SUPERCRITICAL METHANOLYSIS OF WASTE COOKING OIL FOR BIODIESEL PRODUCTION: EXPERIMENTAL ASSESSMENT FOR EVALUATING THE EFFECT OF FREE FATTY ACIDS CONTENT

Omar Aboelazayem[1,2], Mamdouh Gadalla[3,2], Basudeb Saha[1]

[1]Centre of Energy and Environment Research, School of Engineering, London South Bank University, 103 Borough Road, London SE1 0AA, United Kingdom
[2]Department of Chemical Engineering, The British University in Egypt, El-Sherouk City, Cairo 11837, Egypt
[3]Department of Chemical Engineering, Port Said University, Port Said, Egypt

ABSTRACT: In this study, high acid value waste cooking oil (WCO) has been assessed for biodiesel production using supercritical methanol. A comparative analysis between two different WCOs with dissimilar total acid number (TAN) has been conducted. The main factors influencing the reaction have been analysed using Response Surface Methodology (RSM) including methanol to oil (M:O) molar ratio, reaction temperature, reaction pressure and reaction time. Biodiesel yield has been chosen as reaction responses for the comparative analysis. Using RSM, two quadratic models representing the interrelationships between reaction variables and biodiesel yield for both feedstocks have been developed. It has been observed that reaction variables have different effect on biodiesel yield in each feedstock. The optimal reaction conditions have been predicted using numerical optimisation for the WCO with higher TAN. The predicted optimal reaction conditions have been realised at M:O molar ratio, temperature, pressure and time of 25.5:1, 268°C, 110 bar and 21.5 min, respectively. Experiments have been carried out at the optimum conditions for both WCOs, where 97% biodiesel yield has been achieved using WCO with higher TAN while only 81% yield for WCO with lower TAN. These results illustrate the positively effect of FFA content on enhancing biodiesel production using supercritical methanol.
Keywords: Biofuel, Biodiesel, Organic waste, Modelling, Transesterification, Esterification.

1 INTRODUCTION

The increasing demand of carbon, spurred by industrial developments and technology, has led to an extensive increase of fossil fuels consumption including crude oil, natural gas and coal. The tremendous consumption of natural resources has created some problems associated with energy including supply chain instability and huge prices fluctuations. Accordingly, energy security of various sectors has been affected including transportation and power generation. In addition to the energy security aspects, the immense consumption of fossil fuels has affected the ecosystem with huge carbon accumulations. The anthropogenic activities have increased the percentage of greenhouse gases especially carbon dioxide which is considered as the main contributor for the global warming and climatic changes among the entire planet [1].

In an attempt to abate the mentioned environmental problems developed due to the universal carbon imbalance, the research has focused on restricting the consumption of fossil fuels and/or search for applicable replacement with lesser greener effect on environment. Biofuels have been considered as potential replacement for fossil fuels including biodiesel and bioethanol. Harnessing biofuels for fossil fuels replacement provides an ideal solution due to their compatibility with the existing engines without the need to perform any engine modifications [2].

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils, animal fats and recently from microalgae. In comparison with bioethanol, biodiesel has relatively simple conversion process in short period of time which is considered as a significant driving force for commercialisation. Biodiesel production has been readily commercialised from edible oils (first generation biodiesel). However, numerous obstacles have faced further expansion of biodiesel from edible oils including increasing of crop prices, ethical dilemmas for food security, water shortage and increasingly competition with food industry. Accordingly, research has been shifted towards second and third generations from non-edible oils (i.e. castor oil) and microalgae, respectively [3].

In fact, all biodiesel generations share the same conversion process, namely transesterification, biodiesel production from non-edible feedstock is challenging due to the high presence of FFAs and other impurities [3].

Conventional production method using alkaline homogenous catalyst including KOH and NaOH requires extensive pre-treatment for feedstocks with high FFA to avoid saponification side reactions. In addition, using homogenous acidic catalysts is considered as very lengthy process with longer reaction time in comparison to the alkaline catalysed technique. Two steps technique has been established to mitigate the conversion of feedstocks with high FFA to biodiesel. The process includes both esterification and transesterification individual processes. Esterification reaction is implemented as a pre-treatment step to convert FFAs to fatty acids methyl esters (FAME). This is followed by transesterification reaction of triglycerides to FAMEs. However, the higher production cost is considered as the main disadvantage of this technique [2]. Heterogenous catalysts have been implemented as a solution for the problems associated with conventional homogenous catalysed processes. However, it has been reported that most of heterogenous catalysts are very sensitive to water content. Moreover, commercialisation of heterogenous catalysts processes have not been implemented due to the high preparation costs in addition to their catalytic inferiorities in comparison with conventional homogenous catalysts [4].

Non-catalytic technique has been developed to overcome the problems associated with catalytic processes. Oil and alcohol are mixed in the supercritical conditions of alcohol in the absence of catalyst. The main advantage of using non-catalytic technique is the

applicability for converting both FFAs and triglycerides simultaneously through esterification and transesterification, respectively. Accordingly, it is capable to produce biodiesel from feedstocks with high concentration of FFAs. In addition, it has several advantages including short reaction time exclusion of wastewater, elimination of catalyst preparation cost, elimination of soap formation and simplification of the product separation [5].

In this study, WCO has been used as a feedstock for biodiesel production using supercritical methanolysis. Two different feedstocks with different TAN has been used to investigate the effect of FFA concentration on the process. The effect of four reaction variables including M:O molar ratio, temperature, pressure and time on biodiesel yield have been examined. RSM using central composite design (CCD) has been employed to optimise reaction conditions. Two quadratic models have been developed representing an empirical relationship between reaction variables and response.

2 MATERIALS AND METHODS

2.1 Materials

Different WCOs were used through this research work which were categorised as WCO from UK (UK WCO) and WCO from Egypt (EG WCO). UK WCO was supplied by Uptown biodiesel company Ltd., UK. However, EG WCO was collected from various local restaurants and industries in Egypt. 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

Physicochemical properties of the WCOs used through this research were analysed. Kinematic viscosity, density and TAN were analysed using standard procedures including ASTM D-445, ASTM D-4052 and ASTM D-974, respectively. Three replicates of the analysed properties were performed where the average has been reported as final results. Fatty acids compositions of WCO were analysed by converting them to methyl ester using standard methylation method according to BS-EN-ISO-12966-2:2011. The esters compositions were analysed using gas chromatograph (GC) 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 250ºC. 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 minutes. Tables I and II illustrate the composition of both UK WCO and EG WCO, respectively.

Table I: FFA composition in UK WCO

Fatty acid	Composition (wt.%)
Oleic	37
Palmitic	18
Linoleic	29
Arachidic	0.8

Table II: FFA composition in EG WCO

Fatty acid	Composition (wt.%)
Oleic	48.2
Palmitic	41.6
Linoleic	9.3
Myristic	0.8

2.3 Analysis of FFA

The TAN 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.

2.4 Experimental setup

WCOs have been filtered to remove the residuals of 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 was used to perform the experiments. Methanol with specific ratio has been added to the oil inside the reactor and they were heated to a targeted temperature with constant stirring rate of 300 rpm using a mechanical stirrer. 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. The reaction time was counted once the mixture has reached the required temperature and pressure. After the reaction time, the reactor was quenched using an ice bath to stop the reaction. Then, the reactor was depressurised, and the reaction product was separated using a centrifuge (1500 rpm, 3 min per cycle) forming two separate layers. The upper layer represent biodiesel while the bottom layer represented glycerol. This was followed by methanol recovery step using distillation by heating the biodiesel up to 80 °C for 30 min. Finally, biodiesel properties were analysed and compared with the European biodiesel standard (EN14214).

2.5 Experimental design

RSM using CCD was implemented to investigate the effect of reaction variables on reaction responses. Four independent reaction variables were used through the experimental design 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 III.

Table III: 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

RSM was used to predict a model for each feedstock representing an empirical relationship between reaction variables and reaction response. The general quadratic equation of four variables was used to define the predicted model as shown in Eq. (1).

$$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1X_2 + \beta_{13} X_1X_3 + \beta_{14} X_1X_4 + \beta_{23} X_2X_3 + \beta_{24} X_2X_4 + \beta_{34} X_3X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 \quad (1)$$

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.

The adequacy of the predicted models was investigated using analysis of variance (ANOVA) *via* calculating the Fisher's *F*-test and *p*-value at 95% confidence level. Design Expert 10 software (Stat-Ease Inc., Minneapolis, MN, USA) was used for experimental design and statistical analysis.

3 RESULTS AND DISCUSSIONS

3.1 Model development

Thirty experiments have been performed in a randomised order to minimise the effect of unexplained inconsistency. A multiple regression analysis has been performed for the experimentally concluded results where two quadratic regression models have been developed representing reaction response function in reaction variables as shown in Eqs. (2) and (3). Where A, B, C and D represent the M:O molar ratio, temperature, pressure and time, respectively. While Y_1 and Y_2 represent biodiesel yield for UK WCO and EG WCO, respectively.

$$Y_1 = 94.2 + 4.08\ A + 3.17\ B + 1.42\ C + 0.5\ D - 0.25\ AC - 0.5\ AD - 0.5\ BD - 3.77\ A^2 - 4.14\ B^2 - 3.77\ C^2 - 3.14\ D^2 \quad (2)$$

$$Y_2 = 88.64 - 1.31\ A - B - 0.65\ C + 0.32\ D - 2.34\ AB - 0.17\ AC - 1.54\ AD - 1.04\ BC - 0.17\ BD - 0.86\ CD - 0.18\ A^2 + 0.32\ B^2 + 2.23\ C^2 + 1.28\ D^2 \quad (3)$$

3.2 Model fitting and adequacy checking

The predicted models have been subjected to adequacy checking using ANOVA using F-test and p-value that have been used to analyse the significance of the model, reaction variables and variables interactions.

The predicted models have shown highly significant results with p-value of <0.0001 for both models as shown in Tables IV and V.

Table IV: ANOVA for UK WCO quadratic model

	SoS	df	MS	*F*-value	*p*-value
Model	581	14	41.5	65	<0.0001
A	200	1	200	315	<0.0001
B	120	1	120	189	<0.0001
C	24	1	24	38	<0.0001
D	3	1	3	5	0.0473
AB	0	1	0	0	1
AC	0.25	1	0.25	0.39	0.54
AD	1	1	1	1.58	0.22
BC	0	1	0	0	1
BD	1	1	1	1.58	0.23
CD	0	1	0	0	1
A^2	92	1	92	145	<0.0001
B^2	111	1	111	175	<0.0001
C^2	92	1	92	145	<0.0001
D^2	64	1	64	101	<0.0001
Residual	8.88	14	0.63		
Lack of fit	4.08	10	0.41	0.34	0.924
Pure error	5	4	1.2		
Cor Total	590	28			

Table V: ANOVA for EG WCO quadratic model

	SoS	df	MS	*F*-value	*p*-value
Model	407	14	29	122	<0.0001
A	41	1	40.9	171	<0.0001
B	24	1	24	101	<0.0001
C	10	1	10	42	<0.0001
D	3	1	3	11	0.0055
AB	88	1	88	367	<0.0001
AC	0.5	1	0.5	2	0.1831
AD	38	1	38	159	<0.0001
BC	17	1	17	73	<0.0001
BD	0.5	1	0.5	2	0.1772
CD	12	1	12	50	<0.0001
A^2	0.92	1	0.92	4	0.0688
B^2	3	1	3	12	0.004
C^2	136	1	136	570	<0.0001
D^2	45	1	45	188	<0.0001
Residual	4	15	0.24		
Lack of fit	3.14	10	0.31	3.53	0.1
Pure error	0.44	5	0.089		
Cor Total	410	29			

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

3.3 Effect of reaction variables

The 3-D surfaces and contour plots have been used to illustrate the effect of two reaction variables on biodiesel yield for both feedstocks used through this research. The significance of each variable on biodiesel yield for both feedstocks is shown in Tables IV and V.

3.3.1 Effect of M:O molar ratio

It is widely accepted that an excess of methanol is required for supercritical methanolysis [6]. Accordingly, analysing the effect of M:O molar ratio is an important parameter for optimisation process. The effect of M:O molar ratio differs according to the FFA content of the feedstock. For UK WCO with low TAN, it is clearly shown in Figure 1 that M:O molar ratio has positively effect on biodiesel yield from the range between 20:1 till 33:1 where using more methanol beyond that range has

slightly negative effect on biodiesel yield. However, the effect of M:O molar ratio differs while using EG WCO with high TAN. It is clearly shown in Figure 2 that slightly positive effect on biodiesel yield at low temperature while it has negatively effect on biodiesel yield at higher temperatures

Similar results have been reported previously by Rade et al [7]. They have reported that M:O molar ratio has decreasingly effect on biodiesel yield from high TAN feedstock. This attributes to the presence of high concentration of FFA in the feedstock where esterification reaction is enhanced with lower M:O molar ratio.

3.3.2 Effect of reaction temperature

Reaction temperature is an important parameter that affect biodiesel production using supercritical methanolysis. According to ANOVA results shown in Tables IV and V, reaction temperature has highly significant effect on biodiesel yield for both feedstocks. However, the effect of variation of temperature differs for each feedstock. For UK WCO with low TAN, reaction temperature has increasingly effect on biodiesel yield up to 270ºC where decreasingly effect s reported beyond these limits as shown in Figure 1. This result has been reported previously and has been clarified due to the thermal degradation of FAME at temperatures higher than 270ºC [8].

On the other hand, reaction temperature showed different effect on biodiesel yield using EG WCO with high TAN. As shown in Figure 2, reaction temperature has positively effect on biodiesel yield at lower M:O molar ratio while having negatively effect at higher M:O molar ratio. These results contradict with previous studies for the effect of temperature however it attributes to the presence of high concentration of FFA in the feedstock [9].

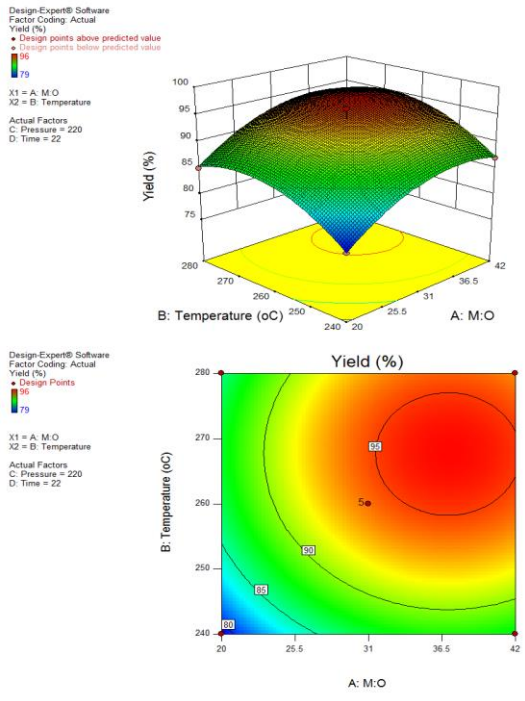

Figure 1: 3-D and contour graphs of M:O molar ratio and reaction temperature *versus* biodiesel yield for UK WCO with low TAN.

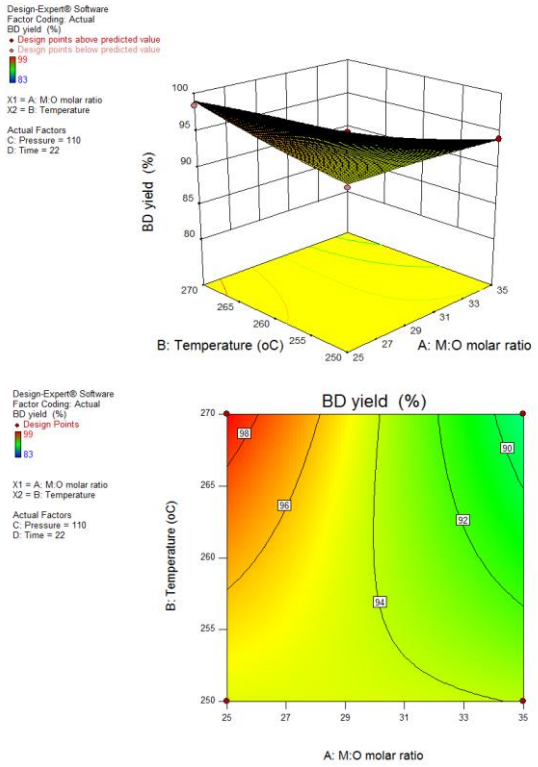

Figure 2: 3-D and contour graphs of M:O molar ratio and reaction temperature *versus* biodiesel yield for EG WCO with high TAN.

3.4 Optimisation of reaction conditions

A numerical optimisation has been implemented to maximise biodiesel yield while minimising reaction variables. The optimisation has been done on EG WCO where the optimum conditions were reported at M:O molar ratio, temperature, pressure and time of 25.5:1, 268°C, 110 bar and 21.5 min, respectively, resulting in biodiesel yield of 97% conversion. The same conditions were applied for UK WCO where biodiesel yield has reported only 81% This attribute to the different concentration of FFA in both feedstocks.

3.5 Physicochemical properties

The final biodiesel produced using both feedstocks have been analysed for physicochemical properties and compared with European Biodiesel Standard, EN14214, for quality checking. Table VI shows a comparison between the produced biodiesel properties from both feedstocks and European Biodiesel Standard.

Table VI: Properties of the produced biodiesel

Property	UK BD	EG BD	EN14214
Kinematic Viscosity (cSt)	4.43	4.62	3.5-5
Density (g/cm^3)	887	884	0.86-0.9
TAN (mg KOH/ g oil)	0.08	0.3	< 0.5

4 CONCLUSIONS

Supercritical methanolysis has been proven as an efficient technique for biodiesel production from high acid value WCO. A comparative analysis has been developed between two feedstocks with dissimilar TANs. It has been observed that reaction variables have different effect on biodiesel yield for different feedstock. Two polynomial models have been developed for each feedstock representing an empirical relationship between reaction variables and response. The optimal reaction conditions have been predicted using numerical optimisation for the WCO with higher TAN. Optimisation of reaction variables has resulted 97% biodiesel yield from EG WCO at M:O molar ratio, temperature, pressure and time of 25.5:1, 268°C, 110 bar and 21.5 min, respectively. Experiments have been carried out at the optimum conditions for UK WCO where only 81% biodiesel yield has been achieved. FFA content has proven as a significant parameter that should be considered as an individual independent parameter for future research.

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10 LOGO SPACE