140.0	180.00	12:1	83.17	Yusuff *et al.*, 2021
CaO/Wheat ran ash	54.6	144.21	12:1	93.60	Gouran *et al.*, 2021
CaO/SiO$_2$/Rice husk biochar	65.0	180.00	9:1	93.40	Zhao *et al.*, 2018
KOH/bentonite	60.0	180.00	6:1	90.70	Soetaredjo *et al.*, 2011
KOH/palm shell activated carbon	64.1	60.00	24:1	97.72	Baroutian *et al.*, 2010
K$_2$CO$_3$-CuO/PKSAC	70.0	120.00	12:1	95.36	Abdullah *et al.*, 2021
Sugarcane leaf ash catalyst	64.0	180.00	19:1	97.00	Arumugam and Sankaranarayanan, 2020
CaO/CaCO$_3$/palm oil mill boiler ashes	60.0	180.00	12:1	94.48	Ho *et al.*, 2012
20%K/PKSA	65.0	60.00	11.39:1	92.74	Present study

decrease. The reduction in biodiesel yield could be due to triglyceride poisoning of the active sites. To determine the cause of deactivation, used catalysts were analysed using FTIR techniques. *Figure 8* depicts the FTIR spectra of fresh 20%K/PKSA, 20%K/PKSA used after the third cycle with WCPO addition. In comparison to the spectrum of a fresh catalyst, the spectrum of a used catalyst after three cycles indicates an additional band between 3000 to 2800 cm^{-1} and a region at 1743 cm^{-1}. These additional spectra correspond to the vibrations of adsorbed species and are comparable to the WCPO spectra's bands. The additional function groups on the reused catalyst were 2923 and 2852 cm^{-1} (-C-H of methylene group) and 1743 cm^{-1} (C=O stretch of lipid and fatty acid), confirmed the triglyceride blockage on active sites and hence negatively affect the catalytic active sites (Yusuff *et al.*, 2021). The results indicate that the washing process using n-hexane and methanol is unable to completely remove the triglyceride accumulation from the surface of the catalyst.

However, the decline in the activity of the catalyst could be due to the leaching of the active phase to the methanol phase. According to Ghasemi *et al.* (2014), the loss of catalyst activity could be attributed to the leaching of potassium content as K$_2$O to the methanol phase. The leached and dissolved of K$_2$O in the methanol would react as a homogeneous catalyst. As a result, the process advantages of heterogeneous catalysts are reduced. Other than that, another study reported by Alonso *et al.* (2007) confirmed that the leaching of the active phase to the methanol phase, the potassium content of K/γ-Al$_2$O$_3$ was measured by ICP-AES in the fresh catalyst and after the reaction. The results confirmed that the K/Al ratio remaining in the catalyst decreased by 40% in the second run and 75% in the fourth run. These results demonstrate that the decrease in catalyst activity between catalytic runs was due to the leaching of active species to the methanol phase. In addition, the leached of K$_2$O was also observed by Saba *et al.* (2016). The XRF results obtained for the spent 35KOH/ZSM5 catalyst showed that 3.8% of the K$_2$O active phase was leached after 1st run and 9.4% after the 4th run in the experiment. These results explain how a yield of FAME decreases as the number of runs increases.
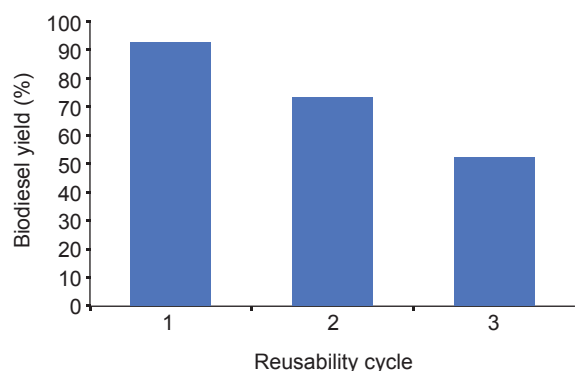

Figure 7. Effect of reusability of 20%K/PKSA on WCPO transesterification at optimal conditions (at 65°C, 60 min reaction time, 15% PKSA, 20% K and 11.39 M/O).
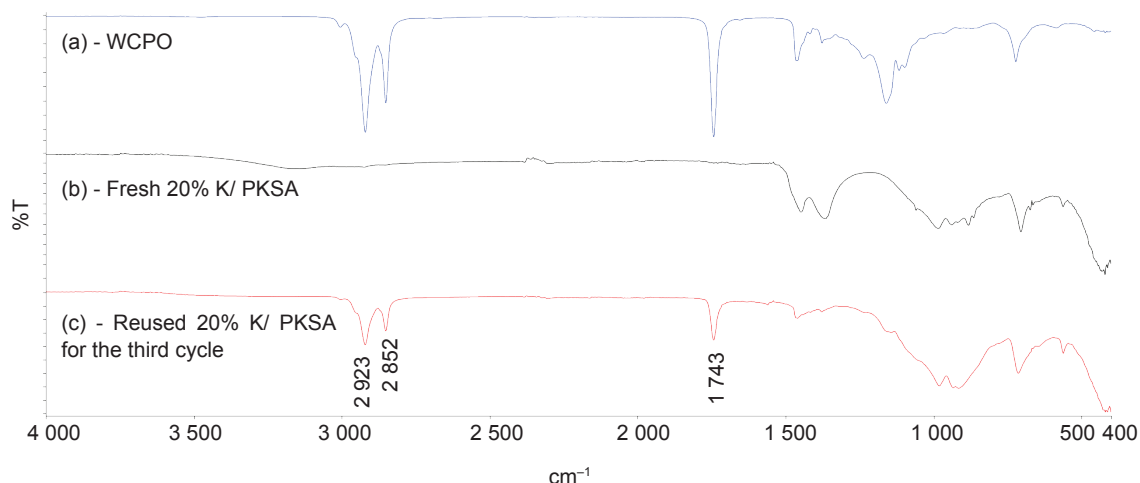
Figure 8. FTIR spectra of (a) WCPO, (b) Fresh 20%K/PKSA catalyst and (c) Reused 20%K/PKSA catalyst for the third cycle.

In this study, the 20%K/PKSA catalyst demonstrated greater stability and reusability for the transesterification process than the eco-friendly catalysts previously reported. For example, when a CaO-fly ash catalyst was used to produce biodiesel from crude palm oil, the yield decreased from 79.76% to 38.93% after the third cycle (Ho *et al.*, 2014). In addition, Olutoye *et al.* (2016) produced biodiesel from used cooking oil and reported that the yield decreased from 83.38% to 21.50% after the third cycle of reuse of the montmorillonite K10-supported BaO catalyst. Yusuff *et al.* (2019) demonstrated that an eggshell-supported alumina catalyst could be reused four times with the product yield decreasing from 77.56% to 18.92%.

CONCLUSION

The study demonstrated that the modified palm kernel shells ash (PKSA) with KOH can produce the WCPO biodiesel by using the response surface methodology on Box-Behnken design. The highest biodiesel yield of 92.74% was obtained at the optimum reaction conditions of 15.00% Catalyst (wt.%), 20% K, and 11.39 M/O at 65°C reaction temperature for 60 min. Analysis of variance showed a high coefficient of determination $R^2 = 0.9945$ and Adj-$R^2 = 0.9846$. This demonstrated that response surface methodology with Box-Behnken design can be an effective method to optimise the process parameter for biodiesel production. Furthermore, the prepared catalyst demonstrated a remarkable reusability profile up to the third cycle with a 52.23% biodiesel yield. The physicochemical properties of synthesised biodiesel properties meet with the established standard in Thailand. This study revealed that modified PKSA

with KOH is an eco-friendly catalyst with the capability for cost-effective applications for biodiesel production. Biodiesel from WCPO could be used as an alternative diesel fuel that can be considered as renewable energy and environmental recycling process of waste oil after frying.

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