BIODIESEL PRODUCTION FROM HIGH ACID VALUE WASTE COOKING OIL USING SUPERCRITICAL METHANOL: ESTERIFICATION KINETICS OF FREE FATTY ACIDS

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ABSTRACT: In this study, low quality waste cooking oil (WCO) with high total acid value has been used for biodiesel production. The main factors affecting the reaction have been analysed using Response Surface Methodology (RSM). A quadratic model representing the interrelationships between reaction variables and free fatty acids (FFA) conversion has been developed. Analysis of variance (ANOVA) has been used to evaluate the significance of the predicted model. Numerical optimisation predicted the optimum conditions for maximum conversion of FFA at methanol to oil (M:O) molar ratio, temperature, pressure and time of 35:1, 260 °C, 110 bar and 16 min, respectively for 98 % conversion. The predicted optimum conditions have been validated experimentally resulting in 97.7 % conversion of FFA with 0.3 % relative error. Kinetic and thermodynamic data of the esterification reaction has been studied resulting in pseudo first-order reaction with reaction rate constant of 0.00103 s^{-1}, activation energy of 34.5 kJ/mol and Arrhenius constant of 1.26 s^{-1}. Finally, a kinetic reactor has been simulated resulting in 97 % conversion of FFA with 0.716 % relative error from the experimental results.

Keywords: Biodiesel, Bioenergy, Transesterification, Vegetable oil, Organic waste, Modelling

1 INTRODUCTION

The increasing demand of energy, oscillation of fossil fuels price and the environmental considerations of fossil fuels have triggered the search for renewable green energy resources. Biofuels have been considered as sustainable and biodegradable energy resources with acceptable environmental impact. Biodiesel, bioethanol and biogas are the commonly used types of biofuels [1].

Biodiesel is a clean burning combustible fuel for diesel engine and is defined as a mono-alkyl ester of long chain fatty acid derived from either animal fats or vegetable oils. It is a renewable, non-toxic and biodegradable fuel which is free of sulphur and aromatic contents [2]. Biodiesel is commonly produced from edible vegetable oils (first-generation biodiesel) which have a direct impact on food security. Numerous researchers reported that higher food commodity prices directly affect poor people. They reported that one of the reasons of food price increasing is the competition between food and biodiesel industries regarding vegetable oils. Accordingly, the research on biodiesel production from either non-edible resource and/or waste vegetable oil (second-generation biodiesel) has been improved. In addition, the main parameter that determines the biodiesel cost is the relevant price of the feedstock. Consequently, non-edible oils and/or waste oils has been considered as prospective feedstock due to their lower prices [3].

Biodiesel production through transesterification reaction is the commonly used technology. Catalytic techniques are still the preferred route for biodiesel production. Catalytic techniques include homogenous, heterogenous and enzymatic processes. Alkaline homogenous catalysed processes are the most commonly implemented plants for biodiesel production. However, using alkaline homogenous catalytic process requires high quality feedstock with low FFA and water content. High concentration of FFA causes saponification side reaction in case of using homogenous alkaline catalyst which then, reduces the biodiesel yield. Nonetheless, the environmental concerns on using chemical catalysts which consume large amount of water for washing step have increased the attention towards bio-catalysed and/or non-catalysed processes [4]. Another technique for using alkaline catalysts with high FFA feedstock is the two-step production process which includes esterification of FFA to fatty acids methyl esters (FAME) then transesterification of triglycerides to FAME [5]. Accordingly, FFA esterification has been considered as the competitive step of biodiesel production from waste vegetable oils with high FFA concentration.

Biosynthesis in supercritical fluids has been considered as a green alternative technology for biofuels production. Non-catalytic biodiesel production using supercritical methanol has been proven as a competitive technique. It is capable to produce biodiesel from feedstocks with high FFA concentration and water content [6]. Saka and Kusdiana (2001) have applied the first biodiesel production using supercritical methanol [7]. Adding carbon dioxide (CO_2) as co-solvent enhances biodiesel yield as it increases the solubility of methanol in oil [6].

WCO has been considered as a potential second-generation feedstock for biodiesel production. Typically, most of the WCO have high FFA concentration which then requires a pre-treatment esterification step before biodiesel production. Esterification reaction of FFA to FAME includes acidic catalysed, enzymatic and non-catalysed processes [8]. In particular, non-catalytic esterification is attracting more attention as it provides easier product separation and decreases the amount of waste water.

In this work, esterification of FFA for high acidity WCO has been investigated. Effects of different reaction variables including M:O molar ratio, temperature, pressure and time on esterification reaction have been examined. RSM using central composite design (CCD) has been employed to optimise reaction conditions. A quadratic model representing FFA conversion as function in reaction variables has been developed. In addition, kinetic and thermodynamic parameters for the esterification reaction have been determined. A kinetic reactor has been finally simulated using the experimental determined kinetic data.

2 MATERIALS AND METHODS

2.1 Materials

WCO was purchased from different local restaurants in Egypt and then mixed together to form a typical realistic mixture. Methanol 99% (MeOH) was purchased from Fisher Scientific UK Ltd. Toluene 99.8%, 2-propanol 99.7%, 0.1 M volumetric standard hydrochloric acid, 0.1 M standardised solution of potassium hydroxide in 2-propanol, p-naphtholbenzein and methyl orange were purchased from Sigma-Aldrich, UK. The standard methyl esters used for preparing calibration curves and heptadecanoic acid methyl ester used as an internal standard were purchased from Sigma-Aldrich, UK. The liquid CO_2 cylinder (99.9%) equipped with dip tube was purchased from BOC Ltd., UK.

2.2 WCO characterisation

The fatty acid composition bonded by glycerol backbone classifies the oil type. The average molecular mass of vegetable oils is directly related to the fatty acids composition. The average molecular mass of the WCO was determined by multiplying mass fraction of fatty acids present in the oil with the individual molecular mass of each fatty acid involved. The compositions of fatty acids were determined by converting them to FAME through a standard methylation process. Derivatisation through methylation process is a recognised characterisation method because of the robustness and reproducibility of the chromatographic data. It has been used commonly for characterising lipids fractions in fats and oil. In addition, it is a relatively cheaper characterisation method as it does not require expensive reagents or equipment [9]. Standard methylation process was carried out according to the British Standard Institution (BSI) method, EN ISO 12966-2:2011.

Table I: FFA composition in WCO

Fatty acid	Composition (%)
Oleic	45.5
Palmitic	39.5
Linoleic	11.3
Myristic	3.7

The derivatisation process started with transferring 50 mg of WCO to a 10-mL ground-glass necked flask. Then, 2 mL of 0.2 M sodium methoxide and boiling chips were added to the flask with fitting a reflux condenser. The mixture was boiled and refluxed until it becomes clear. The mixture was shacked vigorously after adding 1 mL of isooctane then it was left for settling. Sodium chloride solution was added until the upper layer which contains FAME fills the flask neck. The upper layer was then analysed using gas chromatograph (GC) (Thermo-Scientific, Trace 1310) equipped with a capillary column (TR-BD 30 m × 0.25 mm × 0.25 μm) and flame ionisation detector (FID). Both injector and detector temperatures were adjusted at 250 °C. Helium was used as the carrier gas. The temperature programme was started from 60 °C and held for 2 min. Then it ramped with 10 °C/min to 200 °C and directly ramped with 1 °C/min to 210 °C. Finally, the temperature was increased to 240 °C with a ramp rate of 20 °C/min and remained for 7 min. Table I presents the chromatographic results in terms of composition of the FFA existing in WCO.

2.3 Analysis of FFA

Total acid numbers (TANs) of both WCO and products were calibrated using ASTM D974. The analysis was performed by dissolving the sample in a mixture of 2-propanol, toluene and small amount of water to obtain a single-phase solution. Next, the mixture was titrated with 0.1 M KOH in 2-propanol solution with the aid of p-naphtholbenzein as an indicator. The end point was determined when the indicator colour changes from orange to green. The FFA conversion was calculated according to Eq. (1) [9].

$$X = (1 - TAN_1 / TAN_o) \times 100\% \qquad (1)$$

Where TAN_o and TAN_1 represent total acid number of feed and product, respectively.

2.4 Experimental setup

WCO has been collected from local restaurants in Egypt where some solid food particles residuals were remained in the oil. Accordingly, WCO was filtered to remove solid residuals from the cooking process. A 100-mL high pressure reactor made of stainless steel (model 4590, Parr Instrument Company, Moline, IL, USA) which was fitted with a thermocouple (type J), heating mantle, controller (model 4848) and a mechanical stirrer has been used to perform the experiments for supercritical esterification/production of biodiesel. WCO and methanol were added to the reactor with a specified M:O molar ratio then heated to the targeted temperature with continuously stirring at constant rate of 300 rpm. Then, a supercritical fluid pump (model SFT-10, Analytix Ltd., UK) was used to compress CO_2 to the targeted pressure from the cylinder to the reactor. Reaction time starts once the mixture reaches the required temperature and pressure. Start-up possible reaction was not considered throughout all the experiments. The reactor was quenched using an ice bath to stop the reaction after the specified reaction time. The reactor was depressurised and the reaction product was separated using a centrifuge (1500 rpm, 3 min per cycle) forming two separate layers. Biodiesel represents the upper layer, while glycerol represents the bottom one. The unreacted methanol was recovered using distillation by heating the biodiesel up to 80 °C for 30 min. Finally, the pure biodiesel properties were analysed and compared with the European biodiesel standard (EN14214).

2.5 Experimental design

In an attempt to reduce the number of experiments and to determine an accurate relationship between reaction variables and reaction response, the design of experiments (DOE) technique was applied through the experiments. RSM was employed to analyse the operating conditions of esterification reaction and effect of each reaction variable/interactions on the reaction response. The experimental design was developed based on four chosen independent variables including M:O molar ratio, temperature, pressure and time, which were labelled as A, B, C and D, respectively. For each variable, the experimental studied range and the centre point are given in Table II.

Table II: Coded levels for the experimental variables

Factors	Code	Levels		
		-1	0	+1
M:O molar ratio	A	20	30	40
Temperature (°C)	B	240	260	280
Pressure (bar)	C	85	135	185
Time (min)	D	7	22	27

2.6 Statistical analysis

One of the advantages of using DOE is the applicability of predicting a model representing the response variable function in all independent variables. The general quadratic equation of four variables was used to define the predicted model as shown in Eq. (2).

$$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1X_2 + \beta_{13} X_1X_3 + \beta_{14} X_1X_4 + \beta_{23} X_2X_3 + \beta_{24} X_2X_4 + \beta_{34} X_3X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 \tag{2}$$

Where Y is the predicted response value, X_1, X_2, X_3, X_4 are the reaction independent variables, β_o is the constant regression term, $\beta_1, \beta_2, \beta_3, \beta_4$ are the linear coefficient terms, $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}$ are the squared coefficient terms and $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}, \beta_{34}$ are the interaction coefficient terms.

Statistical analysis was employed to investigate the adequacy of the predicted model using coefficient of correlation (R^2), adjusted coefficient of determination (R^2_{adj}) and predicted coefficient of determination (R^2_{pred}). Although, the adequacy of the predicted model was examined by ANOVA via calculating the Fisher's F-test at 95 % confidence level. Operating conditions' optimisation was studied for maximum conversion of FFA. Design Expert 10 software (Stat-Ease Inc., Minneapolis, MN, USA) was used for experimental design, optimisation and regression analysis.

2.7 Physicochemical properties

WCO properties were calibrated as shown in Table III. In addition, properties of biodiesel produced at the concluded optimum conditions were calibrated and compared with European standard of biodiesel, EN14214. The analysed properties were replicated twice and the final results were obtained as an average of the two results.

Table III: WCO Physicochemical properties

Property	Calibration method	Result
Kinematic Viscosity	ASTM D-445	60.5 cSt
Density	ASTM D-4052	0.931 g/cm^3
TAN	ASTM D-974	18 mg KOH/g oil

2.7 Reaction kinetics

Schematic figure for the esterification reaction of FFA to FAME is shown as Fig. 1. Due to the use of excess methanol through the reaction, the change in concentration of methanol was ignored throughout the reaction. Hence, kinetic calculations were based only on the change of FFA concentration through the reaction. Also, the backward reaction rate was not considered through the calculations.
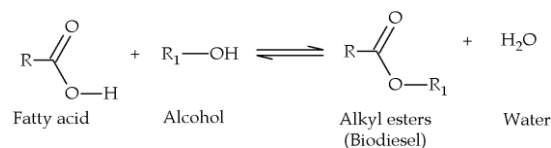
Figure 1: Esterification reaction of fatty acids

2.8 Reactor simulation

Biodiesel production reactor through esterification of FFA to FAME was simulated using Aspen HYSYS® commercial simulation software v8.8 (Aspen Technology Inc., USA). Oleic acid ($C_{18}H_{34}O_2$) from components library of HYSYS was used to represent FFAs in WCO as it represents the main component of the oil as shown in Table I. Accordingly, methyl-oleate ($C_{19}H_{36}O_2$) from HYSYS components' library was considered as the product of the esterification reaction. Continuous stirred tank reactor (CSTR) was chosen to operate the continuous reaction. Non-random two liquid (NRTL) thermodynamic activity model was used as the fluid package of the simulation as the reaction includes a polar component, i.e. methanol. Experimentally determined kinetic and thermodynamic data from this study were used as realistic data for simulating the reactor.

3 RESULTS AND DISCUSSIONS

3.1 Model development

A CCD was employed to design the experiments; the results obtained from each experimental run in terms of FFA conversion are reported in Table III in the penultimate column. As shown in the Table III, the actual experimental conversion varies from 93.75 to 99.25 %. The experiments have been performed in a randomised order to minimise the effect of unexplained inconsistency in the responses. The multiple regression analysis of the responses in Table IV was accomplished using Design Expert software resulting in an empirical relationship between the reaction independent variables and the reaction response as shown in Eq. (3). Where Y, A, B, C and D represent the FFA conversion, M:O molar ratio, temperature, pressure and time, respectively.

$$Y = 96.63 + 0.19\,A + 0.35\,B - 0.5\,C + 0.45\,D + 0.21\,AB - 0.25\,AC - 0.065\,AD - 0.15\,BC + 0.036\,BD + 0.063\,CD + 0.014\,A^2 - 0.029\,B^2 + 0.45\,C^2 - 0.46\,D^2 \tag{3}$$

3.2 RSM analysis and model fitting

In an attempt to report the potential problems associated with the normality assumption, the predicted model has been tested by ANOVA for adequacy checking. The significance of the predicted model has been examined using ANOVA at 95 % confidence level. F-test and p-value have been used to inspect the significance of the model, independent variables and their interactions. The more significance parameters are determined by the higher F-value and the smaller p-value.

The ANOVA for the quadratic polynomial regression model showed a high significance with p-value and F-value of <0.0001 and 38.09, respectively, as shown in Table V. Lack-of-fit analysis has been applied which measures whether the model failed to represent the experimental data at the points which are not included in the regression. A well-fitted model is represented by significant regression analysis and non-significant lack-of-fit analysis. The lack-of-fit analysis result was non-

significant with *p*-value and *F*-value of 0.8451 and 0.49, respectively, as supplied in Table V. The coefficient of correlation (R^2) has recorded 0.9826, which indicates that only 0.0174 of the total variation has been excluded from the fitting of the developed model. Agreement between actual and predicted responses, shown in Table IV, confirms the adequacy of the model. Moreover, Fig. 2 illustrates the experimental actual results *versus* the predicted model results.

Table IV: Coded levels for the experimental variables

Run	A	B	C	D	X_1	X_2
1	30	260	135	17	97.00	96.63
2	35	250	160	22	96.16	96.05
3	35	250	110	22	97.17	97.12
4	35	270	160	22	96.83	96.95
5	35	270	110	12	97.83	97.91
6	35	250	160	12	95.00	95.23
7	25	270	160	22	96.67	96.77
8	30	260	135	17	96.50	96.63
9	25	250	110	22	96.60	96.79
10	25	250	160	22	96.80	96.73
11	30	260	85	17	99.25	99.44
12	25	270	110	12	96.50	96.47
13	25	250	160	12	95.75	95.65
14	30	260	135	17	97.00	96.63
15	35	250	110	12	96.80	96.54
16	30	240	135	17	95.70	95.82
17	30	260	185	17	97.50	97.46
18	35	270	160	12	96.20	95.98
19	30	260	135	17	96.50	96.63
20	30	260	135	27	95.60	95.68
21	30	260	135	7	93.75	93.88
22	25	270	160	12	95.50	95.54
23	20	260	135	17	96.20	96.31
24	25	250	110	12	96.10	95.96
25	30	280	135	17	97.20	97.22
26	30	260	135	17	96.30	96.63
27	40	260	135	17	97.00	97.07
28	25	270	110	22	97.70	97.44
29	30	260	135	17	96.50	96.63
30	35	270	110	22	98.70	98.62

Where X_1, X_2, A, B, C and D represent the actual experimental FFA conversion%, predicted FFA conversion %, M:O molar ratio, temperature, pressure and time, respectively.
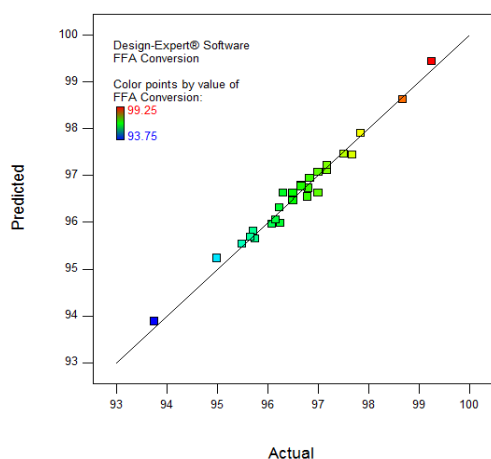
Figure 2: Predicted *versus* experimental actual results

Table V: ANOVA for response surface quadratic model

	SoS	df	MS	*F*-value	*p*-value
Model	30.31	14	2.17	38.09	<0.0001
A	0.88	1	0.88	15.45	0.0013
B	2.93	1	2.93	5161	<0.0001
C	5.91	1	5.91	104.0	<0.0001
D	4.85	1	4.85	85.23	<0.0001
AB	0.73	1	0.73	12.89	0.0027
AC	1.00	1	1.00	17.65	0.0008
AD	0.067	1	0.067	1.180	0.2930
BC	0.38	1	0.38	6.610	0.0213
BD	0.021	1	0.021	0.360	0.5558
CD	0.063	1	0.063	1.100	0.3099
A^2	0.0005	1	0.0005	0.097	0.7597
B^2	0.023	1	0.023	0.400	0.5376
C^2	5.66	1	5.66	99.54	<0.0001
D^2	5.87	1	5.87	103.24	<0.0001
Residual	0.85	15	0.057		
Lack of fit	0.42	10	0.042	0.49	0.8451
Pure error	0.43	5	0.087		

Where, SoS and MS represent the sum of squares and mean square, respectively.

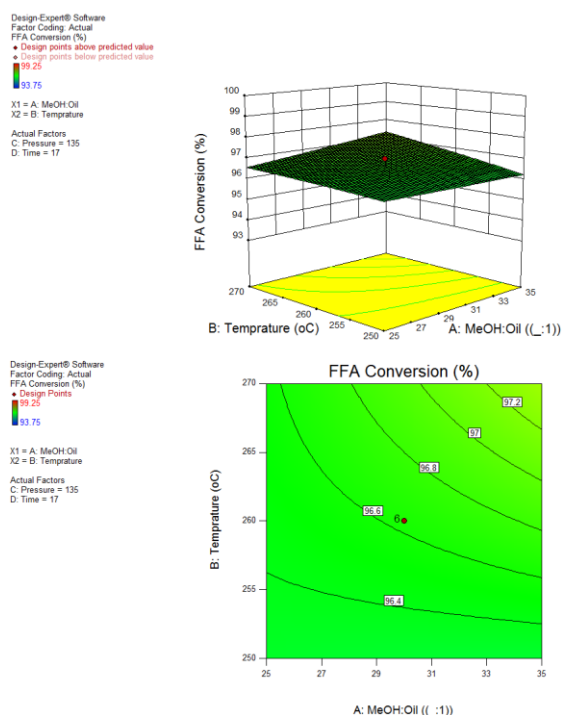### 3.3 Effect of reaction variables

The response 3-D surfaces and contour plots for the above-mentioned model for FFA conversion (Eq. (3)) have been used to observe the effect of process variables and their interaction on the reaction response. For each plot, two independent variables have been checked while keeping the other two variables constant at their centre points. According to the ANOVA results, shown in Table V, M:O molar ratio, temperature, pressure and time exhibited a highly significant effect on the reaction response with *p*-values of 0.0013, < 0.0001 < 0.0001 and < 0.0001, respectively.

3.3.1 Effect of M:O molar ratio

Non-catalytic esterification reactions of FFA to FAME requires large excess of methanol hence, analysing the effect of M:O molar ratio variation as an important optimisation parameter. The effect of M:O molar ratio and temperature and their interaction on conversion of FFA at constant pressure and time could be observed from Fig. 3. It can be clearly observed from Fig. 3 that FFA conversion increases with the increase of M:O molar ratio, in particular, at high temperatures. This relationship confirms the importance of excess methanol in enhancing the reaction.

3.3.1 Effect of reaction temperature

In this study, esterification reaction is operated without the aid of catalyst using supercritical methanol. Accordingly, the minimum temperature of reaction should be 240 °C (critical temperature for methanol). Within the studied range of temperature between 240 °C and 280 °C, the reaction temperature revealed a directly proportional effect on FFA conversion. FFA conversion increase with the increase of temperature, especially at high M:O molar ratio, as depicted in Fig. 3. Optimising the reaction temperature is an essential parameter for minimising the cost of biodiesel production.

Figure 3: 3-D and contour graphs of M:O molar ratio and reaction temperature *versus* FFA conversion
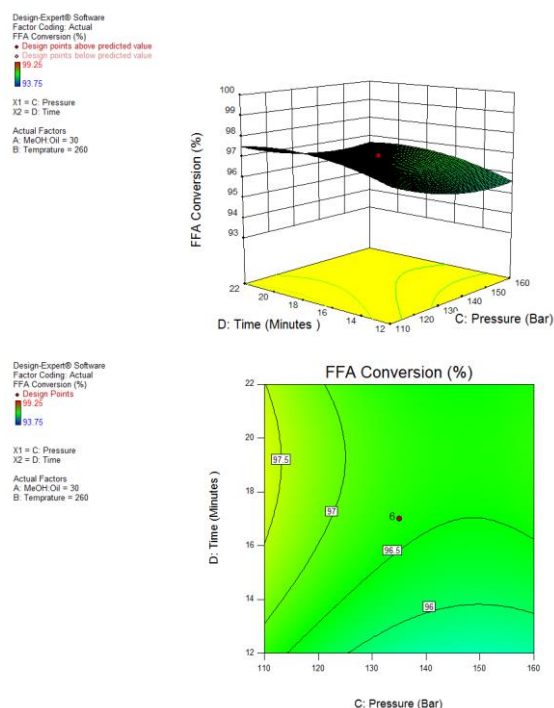
3.3.3 Effect of reaction pressure

CO_2 gas has been used to pressurise the reactor. CO_2 acts as a co-solvent for the reaction as it enhances the solubility of methanol in oil. The studied range of reaction pressure was between 85 to 185 bar as the critical pressure for methanol is 80 bar. It is clearly observed from Fig. 4 that increasing the pressure from 110 to 140 bar showed a negative effect on FFA conversion. However, at higher reaction pressure the effect on FFA conversion is considerably constant. Minimising the reaction pressure reduces the restrictions on the reactor material; and hence, reduces the biodiesel production capital cost.

3.3.4 Effect of reaction time

It is clearly shown from Fig. 4 that increasing the reaction time between 12 to 17 min increases the FFA conversion. While at longer reaction durations than 17 min, FFA conversion has not been affected.

3.4 Optimisation of reaction conditions

The optimum values for the selected independent variables have been concluded by solving the regression equation (Eq. (3)) using Design-Expert® Software. The targets of the optimisation were set to minimise the independent variable to achieve the maximum conversion of FFA. Optimisation has resulted in identifying the optimum conditions for biodiesel production according to the targets set at M:O molar ratio, temperature, pressure and time of 35:1, 260 °C, 110 bar and 16 min, respectively, resulting in FFA conversion of 98 % conversion.

Figure 4: 3-D and contour graphs of reaction pressure time *versus* FFA conversion

3.5 Validation of predicted optimum conditions

The predicted optimum condition has been performed experimentally at M:O molar ratio, temperature, pressure and time of 35:1, 260 °C, 110 bar and 16 min, respectively. Three experiments have been performed and the recorded experimental result is an average between them. The experiments concluded FFA conversion of 97.7 % compared to 98 % of the predicted model. The relative error between the experimental and predicted results is about 0.3 %.

3.6 Physicochemical properties

The final biodiesel product has been analysed for chemical and physical properties and compared with European Biodiesel Standard, EN14214, for quality checking. Table VI shows a comparison between the produced biodiesel properties and European Biodiesel Standard.

Table VI: Properties of the produced biodiesel

Property	Experimental	EN14214
Kinematic Viscosity (cSt)	4.85	3.5-5
Density (g/cm^3)	0.89	0.86-0.9
TAN (mg KOH/ g oil)	0.4	< 0.5

3.7 Reaction kinetics

The experimental results required for kinetics calculations were predicted using the validated quadratic model. For the esterification reaction of FFA, the reaction rate could be described as shown in Eq. (4), where the change of methanol concentration throughout the reaction was neglected. Accordingly, the reaction rate has been assumed to be pseudo first-order function only with the change of FFA concentration throughout the reaction.

$$-r_{FFA} = -d [FFA]/dt = k_f [FFA] \tag{4}$$

Accordingly, a graphical relationship between │Ln [FFA]│ *versus* time within range from 720 to 1080 sec, while keeping the other variables constant at the optimum conditions, has been established. The graphical relationship concluded a straight line with $R^2 = 0.9646$. This result confirms that the reaction follows pseudo-first-order reaction kinetics with reaction rate constant of 0.00103 s^{-1}.

$$k = A\, e^{-E/RT} \tag{5}$$

In addition, thermodynamic parameters of the reaction have been considered through this study (i.e. activation energy and frequency factor). Activation energy of the reaction has been calculated using Arrhenius equation as shown in Eq. (5). Consequently, a graphical relationship between │Ln k│ *versus* temperature within range from 250 to 270 °C has been established. A straight line has been concluded with $R^2 = 0.995$. As a result, activation energy and Arrhenius constant were calculated to be 34.5 kJ/mol and 1.26 s^{-1}, respectively.

3.8 Reactor simulation

Using the concluded optimum conditions for the esterification reaction of FFA and the determined experimental kinetic and thermodynamic data, a kinetic reactor has been simulated to represent the reaction using Aspen HYSYS simulation software platform. Feed stream of the reactor has been defined using the specified optimum M:O ratio (35:1) where methanol and oleic acid molar flow have been defined by 35 and 1 kmol/hr, respectively. Stoichiometric esterification reaction (Fig. 1) set has been defined as the reaction set in the reactor. Activation energy and frequency factor which have been determined experientially (34.5 kJ/mol and 1.26 s^{-1}) through this study were used to define the kinetic required data for the reactor. As a result, the reactor has simulated the reaction with 97 % conversion of oleic acid to methyl oleate with 0.716 % relative error from the experimental results. A scheme of the process flow diagram is represented in Fig. (4), while the feed and product streams details of the reactor are given in Table VII.
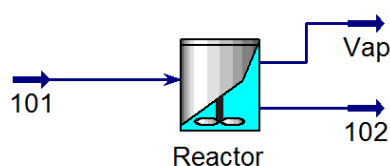
Figure 5: Simulated CSTR using optimum parameters obtained from the experimental study.

Table VII: CSTR streams data

Property	101	102
Temperature (°C)	270.0	265.0
Pressure (bar)	110.0	110.0
Molar flow (kmol/h)	36.00	36.00
Mole fraction		
Oleic acid	0.027	0.001
Methanol	0.972	0.945
Methyl oleate	0.000	0.027
Water	0.000	0.027

4 CONCLUSIONS

FFA esterification reaction using supercritical methanol has been studied. Four independent variables have been investigated through the reaction including M:O molar ratio, temperature, pressure and time. Response variable of the reaction has been identified by FFA conversion. A quadratic polynomial regression model has been developed representing FFA conversion as function in the independent variables. Optimum reaction condition for FFA conversion has been concluded at M:O molar ratio of 35:1, reaction temperature of 260 °C, reaction pressure of 110 bar and 16 min reaction time for 98 % conversion of FFA. The predicted optimum condition has been validated experimentally resulting in FFA conversion of 97.7 %. The experimental validation showed good estimate for the predicted optimum condition with 0.3 % relative error from the experimental results. Kinetic and thermodynamic data have been concluded experimentally resulting in activation energy and frequency factor of 34.5 kJ/mol and 1.26 s^{-1}, respectively. Reactor simulation at the validated optimum conditions using the experimentally determined kinetics has been simulated. Simulation results showed reaction conversion of 97 % with 0.716 % relative error from the experimental attempts.

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7 ACKNOWLEDGEMENTS

8 LOGO SPACE