WASTE COOKING OIL VALORISATION INTO BIODIESEL USING SUPERCRITICAL METHANOLYSIS: CRITICAL ASSESSMENT ON THE EFFECT OF WATER CONTENT

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ABSTRACT: In this work, valorisation of high acid value waste cooking oil (WCO) into biodiesel has been assessed using supercritical methanolysis. The effect of the water content in the feedstock has been critically investigated. Using supercritical methanolysis, the higher water content in the feedstock enhanced the hydrolysis of triglycerides to free fatty acids (FFAs) and the esterification of FFAs into fatty acid methyl esters (FAMEs) has been reported. The effect of water content has been investigated by adding different volumes of water to the feedstock prior to the reaction. Response Surface Methodology (RSM) using Central Composite Design (CCD) has been used to design the experiments and to optimise the experimental variables. Five controllable reaction parameters have been studied including methanol to oil (M:O) molar ratio, reaction temperature, reaction pressure, reaction time and water content. Biodiesel yield has been chosen as reaction response for the experimental runs. The linear effect of reaction parameters and their interactions on biodiesel yield has been analysed. It has been observed that increasing the water content of the feedstock decreases the yield of biodiesel at specific conditions. However, due to the high interactive effect between water content and reaction time, it has been observed increasing effect at longer reaction time. A quadratic model has been developed using the reported experimental results representing biodiesel yield function in all of the experimental parameters. The adequacy of the predicted model has been checked statistically using analysis of variance (ANOVA). Numerical optimisation has been applied to identify the optimal reaction conditions for maximum production of biodiesel. The developed optimal condition has reported 99.8% biodiesel yield at 10:1 M:O molar ratio, 245 °C, 125 bar, 6 vol% of water content within 19 min.

Keywords: Biodiesel, Organic waste, Modelling, Transesterification, Esterification.

1 INTRODUCTION

Fossil fuels including coal, natural gas and oil are the main sources of energy. The dependency of these fuels is of great concern especially on environment. During the last decades, biodiesel has been established as a potential substitute for petroleum based diesel (petro-diesel). Biodiesel is an alternative, reliable and environmentally benign fuel. It could be used in diesel engines as a pure form or blended with petro-diesel without any major modifications needed to be done [1,2]. Biodiesel has many advantages over petro-diesel in terms of biodegradability, higher flash point, lower sulphur and aromatic content. Biodiesel consists of a mixture of fatty acids monoalkyl esters (FAME) obtained from the transesterification of triglycerides from vegetable oils, animal fats and algal lipids [3]. Biodiesel is mainly produced from edible oils, e.g. sunflower, rapeseed, palm and soybean oils. However, increasing consumption of edible crops has resulted in increasing the edible oils prices as it is highly required for both food and biofuels industries [4]. Consequently, to avoid competition between the food and the energy sector, which could highly affect the global food security, non-edible and waste cooking oil (WCO) has gained an extensive interest as a feedstock for biodiesel production [5].

Recently, supercritical technology has been identified as a potential non-catalytic process for biodiesel production. It was firstly reported by Saka and Kusdiana [6] rapeseed oil as a feedstock. The technology has proven an applicable simultaneous conversion of triglycerides and free fatty acids (FFA) into FAME through intensified transesterification reaction. The process is designed to produce biodiesel from low quality crude vegetable oil with high total acid value and water content. Further the process eliminates catalyst preparation and separation steps, produce high yield of biodiesel and shorten the reaction duration time [6]. It has been reported as an ideal technique for feedstock with high acidity including WCO and crude non-edible oils. Several researchers have recently reported supercritical production of biodiesel [7–10].

WCO is considered as an ideal feedstock for biodiesel production *via* non-catalytic transesterification process where it does not require any pre-treatment steps. Feedstock pre-treatment process using conventional catalysed technology includes blending of a high FFA feedstock with other lower FFA feedstock to obtain acceptable concentration of FFA. Feedstock for biodiesel production *via* catalytic transesterification process can be pre-treated with adsorbents to extract FFAs from oil. It could also be pre-treated by converting FFAs to their potassium salt by neutralisation reaction and could be removed by centrifuge. The pre-treatment processes mentioned avoid saponification.

WCO also reduces the cost of biodiesel production as a feedstock. Tsai et al. [11] reported that WCO recorded better results than crude cooking oil using supercritical methanol transesterification. They reported that using WCO at 300 °C and 100 bar in 4 min the biodiesel yield was 65% and for crude cooking oil it was 40 min under the same conditions resulted the same biodiesel yield. They showed that presence of FFAs at higher concentration in WCO feedstock enhances FAME production using supercritical methanol since both esterification and transesterification take place in parallel during the reaction.

Recently, Aboelazayem et al. [12,13] have studied the valorisation of WCOs with different FFAs content into biodiesel using supercritical methanol. They have reported biodiesel yield of 91% from a low acidity feedstock (0.8 mg KOH/g oil) at M:O molar ratio, temperature, pressure and reaction time of 37:1, 253.5 °C, 198.5 bar and 14.8

min, respectively. However, 98% yield has been reported for biodiesel from high acidity WCO (18 mg KOH/g oil) at 25:1 M:O molar ratio, 265 °C temperature, 110 bar pressure within 20 min. The same authors have also compared two WCOs with different acidity at the same reaction conditions. They have reported higher biodiesel yield from high acidity feedstock. They have reported that the rate of esterification reaction has higher value than the rate of transesterification reaction at supercritical methanolysis reaction [14,15].

In the present study, the yield of biodiesel using supercritical methanolysis has been investigated where the effect of the water content in the feedstock has been highlighted. The effects of five controllable variables and their interactions i.e. M:O molar ratio, temperature, pressure, time and water content, have been investigated. Numerical and graphical optimisation have been employed to optimise the reaction variables for biodiesel production with higher yield.

2 MATERIALS AND METHODS

2.1 Materials

WCO was collected from different restaurants and industries in Egypt and mixed together to form a realistic mixture of waste oil. Methanol 99% (MeOH) was purchased from Fisher Scientific UK Ltd. The liquid CO_2 cylinder (99.9%) equipped with dip tube was purchased from BOC Ltd., UK.

2.2 Supercritical synthesis of biodiesel

The detailed procedure for the biodiesel synthesis using supercritical methanol was reported elsewhere [13]. In summary, WCO was heated using a hot plate for 5 min at 25 °C and then filtered to remove any residuals obtained during cooking processes. The filtered WCO was loaded to a 100 mL high-pressure reactor made of stainless steel (model 4959, Parr instrument company, USA). The reactor was fitted with a thermocouple (type J), heating mantle, controller (model 4848) and mechanical stirrer. WCO, methanol and water were weighed and mixed together based on the specific molar ratio to the reactor. The mixture was heated to the desired temperature at a continuous stirring rate of 320 rpm. 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 heating process started before pressurising since the vaporised methanol build-up pressure inside the reactor where the remaining pressure was obtained using pressurised CO_2 gas. The time required to reach the reaction conditions was about 20 min. The reaction time was considered once the reactor reached the targeted temperature and pressure. After the reaction time (specified for each experimental run), the reactor was quenched with cold water and ice bath to stop the reaction. The reactor was then depressurised and the products were fed to a centrifuge (1500 rpm, 3 min per cycle) to separate glycerol and biodiesel. Biodiesel is fed onto a rotary evaporator (Rotavapor, R-210/215, Buchi Labortchnick AG, Switzerland) for distillation at a temperature of 80 °C and pressure of 750 mbar for 20 min to recover the unreacted methanol. The physicochemical properties and the composition of the feedstock are reported elsewhere [12].

2.3 Experimental design

In the present work, the effect of 5 controllable factors on the yield of biodiesel has been investigated. An experimental design using RSM *via* CCD has been applied to minimise the number of experiments and to provide detailed relationships between process variables and response. In addition, the implementation of CCD in experimental design provides the possibility for process optimisation, development of a numerical model and analysing the interactive effect of process variables.

The controllable variables in this work has been identified as M:O molar ratio, temperature, pressure, time and water content, which were labelled as A, B, C, D and E, respectively. Five levels of each variable has been studied following the regulations of CCD method, which includes axial, central and star points. The variables levels have been set based on previous experimental reports [12,16]. The selected five levels for each variable has been coded as -2, -1, 0, +1 and +2, as shown in Table I. The levels of M:O molar ratio range between 0 to 40 with an increment of 10 between each level. However, the lowest level (0) has been replaced by 3 as it represents the minimum stoichiometric M:O molar ratio of 3:1. The identified variables and levels has resulted in development of 32 randomised experiments as shown in Table II. The performed experimental runs has been designed in a randomised manner to minimise the effect of unexplained inconsistency in the responses [17].

Table I: Coded levels for the experimental variables

Factor	Code	Levels				
		-2	-1	0	+1	+2
M:O (molar ratio)	A	0(3)	10	20	30	40
Temperature (°C)	B	235	245	255	265	275
Pressure (bar)	C	65	85	105	125	145
Time (min)	D	5	10	15	25	30
Water content (vol%)	E	0	2	4	6	8

2.4 Statistical analysis

The development of the regression model analysis is referred to as the general full quadratic equation as shown in Eq. (1).

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j>1}^{n} b_{ij}\, x_i x_j + \varepsilon \quad (1)$$

Where Y is the predicted response, b_o is the model coefficient constant, b_i, b_{ii}, b_{ij}, are coefficients for intercept of linear, quadratic, interactive terms respectively, while X_i, X_j are independent variables *(i≠j)*. n is the number of independent variables and ε is the random error. The adequacy of the predicted model has been investigated using different statistical analytical methods including adequacy precision, coefficient of correlation (R^2), adjusted coefficient of determination (R^2_{adj}) and the predicted coefficient of determination (R^2_{pred}). In addition, the statistical significance of the predicted model has been checked using ANOVA *via* Fisher's test, i.e. F-value and p-value, at 95% confidence interval. Further, the lack of fit analysis has been employed to investigate the fitting accuracy of the predicted model to the experimental data.

Design Expert 11 software (Stat-Ease Inc., Minneapolis, MN, USA) has been used for designing experiments, regression analysis, graphical analysis and numerical optimisation.

3 RESULTS AND DISCUSSIONS

3.1 Model development

The developed 32 runs have been performed experimentally to report the actual biodiesel yield results as reported in Table II. The range of the actual results have been reported between 67.8 and 99.7% yield. In order to fit the experimental data to a mathematical model, Design Expert software has been used to perform multiple regression analysis for the experimental results. Four mathematical regression models have been used to fit the experimental results including linear, two factors interactions (2FI), quadratic and cubic polynomials. The software has suggested the development of a quadratic regression model as it has been observed with high fitting to the experimental results amongst the other models. Consequently, a quadratic model has been developed representing an empirical relationship between process response and process variables as shown in Eq. (2).

$$Y = 86.17 + 0.24\,A + 2.23\,B - 2.3\,C + 1.74\,D - 4.22\,E + 1.5\,AB - 0.12\,AC - 3.13\,AD + 0.07\,AE + 1.62\,BC - 0.96\,BD + 0.11\,BE - 1.77\,CD + 4.23\,CE + 5.88\,DE - 0.22\,A^2 - 1.05\,B^2 - 0.22\,C^2 + 0.65\,D^2 - 2.62\,E^2 \quad (2)$$

Where *Y* represents the response variable (biodiesel yield). While, *A, B, C, D and E* represent the independent variables i.e. M:O, temperature, pressure, time and water content, respectively. Further, *AB, AC, AD, AE, BC, BD, BE, CD, CE* and *DE* represent the interaction between independent variables. Finally, A^2, B^2, C^2, D^2 *and* E^2 represent the excess of each independent variable. The overall effects of reaction variables have been observed from the developed model where the positive sign of each variable coefficient represents the synergetic effect of the variable on the response, however, the negative sign represents the antagonistic effect on the response.

3.2 RSM analysis and model fitting

The adequacy of the predicted model has been examined to analyse the fitting accuracy of predicted results to the actual data. In this work, several statistical validations have been employed. The significance of the predicted model has been verified using ANOVA based on p-value test as shown in Table III; significant parameters have a p-value lower than 0.05. The predicted model has been observed as highly significant with p-value of 0.0001. Furthermore, the values of R^2 and R^2_{adj} have been reported as 0.96 and 0.91, respectively. The p-value for the lack of fit analysis, which examines the accuracy of the model fitting, has been investigated. The non-significant result for the lack of fit analysis illustrates the adequacy of the predicted model in fitting the actual data. As observed from the ANOVA results in Table III, lack of fit analysis has been reported as 0.3515 (not significant). In addition, the adequacy precision test, which describes the ratio between the predicted response and the relative error (signal to noise ratio), has been examined. The test has resulted in a value of 16.413, where a value higher than 4 is preferable. Finally, a plot representing the actual *versus* predicted data has been illustrated in Figure 1. The high agreement between actual and predicted results have been represented with minor deviations from the 45° line.

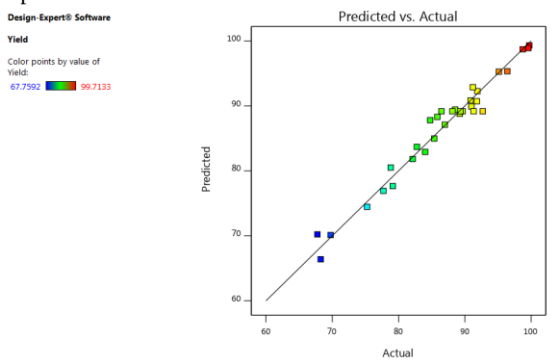

Figure 1. Experimental results *versus* predicted results from the predicted model

Table II: Coded levels for the experimental variables

Run	M:O ratio (A)	Temperature (°C) (B)	Pressure (bar) (C)	Time (min) (D)	Water content (vol%) (E)	Actual yield (%)	Predicted yield (%)
1	30	245	85	10	2	99.71	99.31
2	10	245	85	20	2	99.59	98.90
3	20	255	105	25	4	95.13	95.26
4	20	255	105	15	0	86.99	87.11
5	20	255	105	5	4	85.84	88.30
6	10	265	125	20	2	82.13	81.83
7	10	245	125	10	2	84.01	82.93
8	20	255	105	15	4	89.33	89.17
9	20	255	145	15	4	82.77	83.69
10	20	235	105	15	4	78.83	80.51
11	20	255	105	15	8	67.76	70.23
12	30	245	125	20	2	69.76	70.12
13	20	255	105	15	4	88.12	89.17
14	20	275	105	15	4	88.53	89.43
15	10	265	125	10	6	79.13	77.66
16	30	265	85	20	2	91.89	92.77
17	30	245	125	10	6	75.27	74.46
18	30	265	125	10	2	98.73	98.71
19	40	255	105	15	4	89.23	88.79
20	20	255	105	15	4	89.65	89.17
21	10	245	85	10	6	68.25	66.40
22	30	265	125	20	6	90.87	90.85
23	0(3)	255	105	15	4	84.76	87.80
24	20	255	105	15	4	86.47	89.17
25	10	265	85	20	6	90.99	89.91
26	20	255	105	15	4	92.70	89.17
27	20	255	65	15	4	91.21	92.87
28	30	245	85	20	6	85.38	84.98
29	10	265	85	10	2	96.41	95.33
30	30	265	85	10	6	77.72	76.92
31	20	255	105	15	4	91.33	89.17
32	10	245	125	20	6	91.81	90.72

Table III: ANOVA for response surface quadratic model

	Sum of Squares	df	Mean Square	F-value	p-value	significance
Model	2138.36	20	106.92	17.45	<0.0001	S
A-M:O molar ratio	1.46	1	1.46	0.2390	0.6346	NS
B-Temperature	119.29	1	119.29	19.46	0.0010	HS
C-Pressure	126.62	1	126.62	20.66	0.0008	HS
D-Time	72.70	1	72.70	11.86	0.0055	HS
E-Water	427.28	1	427.28	69.72	< 0.0001	HS
AB	36.25	1	36.25	5.91	0.0333	S
AC	0.2322	1	0.2322	0.0379	0.8492	NS
AD	157.72	1	157.72	25.73	0.0004	S
AE	0.0749	1	0.0749	0.0122	0.9140	NS
BC	42.09	1	42.09	6.87	0.0238	S
BD	14.81	1	14.81	2.42	0.1483	NS
BE	0.2274	1	0.2274	0.0371	0.8508	NS
CD	50.21	1	50.21	8.19	0.0155	S
CE	286.46	1	286.46	46.74	<0.0001	S
DE	554.38	1	554.38	90.46	<0.0001	S
A^2	1.41	1	1.41	0.2302	0.6408	NS
B^2	32.29	1	32.29	5.27	0.0424	S
C^2	1.45	1	1.45	0.2363	0.6364	NS
D^2	12.50	1	12.50	2.04	0.1810	NS
E^2	202.18	1	202.18	32.99	0.0001	S
Residual	67.42	11	6.13			
Lack of Fit	42.76	6	7.13	1.45	0.3515	NS

3.3 Effect of reaction variables

The effects of five process variables on the response have been studied at the following subsections.

3.3.1 Effect of reaction temperature

ANOVA results as presented in Table III shows highly significant effect of reaction temperature on yield and directly proportional relationship between the temperature range and biodiesel yield as shown in Figure 2. Biodiesel yield decreases at a very high temperature due to decomposition of the produced FAME. This phenomenon has been reported by Ghoreishi and Moein [18]. They have observed at a higher temperature more than 271 ^{o}C biodiesel yield starts to decrease. Also, Aboelazayem et al. [13] reported the same observation but at a temperature higher than 270 ^{o}C.

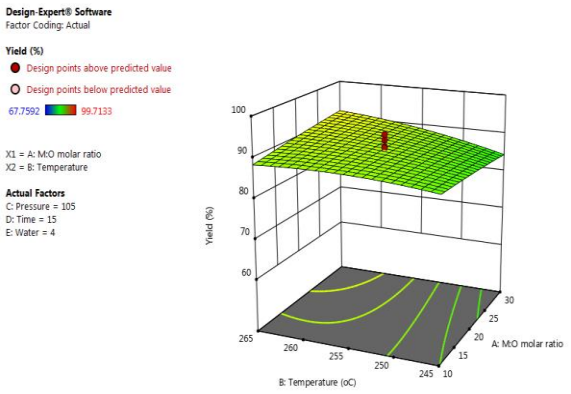

Figure 2: Response surface plot for reaction temperature and M:O molar ratio *versus* biodiesel yield

3.3.2 Effect of reaction pressure

Carbon dioxide gas has been used to pressurise the reaction and also as a co-solvent. The use of carbon dioxide as a co-solvent for the reaction enhances the solubility of methanol to oil [19]. It shows biodiesel yield decreases as reaction pressure increases as shown in Figure 3. Aboelazayem et al. [13] reported that beyond 230 bar the biodiesel yield starts to decrease slightly. In addition, Kurniawan et al. [20] reported that the pressure effect on the supercritical transesterification using compressed nitrogen gas for Jatropha oil is directly proportional until 220 bar and beyond that value the pressure has no effect on the biodiesel yield.

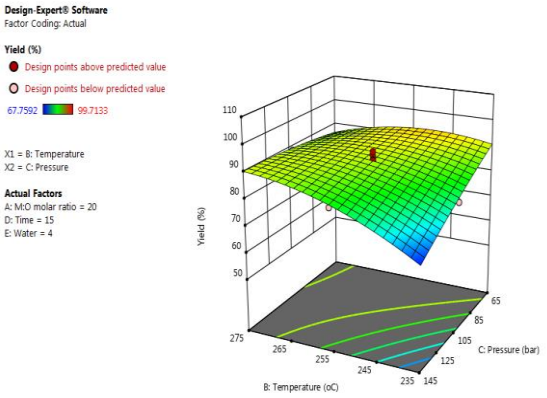

Figure 3: Response surface plot for reaction temperature and pressure *versus* biodiesel yield

3.3.3 Effect of reaction time

The reaction time was considered once the reaction reached a specific condition. The reaction time shows a directly proportional relationship with biodiesel yield as shown in Figure 4. Aboelazayem et al. [13] reported that reaction time more than 24 min, a decrease in biodiesel yield was observed. He et al. [21] explained that the decrease in yield of biodiesel is due to the loss of unsaturated FAME, especially under high temperature.

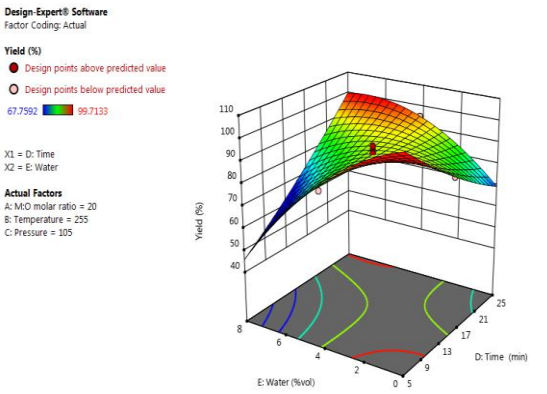

Figure 4: Response surface plot for reaction time and water content *versus* biodiesel yield

3.3.4 Effect of M:O molar ratio

The experimental runs have been carried out at M:O molar ratio between 3:1 and 30:1 in order to study the variation on the yield of biodiesel. The M:O methanol ratio shows a directly proportional relationship with biodiesel yield as shown in Figure 2. Aboelazayem et al. [13] reported that directly proportional relationship with biodiesel yield up until M:O molar ratio value more than 37:1. Ghorieshi and Moein [18] reported that at M:O molar ratio higher than 34:1 the biodiesel yield starts to decrease slightly. The high excess of methanol lowers the critical temperature of the reaction products as methanol has lower critical condition compared to the reaction mixture components. Lowering the critical temperature of the product enhances FAME decomposition and hence reduces biodiesel yield.

3.3.5 Effect of water content

ANOVA results presented in Table III shows highly significant effect on biodiesel yield as shown in Figure 4. It has been observed that the increasing effect of water content has decreasing effect on biodiesel yield. However, due to high interaction effect of water content and other variables, the effect of water content on biodiesel yield has positive influence at higher reaction time. This showed the highly interactive effect of water content and reaction time on biodiesel yield. This might attribute to the high solubility of tocopherols in water where addition of water prevents the decomposition of tocopherols. Kusdiana and Saka [16] reported that the existence of water does not have a significant effect on biodiesel yield.

3.4 Optimisation of reaction conditions

The application of RSM in experimental design has several advantages including the implementation of the developed regression model to predict the optimal conditions as per the desired targets. The optimisation target has been set to maximise the process response (biodiesel yield). However, the process variables have been set minimum values to reduce very high energy consumption that is not economically favourable. The software has used RSM to integrate the process variables *via* the developed model to achieve the optimisation targets.

The numerical optimisation feature in Design Expert software has generated 65 solutions for the desired targets. The solution with the highest desirability has been chosen as the process optimal conditions. The developed optimal condition has reported 99.8% biodiesel yield at 10:1 M:O molar ratio, 245 ^{o}C, 125 bar, 6 vol% of water content within 19 min reaction time. In addition, graphical optimisation has been used to determine the accurate optimal conditions where the combination with the highest desirability has been selected. For instance, the optimum reaction time and temperature have been selected based on the combined positive effect on desirability.

The predicted optimal conditions have been performed experimentally. The experimental results of yield at the predicted optimal conditions have reported similar trend to the predicted results. Additionally, the experimental results at the predicted optimal conditions have reported biodiesel yield of 99.9%, which is considered higher than all of the previous experimental runs.

4 CONCLUSIONS

Biodiesel production by valorising WCO *via* supercritical methanolysis has been studied. It has been observed that water content has high interactive effect with reaction pressure and time on biodiesel yield. For instance, the increasing effect of water content has decreasing effect on biodiesel yield at short reaction time. However, the effect of water content on biodiesel yield has positive influence at longer reaction duration. This could be because presence of water accelerates the hydrolysis reaction and reduces the amount of ester formation. Hence, the produced FFAs from hydrolysis require enough time to be converted to biodiesel. Further, the high solubility of tocopherols in water enhances the yield of biodiesel where addition of water prevents the decomposition of tocopherols. The developed optimal condition has reported 99.8% biodiesel yield at 10:1 M:O molar ratio, 245 ^{o}C, 125 bar, 6 vol% of water content within 19 min.

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8 LOGO SPACE