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Continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid: Optimization using response surface methodology (RSM)

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ABSTRACT

This study aims to develop an optimal continuous process to produce fatty acid methyl esters (biodiesel) from waste cooking oil in a reactive distillation column catalyzed by a heteropolyacid, $H_3PW_{12}O_{40}\cdot 6H_2O$. The conventional production of biodiesel in the batch reactor has some disadvantage such as excessive alcohol demand, short catalyst life and high production cost. Reactive distillation combines reaction and separation to simplify the process operation. The reaction catalyzed by $H_3PW_{12}O_{40}\cdot 6H_2O$ overcomes the neutralization problem that occurs in conventional transesterification of waste cooking oil with high free fatty acid (FFAs) and water content. Response surface methodology (RSM) based on central composite design (CCD) was used to design the experiment and analyzed four operating parameters: total feed flow, feed temperature, reboiler duty and methanol/oil ratio. The optimum conditions were determined to be 116.23 (mol/h) total feed flow, 29.9 °C feed temperature, 1.3 kW reboiler duty, and 67.9 methanol/oil ratio. The optimum and actual free fatty acid methyl ester (FAME) yield was 93.98% and 93.94%, respectively, which demonstrates that RSM is an accurate method for the current procedure.

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1. Introduction

Alternative and renewable sources of energy have become more attractive in recent years due to the depletion of world petroleum reserves, increasing energy demand, increasing environmental concerns due to rising greenhouse gas emissions, and rising petroleum prices [1]. Biodiesel is a renewable fuel that consists of alkyl esters obtained from vegetable oil and animal fat [2]. The main advantages of using biodiesel are its renewability, better lubricity, biodegradability and significant decreases in emitted particulates, unburned hydrocarbons, and carbon monoxide, relative to petrodiesel [3].

Biodiesel is typically produced via transesterification, which is the reaction of vegetable oils with alcohol to produce alkyl esters and glycerol by using an appropriate catalyst [4]. The overall reaction scheme for the methanolysis of triglycerides consists of a sequence of three reversible reactions (R1–R3), where TG, DG and MG refer to tri-, di-, and monoglycerides, respectively, G represents glycerol, and FAME represents fatty acid methyl esters or biodiesel [5,6].

$$\mathrm{TG} + \mathrm{MeOH} \overset{catalyst}{\leftrightarrow} \mathrm{DG} + \mathrm{FAME} \tag{R1}$$

$$\mathrm{DG} + \mathrm{MeOH} \overset{catalyst}{\leftrightarrow} \mathrm{MG} + \mathrm{FAME} \tag{R2}$$

$$\mathrm{MG} + \mathrm{MeOH} \overset{catalyst}{\leftrightarrow} \mathrm{G} + \mathrm{FAME} \tag{R3}$$

Compared to petroleum-based diesel, the high price of biodiesel produced from virgin oils is a major hurdle to commercialization [7,8]. Since the price of waste cooking oil (WCO) is 2–3 times less than virgin vegetable oil, use of low-cost feedstock such as WCO could decrease biodiesel production cost since the feedstock cost often accounts for over half the finished cost of the biodiesel [9]. The production of waste cooking oil has increased due to increasing food consumption in restaurant and food [7,8]. The conversion of WCO into biodiesel not only eliminates the environmental impacts caused by the disposal of these waste oils but also decrease the production cost of biodiesel significantly [7,8].

Biodiesel is currently produced in batch processes which are penalized by important shortcomings such as: high alcohol demand required to shift equilibrium towards fatty esters, necessity of catalyst neutralization causing a salt waste stream, high separation costs of fatty ester products from the reaction mixture, high costs caused by complex processes including multiple reactors and separation units [7,10,11]. As a result, process intensification technologies like reactive distillation have become more attractive in recent years [12].

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Reactive distillation (RD) is the combination of reaction and distillation in a single unit, thus increasing mass transfer while simplifying the process operation [13,14]. It may be advantageous for reactions with a large excess of one or more reactants, or when removal of one or more products is necessary for completion of reaction, or when product recovery or by-product recycle is complicated [15].

In recent literature, many investigations about reactive distillation can be found, but information on the (trans)esterification of long chains fatty acids by reactive distillation is rare. Bock et al. [16] conducted experimental production of myristic acid with isopropanol by using homogenous acid-based catalysts such as sulfuric acid in a two-column facility. Steinigeweg and Gmehling [17] explored biodiesel production by reactive distillation process from decanoic acid and methanol using a heterogeneous catalyst, Amberlyst. Conceptual design of RD column to produce 2-ethylhexyl dodecanoate using sulfated zirconia as a solid acid catalyst was investigated by Omota et al. [11]. Bhatia et al [12] carried out esterification of palmitic acid (PA) with isopropanol to make isopropyl palmitate (IPA) in a pilot plant scale obtaining high conversion. Singh et al. [1] investigated biodiesel production from canola oil and methanol using potassium hydroxide as catalyst by reactive distillation.

The catalyst has a significant role in transesterification of vegetable oil. Two types of catalyst are typically used for transesterification viz basic catalyst and acid catalyst Banerjeea and Chakraborty [4]. Compared to virgin vegetable oil, the production of biodiesel from WCO by using base catalyst is challenging due to large amount of FFAs and water content in this oil. High FFA content in the raw material results in undesirable side reactions such as saponification, which leads to serious problems of product purification and catalyst removal [18]. Therefore, high FFA content in the feedstock lowers ester conversion and yield significantly. Liquid acid catalysts are more effective if the quantity of FFAs in the raw material is more than 1%. Sulfuric acid and hydrochloric acid are often used as homogenous catalysts for acid-catalyzed transesterification. By using acid-based catalyst, the rate of reaction is very slow, requiring 48–96 h even at high methanol to oil (30–150:1) ratio and a reflux of methanol. Moreover, the mineral acids are corrosive for equipment and generate large amounts of salt due to neutralization. A solid acid catalyst could eliminate these problems and have some advantages compared to liquid acid catalysts such as reusability, better separation, less environmental impact and less corrosion of equipment.

Among solid acid catalysts, heteropolyacids (HPAs) are quite active for heterogeneous reactions. HPA is 2–4 times more active than mineral acids and shows higher selectivity [19]. Compared to molybdenum HPAs, tungsten HPAs are usually used due to better acidity, higher thermal and lower oxidation potential. Among the keggin type heteropolyacid series, PW12 shows highest catalytic activity if the catalyst acid strength controls the rate of reaction [20]. There are few reports on transesterification of triglyceride catalyzed by heteropolyacid in a batch reactor. Narasimharao et al. [21] used insoluble Cs salt of heteropolyacids for transesterification of triglyceride and Coa et al. [19] investigated the transesterification of WCO using $H_3PW_{12}O_{40}(6H_2O)$ as catalyst in a batch reactor.

However, no reports were found on biodiesel production from WCO by using heteropolyacid catalyst in a reactive distillation column. The present work focused on the operating parameters that affected acid-catalyzed transesterification of waste cooking oil with methanol in a continuous reactive distillation column. The aim of this study was to better understand the relationship between operating conditions and the response FAME yield, and to find the optimal condition of the process by using response surface methodology (RSM). An important branch of experimental design is RSM. It is a critical method to develop new processes, optimize their performance and improve design and formulation of new products [22,23]. The optimization of biodiesel production in a reactive distillation column improves the conversion and yield and reduces the production cost of the process.

2. Material and methods

2.1. Materials

WCO used in this study was collected from local domestic consumers. The oil composition based on fatty acid content was identified by gas chromatography (GC) according to The American Oil Chemical Society official methods [24]. Furthermore, the used cooking oil was characterized by moisture content, acid value, and iodine value. Moisture content and acid value were determined according to EN 12937 and ASTM D664 methods, respectively. Properties of WCO used in our study are shown in Table 1. The catalyst, 12-Tungstophosphoric acid hydrate (99%), was purchased from Kinbester Co. Ltd. (China) while methanol of purity 99.8% was obtained from Mallinckrodt Chemicals (USA).

2.2. Statistical methods

Transesterification of WCO with 12-Tungstophosphoric acid was developed and optimized following the response surface methodology (RSM) to produce biodiesel in the reactive distillation column. RSM was utilized to design experiments, model and optimize FAME yield as a response. A central composite design (CCD) with four factors was utilized to determine the effect of variables on FAME yield. The CCD is a suitable design for sequential experiments to obtain appropriate information for testing lack of fit without a large number of design points [22,23]. The four factors, or independent variables, were coded at three levels between −1 and +1, where −1 corresponds to the minimum and +1 corresponds to the maximum value of each variable, as noted in Table 2. The four factors investigated were total feed flow (*A*), reboiler duty (*B*), feed temperature (*C*), and methanol/oil ratio (*D*). Prior to experimental design, feasibility experiments were performed to determine the ranges of feed flow rate, reboiler duty, feed

Table 1
Physical and chemical properties of canola oil WCO.

Property	WCO
Fatty acid composition (%)	
Myristic C14:0	1.1
Palmitic acid C16:0	22.5
Palmitoleic 16:1	4.1
Stearic acid C18:0	4.4
Oleic acid C18:1	54.7
Linoleic acid C18:2	11.2
Linolenic acid C18:3	1.1
Density at 25 °C	0.926
Viscosity (mm^2/s) at 40 °C	49.93
Acid value (mg KOH/g)	7.45
Saponification number (mg KOH/g)	206
Iodine number (mg KOH/g)	78
Moisture content (%)	1

Table 2
Experimental design of biodiesel production from WCO by RD column.

Independent variable	Low actual value	High actual value
A: total feed flow rate (mol/h)	115	150
B: reboiler duty (kW)	1	1.5
C: inlet temperature (°C)	20	30
D: methanol/oil ratio	30	70

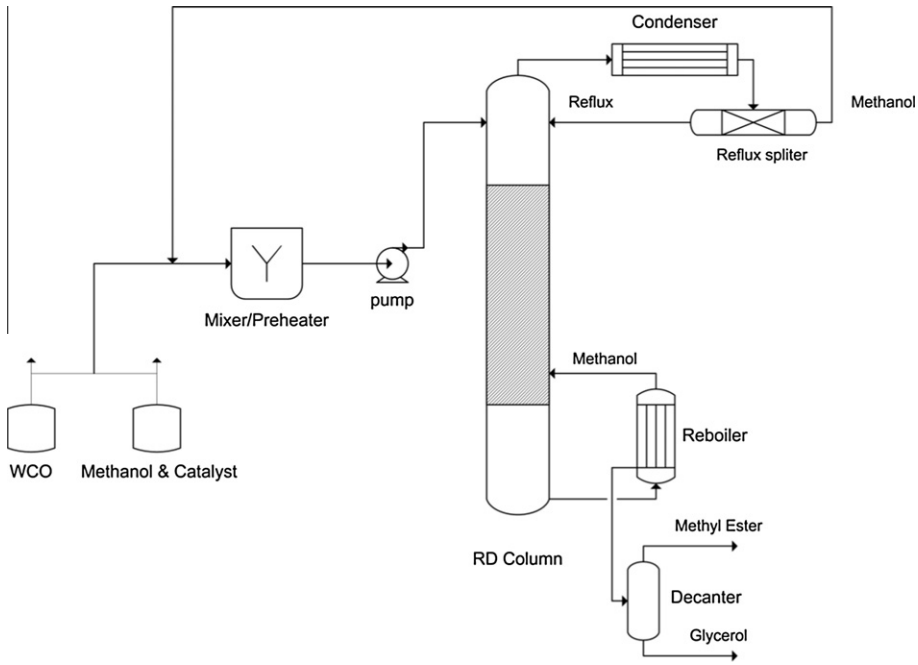

Fig. 1. Schematic diagram of reactive distillation system.

temperature and methanol:oil ratio. The ranges in Table 2 were chosen based on the feasibility experiments.

The total number of experiments was thirty ($2^k + 2k + 6$) where k is the number of factors and equals four. Twenty-four experiments and six replication experiments at design center were carried out randomly to estimate the error. The test factors were coded based on Eq. (1) in the regression equation:

$$X_i = \frac{U_i - U_i^o}{\Delta U_i} \tag{1}$$

U_i is independent variable real value, X_i is independent variable coded value, U_i^o is independent variable real value in center point of the independent variable and ΔU_i is the step change in U_i. Thus, the coded variables range from −1 to +1.

To formulate a simple model suitable for optimization, the response is related to the selected variables by linear and quadratic terms, as follows:

$$\eta = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} x_i x_j + e_i \tag{2}$$

η is response, x_i and x_j the independent factors, β_0 the constant coefficient, β_j, β_{jj} and β_{ij} the coefficient for linear, quadratic and interaction effect and e_i is the error. The coefficients of determination R^2 and R^2_{adj} in Eqs. (3) and (4) indicated the quality of the fit of polynomial. The statistical significance was checked with Eqs. (5) and (6), and also by F-value and p-value [25]:

$$R^2 = 1 - \frac{SS_{resedual}}{SS_{model} + SS_{resedual}} \tag{3}$$

$$R^2_{adj} = 1 - \frac{SS_{residual}/DF_{residual}}{(SS_{model} + SS_{residual})/(DF_{model} + DF_{resedual})} \tag{4}$$

$$\text{Adequate precision} = \frac{max(\hat{Y}) - min(\hat{Y})}{\sqrt{\bar{V}\hat{Y}}} \tag{5}$$

$$\bar{V}(\hat{Y}) = \frac{1}{n}\sum_{1}^{n} V(\hat{Y}) = \frac{P\sigma^2}{n} \tag{6}$$

In these equations, DF is the degree of freedom, P is the number of model parameter, SS is the sum of squares, σ^2 is the residual mean square from ANOVA result and n is number of experiment. The response FAME yield was measured at the end of experiment. The Design-Expert 7.1 software was used in this study to plot response surface and analyzed experimental data.

3. Experimental

3.1. Experimental set up

The experiment was carried out in a pilot plant scale reactive distillation glass column with eight trays and inner diameter of 80 mm as shown in Fig. 1. A horizontal kettle type reboiler with electrical heating provides an infinitely variable output between 0 kW and 6 kW, and was used to supply vapor in the column. The total condenser and a reflux splitter were used to supply reflux in the column. The feed stream was introduced as a liquid to the top of tray 1 to maximize the liquid phase reaction zone in the column.

Two chemical magnet pumps (Senso, PMD-611) were used to feed methanol and WCO mixture containing catalyst into the column. The temperatures of the column, reboiler, feed tank and condenser were measured using thermocouples. The circulating water bath (Cole–Parmer) was used to preheat reactant mixture. The important specifications of the column are presented in Table 3. Feasibility experiments were conducted to determine the ranges of feed flow rate, reboiler duty, feed temperature and methanol:oil ratio. The range of feed flow was set by the column capabilities. At flows above 167.5 mol/h, the trays would flood, and at flows below 97.5 mol/h, the trays had no liquid holdup. The range of feed temperature was governed by practical considerations. A maximum of 35 °C was used because at higher T, the feed mixer would begin to act as a reactor, and that would invalidate the evaluation of the RD column. Below 15 °C, the cold feed clearly condensed the methanol vapor, greatly reducing conversion. The range of reboiler duty was based on the fluid behavior in the reboiler. Below a reboiler duty of 0.75 kW there was little or no boiling of the liquid in the reboiler. Above a reboiler duty of 1.75 kW, the boiling liquid

Table 3
Column specification and operating conditions.

Component	Methanol/WCO/methyl oleate/glycerol
No. of separation stages including reboiler	9
Inner diameter	80 mm
Total height of the tray column	3 m
Upper feed point	
Feed flow rate (mol/h)	115
Feed temperature (°C)	25
Pressure (atm)	1
Condenser type	Total
Reboiler type	Partial

splashed over into the down flow from the bottom tray, and the column temperatures at the top rose well above 65 °C, the boiling point of pure methanol. The range of methanol/oil ratio was chosen based in Fig. 3 in Cao et al. [19]. At low ratios the conversion clearly decreased steeply while at ratios above 70, the conversion plateaued.

3.2. Experimental procedure

A pure methanol circulation was initiated in the column by first loading methanol into the reboiler. Reboiler duty was set on a desirable value to maintain vapor through the column. After 30 min, the methanol vapor reached the top of column at 65 °C and totally condensed. The liquid methanol was refluxed to fill all the trays.

The pre-heater was then filled with WCO and heated to 50 °C, and the warm WCO was stored in the pump inlet tank. Methanol was then mixed with 12-Tungstophosphoric acid (10 wt% with respect to WCO) to form one-phase solution and the solution was stored in the pump inlet tank. The solution of methanol and 12-Tungstophosphoric acid, and the WCO, were then separately pumped in the proper ratio into the preheater/mixer and mixed at 300 rpm before feeding into the column. The residence time in the preheater/mixer depended upon the feed rate, but never exceeded 60 min. In a previous report using the same catalyst and 70:1 methanol/oil ratio, conversion of waste vegetable oil only reached 45% after 8 h at 65 °C [19]. Since the maximum inlet temperature was 35 °C and the maximum residence time was 60 min in this work, the amount of reaction that occurred in the preheater/mixer was deemed negligible.

Steady state was attained after approximately 4 h, as determined in run 1 by taking samples every ½ h. To account for any run-to-run variations, each experimental run lasted 12 h, and the data presented below was determined from samples collected at the 12-hour time point.

Samples were collected from the liquid bottoms product exiting the reboiler and cooled to 0 °C immediately to prevent further reaction. Each sample was left for 12 h in a decanter to separate into a methyl ester upper layer and a glycerin lower layer. The catalyst settled to the bottom of the decanter. The catalyst was separated easily, washed with methanol to extract polar components such as glycerin, and dried by air to be reused in next experiment. For separation of residual methanol, the methyl ester layer was placed in a rotary evaporator at 65 °C for 30 min. Following the rotary evaporator, the crude methyl esters were washed with 50 °C distilled water many times (up to 10) in a separatory funnel to reach neutral pH. A bed of anhydrous sodium sulfate was used to dry methyl ester [26]. Finally, the methyl ester was stored in a bottle to be characterized. The methanol collected from top of the column was continuously recycled to the process.

The methyl ester yield reported below was calculated as the molar yield by simply dividing the moles of FAME produced by three times the moles of vegetable oil fed to the column. The factor

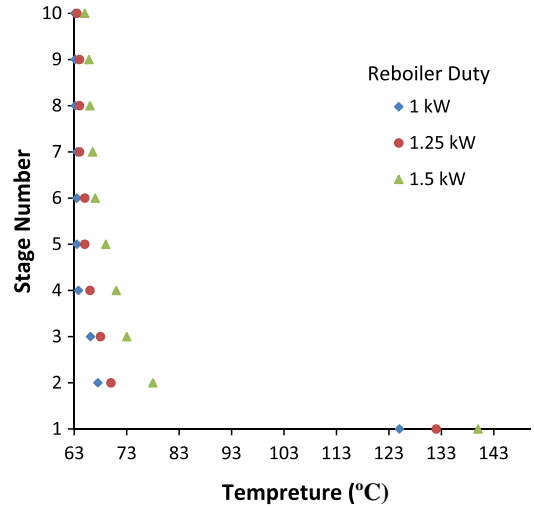

Fig. 2. Temperature profile along the height of the column for runs 2, 3 and 8.

of three is necessary because three moles of FAME are produced from each mole of completely reacted vegetable oil. In order to calculate the number of moles of FAME produced and the number of moles of vegetable oil fed to the column, the molecular weights were estimated using the fatty acid profile reported in Table 1.

3.3. Sample analysis

Most of the chemical and physical properties of the collected methyl esters were analyzed using tests that are part of the European standard EN-14214:2004 to determine several physical properties. ISO-3104:2003 and ISO-3675:1988 were carried out to measure the kinematic viscosity at 40 °C and the density at 15 °C, respectively. By titration based on EN-14104:2003 the acid value (*Av*) was calculated. The iodine value (*Iv*) was determined by EN-14111:2003. The Karl-Ficher method ISO-12937:2000 was used to calculate the water content. To determine saponification value (*Sv*) of biodiesel, titration by ISO-3657:2002 was used. The cetane index (CI) was determined by using the Krisnangkura's [27] equation as follows: $CI = 46.3 + 5458/(Sv - 0.225)\,Iv$. An example of the measured properties of obtained methyl ester are shown in Table 4 for run 19, which gave the highest biodiesel yield of all the experiments. The reported values provide a reasonable assessment of the biodiesel produced in the experiments reported below.

4. Results and discussion

4.1. Experimental results

The relationships between FAME yield and four independent variables (total feed flow, reboiler duty, feed temperature and methanol/oil ratio) were studied. The experimental design listed in Table 5 also provides the FAME yield for each experimental run. The reported yields are probably lower than actually realized since some fraction of the biodiesel was lost in the water wash operation necessary to purify the product for analysis.

The temperature distribution throughout the column is shown in Fig. 2 for runs 2, 3, and 8, where the reboiler duty was varied from 1 kW to 1.5 kW. As the reboiler duty increased from 1 to 1.5 kW, the reboiler temperature increased from 124 °C to 141 °C, indicating that the methanol fraction was low in the reboiler, and then decreased further at higher reboiler duties. Interestingly, the tray temperatures increased very little as the reboiler duty increased from 1 to 1.25 kW. With an increase of the reboiler duty from 1.25 kW to 1.5 kW, the tray temperatures in the lower trays

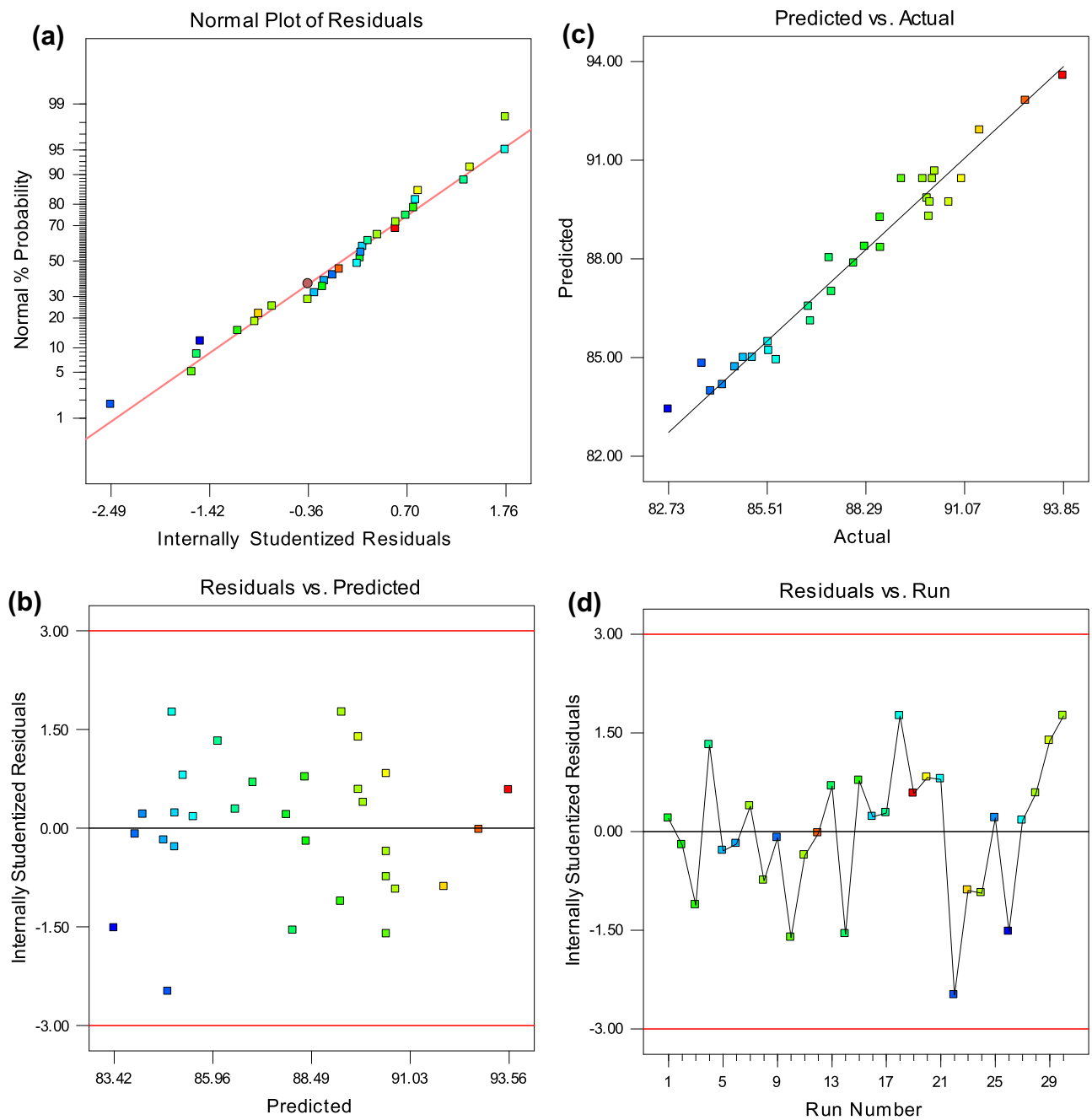

Fig. 3. (a) Normal% probability and studentized residual plot. (b) The studentized residuals and predicted response plot. (c) The actual and predicted plot. (d) The outlier *t* plot.

Table 4
Major properties of the biodiesel.

Property	Biodiesel	Requirements
Density at 25 °C (g/cm^3)	0.883	0.886 ± 0.005 (JUS EN 14214)
Viscosity at 40 °C (mm^2/s)	4.53	3.5–5 (JUS EN 14214)
Acid value (mg KOH/g)	0.272	<0.5 (JUS EN14214)
Saponification number (mg KOH/g)	205	–
Iodine number (mg KOH/g)	81	<120 (JUS EN 14214)
Cetane index	75.5	–
Moisture content (%)	0.12	<0.05% JUS standards

increased substantially, indicating much reduced methanol fractions in the reacting liquid phase.

4.2. Regression model and statistical analysis

The response obtained in Table 5 was correlated with the four independent variables using a polynomial equation, Eq. (2). Least squares regression was used to fit the obtained data to Eq. (2). The best fit model is:

$$Yield = 90.07 - 1.61A + 0.45B + 1.62C + 1.12D + 0.03AB - 0.32AC - 0.26AD + 0.15BC - 0.18BD + 0.68CD - 0.26A^2 - 1.35B^2 - 0.57C^2 - 0.67D^2 \quad (7)$$

Table 5
Experimental design results for transesterification of waste cooking oil.

Run	Block	Total feed flow rate (mol/h)	Reboiler duty (kW)	Inlet temperature (°C)	Methanol/oil ratio	Response FAME yield (*Y*) (wt%)
1	Block 1	115	1	20	70	87.95
2	Block 1	150	1	30	70	88.26
3	Block 1	150	1.5	30	70	88.7
4	Block 1	115	1	20	30	86.73
5	Block 1	150	1.5	20	70	84.84
6	Block 1	150	1	20	70	84.61
7	Block 1	115	1.5	30	30	90.02
8	Block 1	132.5	1.25	25	50	89.9
9	Block 1	150	1	20	30	83.92
10	Block 1	132.5	1.25	25	50	89.3
11	Block 1	132.5	1.25	25	50	90.17
12	Block 1	115	1	30	70	92.79
13	Block 1	115	1.5	20	30	87.33
14	Block 1	115	1.5	20	70	87.26
15	Block 1	115	1	30	30	88.7
16	Block 1	150	1.5	20	30	85.1
17	Block 1	150	1.5	30	30	86.68
18	Block 1	150	1	30	30	85.77
19	Block 1	115	1.5	30	70	93.84
20	Block 1	132.5	1.25	25	50	90.99
21	Block 2	132.5	1.75	25	50	85.56
22	Block 2	132.5	1.25	25	10	83.68
23	Block 2	97.5	1.25	25	50	91.5
24	Block 2	132.5	1.25	35	50	90.23
25	Block 2	132.5	1.25	15	50	84.25
26	Block 2	132.5	0.75	25	50	82.72
27	Block 2	167.5	1.25	25	50	85.54
28	Block 2	132.5	1.25	25	50	90.1
29	Block 2	132.5	1.25	25	50	90.63
30	Block 2	132.5	1.25	25	90	90.07

ANOVA evaluations of this model, shown in Table 6, imply that this model can describe the experiments. To measure how well the suggested model fit the experimental data, the parameters *F*-value, R^2, *p*-value, and lack of fit were used [28].

As can be seen in Table 6, *F*-value was 27.84 and implied that the quadratic model was significant. Moreover, each term in the model was also tested for significance. A *p*-value smaller than 0.05 implies that the corresponding model term is significant. From Table 6 it is clear that the linear terms for inlet temperature (*C*), total feed flow (*A*), and methanol/oil ratio (*D*) have large effects on FAME yield due to high *F*-values. The *p*-values <0.0001 show that there is only a 0.01% chance that a model *F*-value this large is the product of noise in the experiment. In addition, the linear term for reboiler duty (*B*) is also significant but with a smaller effect on the FAME yield due to its smaller *F*-value than the other linear terms. However, the quadratic term for the reboiler duty (B^2) has a large *F*-value and a *p*-value <0.0001. Thus, the effect of reboiler duty on the FAME yield is most strongly modeled with the quadratic term. The quadratic terms for inlet temperature (C^2) and methanol/oil ratio (D^2) are also significant but with *F*-values smaller than their corresponding linear terms. The quadratic term for the total feed flow (A^2) is insignificant. The only significant coupling term is between inlet temperature and methanol/oil ratio (*CD*), indicating an interaction between those two variables. Furthermore, the lack of fit *F*-value was 1.64, indicating that lack of fit is not significant relative to pure error [29]. The regression equation and coefficient of determination were evaluated to test the fit of model [30].

The distribution of residuals was analyzed to evaluate the adequacy of the model by first determining if the residuals followed a normal distribution. Residuals are the deviation between predicted and actual values and are expected to follow a normal distribution if the experimental errors were random [31]. First, the residuals were normalized with respect to their standard deviations (studentized). A normal distribution function was then fit to the studentized residuals. Then, the studentized residual predicted by the best-fit normal distribution was plotted against the experimentally obtained studentized residual in Fig. 3a. The straight line formed in Fig. 3a indicates that the studentized residuals follow a normal distribution [31]. In cases where the residuals do not follow a normal distribution, an *S*-shape curve is often formed, and this type of curve often results from the use of an incorrect model or if an additional transformation of the response is necessary [31].

Fig. 3b plots the studentized residuals versus predicted FAME yield. This plot is expected to be a random scatter, indicating that the variation in the original observations is not related to the value of the response [31]. If the variation in the original observations is related to, for example, the mean value of the responses, this plot generally shows a funnel shape. The random scatter of the residuals in Fig. 3b further indicates that the suggested model is an appropriate description of the process.

The actual and predicted FAME yields are plotted in Fig. 3c. Actual values are data for each specific run from Table 6, and predicted values are produced by the model, Eq. (7). In experimental design, R^2 is a calculation of amount of variation around the mean described by the model. However, a large value of R^2 can be misleading if the model contains extraneous terms [22,23]. By adding factors to the model, R^2 always increases whether the added factor is significant or not. Generally, the adjusted R^2 value defined in Eq. (4) does not increase as factors are added to the model. In fact, large differences between R^2 and R^2_{adj} indicate that non-significant terms are involved in the model [22,23]. The data in Fig. 3c lead to values of R^2 and R^2_{adj} of 0.9653 and 0.9307, respectively. In addition, the adjusted determination coefficient is very high to prove the high significance of the model.

In Fig. 3d, the outlier *t* plot for all runs of biodiesel production is shown. The outlier *t* plot simply indicates the magnitude of the residuals for each run to determine if any of the runs had particularly large residuals. Typically, a threshold of three standard deviations is employed as a definition of an outlier. Most of the

Table 6
ANOVA for the regression model and respective model terms.

Source	Sum of squares	*DF*	Mean square	*F* value	*p*-value prob > *F*	
Block	3.39983	1	3.39983			
Model	230.4418	14	16.46013	27.84283	<0.0001	Significant
A	62.27095	1	62.27095	105.3333	<0.0001	
B	4.764533	1	4.764533	8.059359	0.0131	
C	63.30027	1	63.30027	107.0744	<0.0001	
D	29.90657	1	29.90657	50.58791	<0.0001	
AB	0.014787	1	0.014787	0.025012	0.8766	
AC	1.646987	1	1.646987	2.785931	0.1173	
AD	1.055654	1	1.055654	1.785671	0.2028	
BC	0.36078	1	0.36078	0.610271	0.4477	
BD	0.546343	1	0.546343	0.924156	0.3527	
CD	7.340306	1	7.340306	12.41636	0.0034	
A^2	1.794722	1	1.794722	3.035829	0.1034	
B^2	49.96898	1	49.96898	84.5241	<0.0001	
C^2	9.045652	1	9.045652	15.30101	0.0016	
D^2	12.18431	1	12.18431	20.61014	0.0005	
Residual	8.276523	14	0.59118			
Lack of fit	6.652339	10	0.665234	1.638322	0.3354	Not significant
Pure error	1.624184	4	0.406046			
Cor total	242.1182	29				

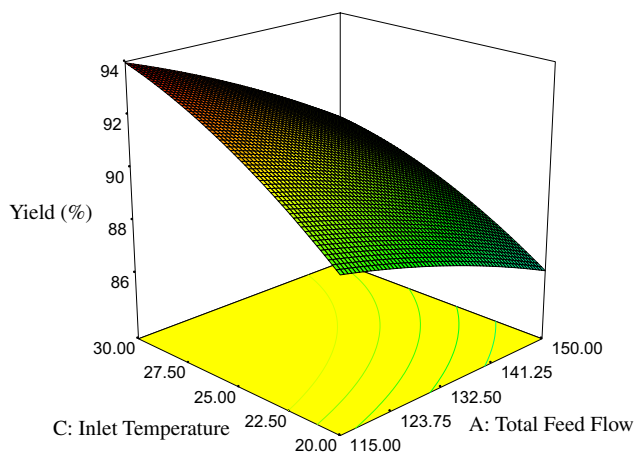

Fig. 4. The effect of total feed flow and inlet temperature on FAME yield, for reboiler duty of 1.25 and methanol/oil ratio of 50.

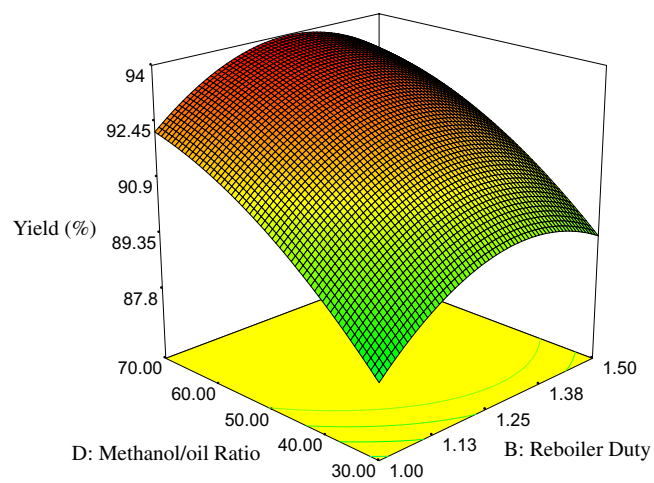

Fig. 5. The effect of reboiler duty and methanol/oil ratio on FAME yield for a total feed flow of 132.5 and inlet temperature of 25.

standard residuals should lie in the interval of ±3.00. An outlier beyond this interval indicates a potential error in the model or an operational error in the experimental data. In Fig. 3d, there were no data outside the interval 3, which indicates that the model is consistent with all the data.

4.3. Influence of inlet feed temperature and total feed flow

Statistical analysis of the experimental data identified inlet feed temperature (*C*) as the most important variable in the response analysis. As shown in Eq. (7) and Table 6, inlet feed temperature has a large, linear, positive effect on the FAME yield response. The quadratic influence of this factor has a minor negative effect on the FAME yield. To achieve higher yield, the feed was heated to avoid methanol condensation through the column. Furthermore, a significant way to deliver the heat to the reaction was to increase the temperature of WCO feed.

A response surface plot for FAME production in Fig. 4 depicts the change of FAME yield with varying total feed flow and inlet feed temperature, plotted for the case where methanol/oil ratio is 65 and reboiler duty is 1.25 kW. The maximum FAME yield of 93.8% was obtained at 30 °C feed temperature.

The total feed flow has a negative effect on the FAME yield because an increase in the feed flow decreases the residence time of reactants in the column. In a reactive distillation process, the aim was to optimize the residence time of reactants in the column while minimizing pressure drop through the column. The residence time for the reactants inside the column was strongly influence by the feed flow rate. At lower feed flows, the increased residence time led to improved FAME yield. As shown in Fig. 4, the maximum FAME yield of 93.8% was obtained at the minimum feed flow of 115 (mol/h).

4.4. Effect of methanol/oil ratio and reboiler duty

Methanol/oil ratio has a positive effect on the FAME yield. The quadratic influence of this factor has significant negative effect on the FAME yield, but its value is smaller than the positive, linear effect. In the transesterification reaction, stoichiometry requires three moles of alcohol to react with one mol of WCO to produce three moles of ester. Since the reactions are reversible, a higher ratio of methanol/oil shifts the equilibrium towards the right hand side of reactions (R1–R3, producing more methyl ester product.

Table 7
Constraints of each variable for the numerical optimization and optimal conditions for maximal FAME yield.

Type of variable	Goal	Lower limit	Upper limit	Optimal conditions no. 1	Optimal conditions no. 2	Optimal conditions no. 3
Total feed flow rate	In range	115	150	115.98	117.18	116.23
Inlet feed temperature	In range	20	30	29.53	29.79	29.94
Methanol/oil ratio	In range	30	70	66.93	69.73	67.93
Reboiler duty	In range	1	1.5	1.29	1.28	1.3
FAME yield	Maximum			93.85	93.92	93.99

Fig. 5 shows the influence of reboiler duty and methanol/oil ratio on FAME yield for the case where the inlet feed temperature is 25 °C and the inlet flow is 117 (mol/h). By increasing methanol/oil ratio, FAME yield increased. The maximum FAME yield of 93.81% was achieved when the ratio of methanol to oil was 65.

The reboiler duty has a minor, linear, positive effect on the FAME yield response. The quadratic influence of this factor has a large negative effect on the FAME yield. Increasing reboiler duty up to 1.25 kW enhances the FAME yield due to small increases in the column temperature (see Fig. 2). Nevertheless, increasing the reboiler duty from 1.25 to 1.5 kW decreases the FAME yield due to vaporization of methanol in the column, thereby lowering methanol availability in the liquid phase of the reaction zone. Fig. 5 shows that the maximum FAME yield of 93.81% was achieved with the reboiler duty set on 1.25 kW. The temperature effects seen in Fig. 2 and the regression model are consistent with results seen previously in batch processing of WCO using heteropolyacid [19].

5. Process optimization

Numerical optimization is a function in the DE software to find the combination of all factors that fulfill the desired requirements simultaneously. To do this, the upper and lower limit of each variable (feed flow, feed temperature, methanol/oil ratio, reboiler duty) and its response were provided according to the contour and surface plots. The maximum response was the ultimate goal of this optimization. Table 7 shows the constraints of each factor and the desired response FAME yield.

The three possible solutions that satisfied all of the specified conditions for the FAME yield are indicated in Table 7. In the present work, solution number 3 (feed flow rate 116.23 mol/h, feed temperature 29.94 °C, methanol/oil ratio 67.93 and reboiler duty 1.3 kW) was chosen due to the highest predicted FAME yield. The optimum values found at the edge of variable ranges was due to restricted capability of the apparatus. A more robust optimum may be found for a newly designed reactor using the methodology illustrated above.

In this preliminary investigation of the use of 12-Tungstophosphoric acid in a reactive distillation column, many important variables were not explored. For example, the feed location, the reflux ratio, the number of trays, and the catalyst concentration were all held constant. Therefore, substantial improvement in yield and conversion is most likely possible, allowing the development of a single reactor for processing waste oils containing substantial free fatty acid.

6. Conclusion

Transesterification of WCO with 12-Tungstophosphoric acid was conducted following response surface methodology (RSM) to produce biodiesel in the RD column. Optimizing four operating parameters, feed flow, reboiler duty, feed temperature and methanol/oil ratio, led to a maximum FAME yield of 93.98%. The 12-tungestophosphoric acid was found to be an active and reusable catalyst to produce biodiesel in the RD column. This process is environmentally friendly due to the recycle of pure methanol from the condenser and recycle of the catalyst from the product stream. Further work is warranted to determine the economics for biodiesel production from low price waste cooking oil with high FFAs and moisture content at industrial scale.

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