Valorisation of high acid value waste cooking oil into biodiesel using supercritical methanolysis: Experimental assessment and statistical optimisation on typical Egyptian feedstock

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ABSTRACT

In this study, valorisation of high acid value waste cooking oil into biodiesel has been investigated. Non-catalytic transesterification using supercritical methanol has been used for biodiesel production. Four controllable independent process variables have been considered for analysis including methanol to oil (M:O) molar ratio, temperature, pressure and time. Uncommon effects of process variables on the reaction responses, e.g. biodiesel and glycerol yields, have been observed and extensively discussed. Response surface methodology (RSM) *via* Central Composite Design (CCD) has been used to analyse the effect of the process variables and their interactions on the reaction responses. A quadratic model for each response has been developed representing the interrelationships between process variables and responses. Analysis of Variance (ANOVA) has been used to verify the significance effect of each process variable and their interactions on reaction responses. Optimal reaction conditions have been predicted using RSM for 98% and 2.05% of biodiesel and glycerol yields, respectively at 25:1 M:O molar ratio, 265^{o}C temperature, 110 bar pressure and 20 minutes reaction time. The predicted optimal conditions have been validated experimentally resulting in 98.82% biodiesel yield, representing 0.83% relative error. The quality of the produced biodiesel showed excellent agreement with the European biodiesel standard (EN14214).

KEYWORDS

Biodiesel, Biomass valorisation, Waste cooking oil, Supercritical methanolysis, Optimisation, Response Surface Methodology.

HIGHLIGHTS

- Successful valorisation of high acid value waste cooking oil into biodiesel.
- Effect of reaction parameters on responses has been comprehensively discussed.
- Reaction optimal conditions has been predicted using Response Surface Methodology.
- Excellent correlation between predicted and experimental optimal conditions.

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1. INTRODUCTION

The increasing demand of energy from the domestic and industrial sectors combined with possible scarcity of petroleum based fuels in the near future have boosted the research for alternative sustainable fuels [1]. Moreover, the growing concerns for the environment and the critical need to reduce carbon emissions, which are the main cause of global warming, have developed numerous agreements between countries aiming to control emissions and to promote development of environmental benign fuels from renewable resources [2,3].

Petroleum diesel is a fuel with complex composition, which is widely used in different sectors including transportation, industrial, agricultural and commercial sectors. It consists of paraffinic, olefinic and aromatic hydrocarbons as main components along with different impurities e.g. sulphur, nitrogen and metallic atoms [4]. Of the alternative fuels, biodiesel is considered as a promising eco-friendly replacement for petroleum diesel fuel [5]. Recently, biodiesel has attracted huge attention due to its biodegradability, non-toxicity, availability from renewable sources and lesser emissions of CO_2 into the atmosphere than petroleum diesel. This non-conventional fuel, composed of fatty acid alkyl esters (FAAEs), is derived from biological renewable resources including vegetable oils. animal fats and microbial oils [6].

Biodiesel has been considered as a promising alternative fuel because it has similar physicochemical properties to petroleum diesel which can be used as substitute without the need for engine modifications. The significant advantage of using biodiesel in diesel engines is the decrease of hydrocarbons, polyaromatic, carbon oxides and sulphur emissions leading to reduction of greenhouse gases while providing similar properties in terms of fuel efficiency [7,8]. Biodiesel is mainly synthesised from oils extracted from traditional oilseeds e.g. sunflower, soybean, and palm. Moreover, any matter containing triglycerides could be considered as a potential feedstock for biodiesel including waste cooking oil (WCO) and lipids derived from either fish or animals [9]

List of Abbreviations: 2

2FI: Two Factors Interactions; ANOVA: analysis of variance; CCD: Central Composite design; DOE: Design of Experiments; FAME: fatty acids methyl esters; FFA: Free Fatty Acid; FID: Flame Ionisation Detector; M:O: methanol to oil ratio; R^2: Coefficient of Correlation; RSM: response surface methodology; TAN: total acid number; WCO: waste cooking oil; df: Degrees of freedom.

Currently, edible oils are the main resources for biodiesel production. However, the use of edible oils has a strong influence on the global food security by reduction of food resources and increasing the price of edible oils. Thus, focus has been shifted towards second generation feedstock including non-edible oils and WCO [10].

Valorisation of bio-waste including agro-industrial, municipal and domestic waste into biodiesel make the process eco-friendly and sustainable. It simultaneously assists waste management while minimising the production cost. WCO, which is much cheaper than fresh vegetable oils, is considered as promising replacement feedstock for edible oils. Disposal of WCOs and fats have been reported as a major problem in many parts of the world. Some developed countries have set some policies to prevent the disposal of WCO through drainage [11].

Generally, the physicochemical properties of WCO is nearly similar to its fresh edible oil. However, the main obstacles in WCO properties are high free fatty acids (FFAs) and water contents due to frying process. During cooking process, edible oils are heated to high temperature in the presence of air for relatively long time. Accordingly, FFAs concentration increases in the oil because of hydrolysis of triglycerides. Moreover, some physical changes occur for WCO including increase in viscosity and surface tension, change in colour and higher tendency of fat formation. These changes are relative to the cooking process where the more use of edible oils in frying results in higher FFA and water contents [12].

There are four basic techniques for biodiesel production including alkaline catalysed transesterification, direct acid catalysed transesterification, enzymatic catalytic conversion of oil to fatty acids and subsequently to biodiesel and non-catalytic transesterification using supercritical technology. Among all these techniques, homogeneous alkaline transesterification is considered as the most commonly used method for biodiesel production. Moreover, methanol is the preferred alcohol in transesterification reaction due to its lower molecular weight and cost [13,14].

Alkaline and acidic transesterification techniques require lower cost with less reaction time in comparison with enzymatic technique [15]. Homogeneous alkaline technique produces biodiesel with high purity and yield with moderate reaction temperature in reasonable reaction time. However, this technique requires feedstock with low FFA content to avoid saponification side reactions [16,17]. Accordingly, two-steps transesterification technique has been developed to overcome the high FFA content in feedstock. Firstly, acid catalysed esterification of FFA to FAAE occur as a pre-treatment step. This is followed by an alkaline catalysed transesterification of triglycerides to FAAEs. Although, the long reaction time and low recovery of catalyst were considered as main disadvantages of two-steps proposed technique [12]. Lewis acid catalysed technique has been proposed to overcome

the disadvantages of two-steps transesterification technique. However, it requires high reaction temperature with relatively low production yield [18]. Heterogeneous alkaline catalysed technique has been developed to overcome the feedstock restriction and to ease the catalyst separation complications. Many researchers reported successful biodiesel production using heterogeneous catalysts with high product yield. However, the high preparation cost of catalysts including very high temperatures for calcination processes (800-900^{o}C) is considered as the main disadvantages of heterogeneous catalysed technique [10,19].

Previous works have been reported for biodiesel production from WCO using various transesterification techniques. El-Gendy et al. [20] have studied the optimisation of biodiesel production from waste cooking oil using CaO obtained from calcination of eggshells. They have obtained 96% yield of biodiesel at 6:1, 3 wt%, 60 min and 200 rpm for M:O molar ratio, catalyst weight percentage reaction time and stirring rate, respectively. Wang et al. [21] achieved have 90% conversion of WCO to biodiesel using 4 wt% of H_2SO_4 with M:O molar ratio of 1:20 after 10 h reaction time. El-Gendy et al [14] have used KOH as an alkaline catalyst for biodiesel production from WCO. They have optimised the process variables to achieve 99% biodiesel yield at M:O molar of 7.5:1, KOH weight of 0.0875 wt%, temperature of 52^{o}C in 1.17 h and 200 rpm stirring rate.

Recently, alternative methods have been reported for biodiesel production including supercritical technology [13], ultrasonic reactor [22], microwave radiation [23] and membrane reactor [24]. Specifically, supercritical methanol transesterification has been developed as an alternative technique for biodiesel production where biodiesel is produced in high yield without any pre-treatment processes. Supercritical methanol transesterification has a number of advantages, including elimination of wastewater generation resulted from catalyst recovery and leading to high purity biodiesel. It also eliminates saponification side reactions resulted from alkaline homogenised technique. Accordingly, supercritical methanol transesterification is considered as an ideal technique for biodiesel production from WCO with high FFAs content [25,26].

Aghbashlo et al [27] have optimised biodiesel production from WCO using ultrasonic reactor in the presence of KOH as a catalyst. They have achieved 97% conversion of triglycerides at M:O molar ratio of 6:1 and reaction temperature of 60^{o}C within only 10 minutes. Milano et al [28] have studied conversion of mixture of WCO and *Calophyllum inophyllum* oil using microwave irradiation-assisted alkaline catalysed method. They have reported 97.65% yield of biodiesel within 7.15 minutes at M:O volumetric ratio, catalyst concentration and stirring rate of 59.60% (v/v), 0.774 wt% and 600 rpm, respectively. Ghoreishi and Moein [29] have optimised biodiesel production from WCO using supercritical methanol. They reported 95% biodiesel optimum yield at 271.1^{o}C, 23.1 MPa ,

M:O molar ratio of 33.8:1 within 20 minutes. Aboelazayem et al. [30] have reported optimum conditions for biodiesel production from WCO using supercritical methanol. They have achieved 91% biodiesel yield at 37:1 M:O molar ratio, 253.5 ^{o}C, 198.5 bar within 14.8 min. However, there is a gap in the literature regarding non-catalytic biodiesel production from high acid value WCO as it is readily available from food industries (TAN varies based on the duration of cooking process).

RSM is based on experimental design with a final goal of assessing the optimal variables for specific target of the response, using minimum experiments. RSM investigates the interaction effect between several illustrative variables on one or more response variables. RSM is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response [31,32].

The present study is focused on solving a real world problem for sustainable production of bioenergy from very low quality feedstock. The main aim of this study is to investigate the feasibility of supercritical methanolysis for biodiesel synthesis from very low quality WCO with high acid value. As high acidity WCO requires pre-treatment esterification step prior to transesterification reaction, the applicability of supercritical methanolysis to operate simultaneous transesterification of triglycerides and esterification of FFAs of very low quality WCO to FAME has been investigated. As per using very low quality WCO, this work has highlighted unusual influence of different reaction parameters and their interactions on biodiesel and glycerol yields. In addition, two quadratic models have been developed representing response variables function in reaction parameters. RSM using CCD has been used for designing the experiments, modelling and optimisation. Four independent process variables have been considered in this study, i.e. M:O molar ratio, temperature, pressure and time. ANOVA has been used to assess the adequacy of the predicted models and the effect of each process variable and their interactions on reaction responses. Optimisation of reaction variables has been carried out to maximise the production of biodiesel. Finally, the predicted optimum conditions have been validated experimentally.

2. MATERIALS AND METHODS

2.1. Materials

WCO was collected from Egyptian local restaurants and food industries. Methanol (99% purity) was purchased from Fisher Scientific, UK. The standard methyl esters used for preparing calibration curves and the heptadecanoic acid methyl ester used as an internal

standard were purchased from Merck, UK. The liquid CO_2 cylinder (99.9%) equipped with a dip tube was purchased from BOC Ltd., UK.

2.2. Experimental procedures

2.2.1. Supercritical methanolysis

WCO was heated to 30ºC using a hot plate for liquefaction and then filtered to remove any residuals from cooking processes. The filtered WCO was used directly in the reactor without any pre-treatment steps. The reaction was carried out in a 100 mL high pressure reactor made of stainless steel (model 4590, Parr Instrument Company, USA) which is fitted with a thermocouple (type J), heating mantle, controller (model 4848) and a mechanical stirrer. A schematic of the experimental setup is shown in Figure 1. WCO was weighed and mixed with methanol (based on specific molar ratio). Then, the mixture was fed to the reactor and heated to the target temperature with continuous stirring at a constant rate of 300 rpm. After reaching the target temperature, vaporised methanol had already built up pressure inside the reactor which was still below the targeted pressure. A supercritical fluid pump (model SFT-10, Analytix Ltd., U.K) was used to compress CO_2 from a cylinder to the reactor in order to achieve the targeted pressure. The time required for reaching the desired temperature and pressure was approximately 15 min in all experiments. Reaction residence time counts once reaching the desired reaction conditions. After the specified residence time, the reactor was quenched using an ice bath to stop the reaction and then the reactor was depressurised. Unreacted methanol was recovered using simple distillation at 80ºC for 30 minutes. The reaction products were separated using a centrifuge (1500 rpm, 3 min per cycle) to biodiesel and glycerol. Finally, biodiesel and glycerol contents were measured for yields calculations. Biodiesel and glycerol yields were calculated using Equation (1) [29].

$$Yield\ (\%) = \frac{Total\ weight\ of\ pure\ product}{Total\ weight\ of\ waste\ cooking\ oil\ used} \times 100 \quad (1)$$

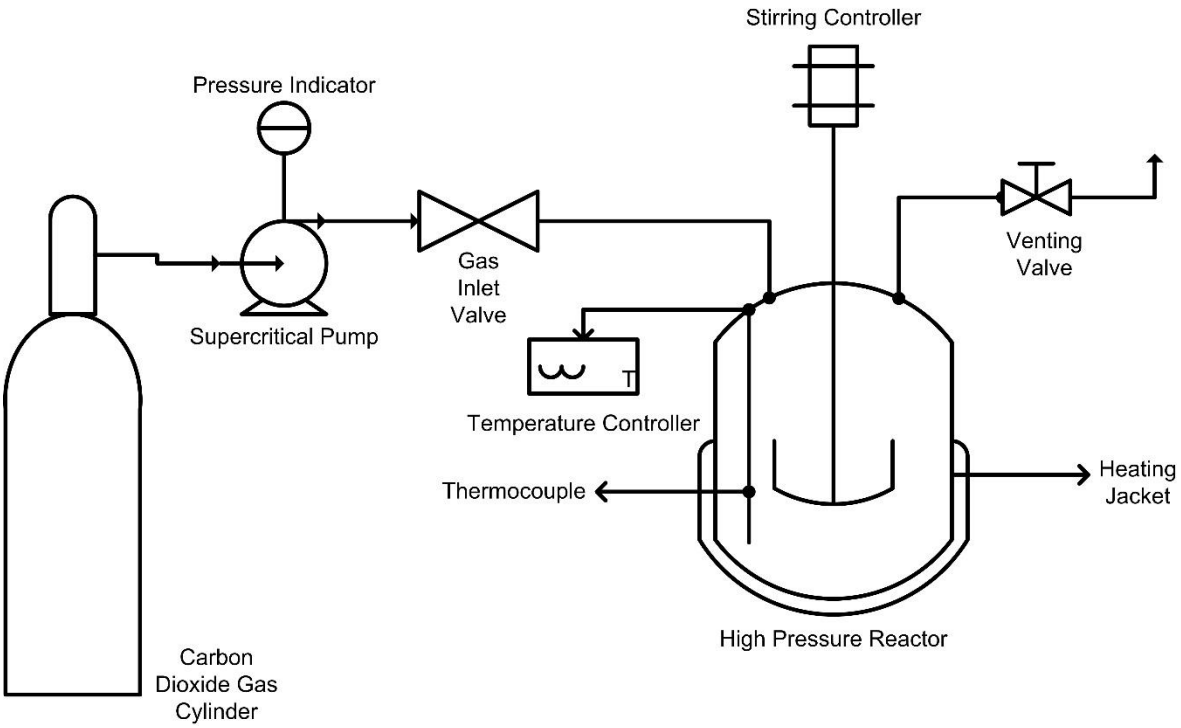

Figure 1. A schematic of the experimental setup

2.2.2. WCO and biodiesel characterisation

Standard procedures were followed to characterise properties of WCO and the produced biodiesel including ASTM D-974, ASTM D-445 and ASTM D-4052 for measuring total acid number (TAN), kinematic viscosity and density, respectively. The determined properties of biodiesel were compared with the European biodiesel standard (EN14214). The analysed properties were replicated twice and the final results were obtained as an average of the two results. Table 1 illustrates the main physicochemical properties of WCO used for the experimental analysis.

Compositions of fatty acids for WCO were analysed by converting them to methyl esters according to BS-EN-ISO-12966-2:2011. Methyl esters content for WCO and produced biodiesel were analysed using a 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 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. Table 2 illustrates the fatty acids composition of WCO used for the experimental analysis.

Table 1. Physicochemical properties of WCO

Property	Calibration Method	Results
Kinematic viscosity	ASTM D-455	60.5 cSt
Density	ATM D-4052	0.931 g/cm^3
TAN	ASTM D-947	18 mg KOH/ g oil

Table 2. Composition of the fatty acids in WCO

Fatty Acid	Wt (%)
Palmitic acid	41.6
Oleic acid	48.2
Linoleic acid	9.3
Myristic acid	0.8

2.3. Experimental design

RSM was applied for the design of experiments (DOE) in order to optimise reaction parameters for higher biodiesel yield. The effect of four independent variables and their interactions on reaction responses (biodiesel and glycerol yields) were investigated using RSM based on four factors and five levels of CCD. The CCD method of RSM is the most popular optimisation tool for reaction conditions. It includes full or fractional designs with centre points that are integrated with a group of axial points, which allow better predictions of the curvature in the resulting model. In this study, the range of the selected independent variables was studied within five levels, which were coded as -2, -1, 0, 1, 2, as shown in Table 3.

Table 3. Experimental design variables and their coded levels

Factor	Code	Levels				
		-2	-1	0	+1	+2
M:O (molar ratio)	A	20	25	30	35	40
Temperature (°C)	B	240	250	260	270	280
Pressure (bar)	C	85	110	135	160	185
Time (min)	D	7	12	17	22	27

According to the CCD design, a 4 factors 5 levels CCD design was implemented and total 30 experiments were carried out in this study as shown in Table 4. The total number of experiments was calculated based on Equation 2.

$$\textit{Total number of experiments} = 2^n + 2n + m \quad (2)$$

where n is the number of independent variables and m is number of replicated centre points. This study included 4 independent variables and hence, enough information should be

provided to assist the prediction of second-order polynomial models for biodiesel and glycerol yields as responses. Thus, 16 factorial points and 8 axial points developed 30 experiments that were performed randomly including 6 replicates at the centre point for precise experimental error predictions. The experimental runs were performed in a randomised order to minimise the effect of unexplained inconsistency in the responses [23]. The analysed reaction variables were M:O molar ratio (A), temperature (B, ^{o}C), pressure (C, bar) and time (D, min) while reaction responses were biodiesel yield (Y_1, wt%) and glycerol yield (Y_2, wt%).

2.4 Statistical Analysis

Regression analysis was performed using general quadratic polynomial equation to define the model as shown in equation (3).

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j>1}^{n} b_{ij}\, x_i x_j + \mathcal{E} \quad (3)$$

where Y is the predicted response (i.e. biodiesel and glycerol yields), 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_i are independent variables ($i \neq j$). n is number of independent variables and ε is the random error.

Model accuracy was checked by coefficient of correlation (R^2), adjusted coefficient of determination (R^2_{adj}) and the predicted coefficient of determination (R^2_{pred}). Investigation of the statistical significance was analysed using ANOVA by calculating the Fisher's F-test at 95% confidence level. Design Expert 10 software (Stat-Ease Inc., Minneapolis, MN, USA) was used to design the experiments, regression analysis, graphical analysis and numerical optimisation.

279 Table 4. Experimental design matrix with the actual and predicted yields
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Run	M:O ratio (A)	Temperature (°C) (B)	Pressure (bar) (C)	Time (min) (D)	Actual BD Yield %	Predicted BD Yield %	Actual GL Yield %	Predicted GL Yield %
1	30	260	135	17	89.21	88.63	10.82	11.50
2	35	250	160	22	92.12	92.63	7.92	7.82
3	35	250	110	22	94.00	93.91	7.10	6.21
4	35	270	160	22	83.00	83.51	17.72	16.61
5	35	270	110	12	89.70	90.01	10.50	9.37
6	35	250	160	12	96.95	96.44	3.20	3.45
7	25	270	160	22	94.50	94.22	4.37	5.36
8	30	260	135	17	88.40	88.63	11.60	11.50
9	25	250	110	22	94.10	94.57	5.96	5.31
10	25	250	160	22	94.20	93.98	5.70	6.01
11	30	260	85	17	99.00	98.84	0.52	1.32
12	25	270	110	12	94.40	93.88	4.50	5.34
13	25	250	160	12	91.40	91.63	8.40	7.97
14	30	260	135	17	88.60	88.63	11.63	11.50
15	35	250	110	12	94.00	94.27	5.82	5.57
16	30	240	135	17	92.00	91.90	8.15	8.83
17	30	260	185	17	96.20	96.25	4.30	3.55
18	35	270	160	12	88.50	88.02	9.50	10.89
19	30	260	135	17	88.40	88.63	11.5	11.50
20	30	260	135	27	95.00	94.40	4.36	4.98
21	30	260	135	7	92.60	93.10	5.50	4.95
22	25	270	160	12	92.40	92.57	5.90	5.97
23	20	260	135	17	90.50	90.51	9.32	9.09
24	25	250	110	12	89.20	88.77	10.70	10.99
25	30	280	135	17	87.90	87.89	12.60	11.97
26	30	260	135	17	88.60	88.63	11.68	11.50
27	40	260	135	17	85.40	85.29	14.65	14.93
28	25	270	110	22	98.40	98.99	2.08	1.01
29	30	260	135	17	88.60	88.63	11.80	11.55
30	35	270	110	22	89.20	88.96	10.20	11.37

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3. RESULTS AND DISCUSSION

3.1. Development of regression model equation

Design Expert software has fitted four models for each response including; linear, two factors interactions (2FI), quadratic and cubic polynomials. Among the fitted models of each response, one model has been selected based on different statistical tests including; lack of fit analysis, adjusted coefficient of determination (R^2_{adj}), predicted coefficient of determination (R^2_{pred}) and associated aliased coefficients. The software suggested the quadratic model for both biodiesel and glycerol yield responses. Equations 4 and 5 represent the developed quadratic models with empirical relationships between responses and reaction variables within specific levels in terms of coded factors shown in Table 3.

$$Y_1 = 88.64 - 1.31\,A - B - 0.65\,C + 0.32\,D - 2.34\,AB - 0.17\,AC - 1.54\,AD - 1.04\,BC - 0.17\,BD - 0.86\,CD - 0.18\,A^2 + 0.32\,B^2 + 2.23\,C^2 + 1.28\,D^2 \quad (4)$$

$$Y_2 = 11.51 + 1.46\,A + 0.79\,B + 0.56\,C + 0.01\,D + 2.36\,AB + 0.22\,AC + 1.58\,AD + 0.91\,BC + 0.34\,BD + 0.93\,CD + 0.13\,A^2 - 0.27\,B^2 - 2.27\,C^2 - 1.64\,D^2 \quad (5)$$

where Y_1 and Y_2 represent biodiesel and glycerol yields, respectively. While, A, B, C and D represent the process variables including M:O molar ratio, temperature, pressure and time, respectively.

The regression equations illustrate the effect of the reaction variables on each the response. The positive sign of each term indicates synergetic effect while the negative sign indicated antagonistic effect [14]. The linear coefficient represents the effect of the reaction variable on the response while the coefficient of variables interaction represents the interactive effect of the process variables. Finally, the quadratic coefficient represents the effect of variable excess on the response.

As shown in Equation 4, M:O molar ratio, temperature and pressure have negative effect on biodiesel yield with negative sign coefficients where the increase of these variables have decreasingly effect of biodiesel yield. However, in Equation 5 all the linear coefficients have positive signs, which indicate that while increasing any of the process variables, e.g. M:O molar ratio, temperature, pressure and time, glycerol yield increases. It can be seen in Equations 4 and 5 that variation of M:O molar ratio (A) has the highest effect of both biodiesel and glycerol yields, where it has the largest coefficient among other variables.

3.2. Model adequacy checking

The adequacies of the predicted models have been investigated to report any error associated with the normality assumptions. Various analyses have been applied to check the adequacy of the predicted model. The coefficient of correlation (R^2) evaluates the accuracy of the predicted model whereas value of R^2 gets closer to unity indicates the high similarity between predicted values of the model and the actual experimental value. The values of R^2, R^2_{adj}, R^2_{pred} have been evaluated for biodiesel yield predicted model as 0.9913, 0.9831 and 0.9543, respectively. In addition, they have been assessed for glycerol's yield model as 0.99, 0.981 and 0.941, respectively. These results indicate that 99.13% and 99% of the total variation is qualified to the experimental variables for both biodiesel and glycerol yields, respectively. Adequacy precision value is a measure of the range for the predicted response value in comparison with its relative error (signal to noise ratio) where a value greater than 4 is desirable. The value of adequacy precision has been evaluated as 44.77 and 22.79 for models representing biodiesel and glycerol yields, respectively. These results verify that the predicted models could be used to navigate the design space.

Statistical data obtained through variance analysis have been used to determine the significance of the predicted models. Moreover, the significance effect of reaction parameters and their interactions were determined. The parameter values from ANOVA are tabulated in Tables 5 and 6.

Table 5. Analysis of variance for biodiesel yield for the developed model

Source	Sum of Squares	df	Mean Square	F-value	P-value	Significance
Model	406.8013	14	29.05723	121.5205	7.94E-13	HS
A-MeOH:Oil	40.8987	1	40.8987	171.0428	1.32E-09	HS
B-Temperature	24.1402	1	24.1402	100.9569	4.69E-08	HS
C-Pressure	10.0492	1	10.0492	42.02685	1.03E-05	HS
D-Time	2.515538	1	2.515538	10.52025	0.005456	S
AB	87.75006	1	87.75006	366.9802	5.88E-12	HS
AC	0.465806	1	0.465806	1.948052	0.183115	NS
AD	37.91481	1	37.91481	158.5638	2.23E-09	HS
BC	17.36806	1	17.36806	72.63508	3.92E-07	HS
BD	0.479556	1	0.479556	2.005556	0.177154	NS
CD	11.95431	1	11.95431	49.99419	3.81E-06	HS
A^2	0.918765	1	0.918765	3.842372	0.068819	NS
B^2	2.755907	1	2.755907	11.5255	0.003999	S
C^2	136.3358	1	136.3358	570.1711	2.39E-13	HS
D^2	44.90241	1	44.90241	187.7867	6.91E-10	HS
Residual	3.586708	15	0.239114			
Lack of Fit	3.141958	10	0.314196	3.532275	0.088105	NS
Pure Error	0.44475	5	0.08895			
Cor Total	410.388	29				

According to Tables 5-6, the significance of each model has been evaluated based on both p-value and F-test at 95% confidence level. The smaller the p-value than 0.05, the more significance of the corresponding parameter. It has been observed that both models are highly significant with p-values of <0.0001. These values have ensured the significance of the models in representing the experimental results. Lack-of-fit analysis is one of the ANOVA techniques which measure the failure of the regression model in representing the experimental data points. The non-significant value for lack-of-fit test indicates a high fitting model. Lack-of-fit values for both models have been observed as 0.088 and 0.22 for both biodiesel and glycerol yields models, respectively. The non-significance of the test illustrated that the models have represented most of the experimental data successfully. Moreover, Figure 2 (a and b) illustrated a graphical representation for experimental actual values *versus* predicted values using the developed models for both biodiesel and glycerol

yields, respectively. The similarity between actual and predicted values has ensured the accuracy of the model in predicting the response variable.

Table 6. Analysis of variance for glycerol yield for the developed model

Source	Sum of Squares	df	Mean Square	F-Value	P-value	Significance
Model	432.8486	14	30.91776	33.51097	9.33E-09	HS
A-MeOH:Oil	51.07084	1	51.07084	55.35437	2.08E-06	HS
B-Temperature	14.83654	1	14.83654	16.08094	0.001136	HS
C-Pressure	7.492838	1	7.492838	8.121295	0.012172	S
D-Time	0.002604	1	0.002604	0.002823	0.958331	NS
AB	89.25526	1	89.25526	96.74149	6.21E-08	HS
AC	0.805506	1	0.805506	0.873068	0.364906	NS
AD	40.03726	1	40.03726	43.39536	8.62E-06	HS
BC	13.26781	1	13.26781	14.38064	0.001771	HS
BD	1.829256	1	1.829256	1.982684	0.179495	NS
CD	13.85701	1	13.85701	15.01925	0.001494	HS
A^2	0.449536	1	0.449536	0.487241	0.49584	NS
B^2	2.066436	1	2.066436	2.239757	0.155246	NS
C^2	140.8054	1	140.8054	152.6153	2.9E-09	HS
D^2	73.38816	1	73.38816	79.54355	2.2E-07	HS
Residual	13.83924	15	0.922616			
Lack of Fit	13.22769	10	1.322769	2.81489	0.22476	NS
Pure Error	0.61155	5	0.12231			
Cor Total	446.69	29				

where HS: highly significant, S: significant and NS: not significant

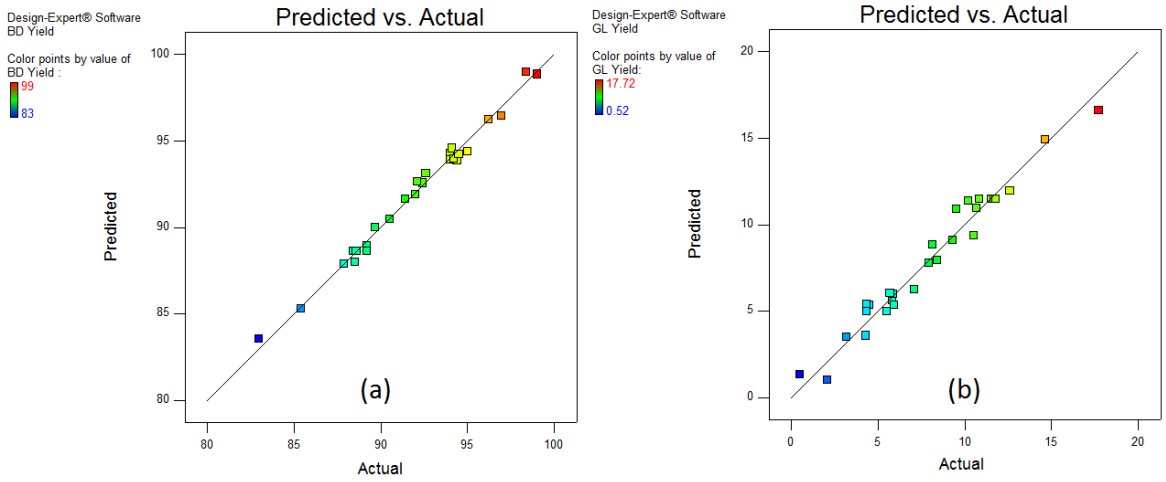

Figure 2. Predicted *versus* actual values for biodiesel yield model (a) and glycerol yield model (b)

Table 5 shows that all studied factors have significant individual (linear) effect on biodiesel yield where reaction time variable has showed the least significance effect than other variables with p-value of 0.005. The analysis also showed that there is a significant effect on biodiesel yield for variables interaction of M:O molar ratio - temperature (AB), M:O molar ratio - time (AD), temperature - pressure (BC) and pressure – time (CD). Moreover, it has been observed that both pressure and time showed significant quadratic effect on biodiesel yield.

According to Table 6, temperature, pressure and time showed significant individual effect on glycerol yield while reaction time showed insignificant effect on glycerol yield. Only temperature and pressure showed significant quadratic effect on glycerol yield. Although, analysis showed that there is a significant effect on glycerol yield between variables interactions of M:O molar ratio - temperature (AB), M:O molar ratio - time (AD), temperature - pressure (BC) and pressure – time (CD).

In an attempt to simplify the developed models, the insignificant variables have been excluded. According to ANOVA results presented in Tables 5 and 6 for the predicted models (Equations 4 and 5), the insignificant parameters, with p-values higher than 0.05 have been highlighted. It is shown in Table 5 that there is insignificant interactive effect on the response for both parameters AC and BD. In addition, the excess of M:O molar ratio (A) has statistical insignificant effect on biodiesel yield. On the other hand, reaction time (D) has insignificant effect on glycerol yield as shown in Table 6, however, it cannot be excluded to maintain the model hierarchal structure [33]. Additionally, the interactions between AC and BD along with the excess of two variables including M:O molar ratio and temperature showed statistically insignificant effect on glycerol yield. Consequently,

simplified reduced models have been developed for both biodiesel and glycerol yields by excluding the mentioned insignificant parameters as shown in Equations 6 and 7.

$$Y_1 = 88.43 - 1.31\,A - B - 0.65\,C + 0.32\,D - 2.34\,AB - 1.54\,AD - 1.04\,BC - 0.86\,CD + 0.34\,B^2 + 2.26\,C^2 + 1.31\,D^2 \quad (6)$$

$$Y_2 = 11.36 + 1.46\,A + 0.79\,B + 0.56\,C + 0.01\,D + 2.36\,AB + 1.58\,AD + 0.91\,BC + 0.93\,CD - 2.25\,C^2 - 1.62\,D^2 \quad (7)$$

It is necessary to check ANOVA assumptions as it has been used to validate the predicted models. ANOVA assumptions summarised in; normality of residuals, homoscedasticity (equal variance) of residuals and random errors [33]. Normality of residuals has been investigated using normal plot where they approximately form straight line as shown in Figure 3. This test ensures the validity of the first assumption where residuals are normally distributed for both biodiesel and glycerol models. Secondly, the homoscedasticity has been investigated where pressure variable (C) has been chosen as a variable sample representing the variance equality at different levels. The homoscedasticity has been examined using residuals *versus* predicted values plot. The equal range of residuals at each level concluding the homoscedasticity of the variable results as shown in Figure 4. Finally, the randomisation of errors has been investigated using the plot of residuals *versus* actual responses values. As shown in Figure 5, residuals were distributed randomly where they do not follow any specific trend. These randomised distributions validate the third assumption of ANOVA.

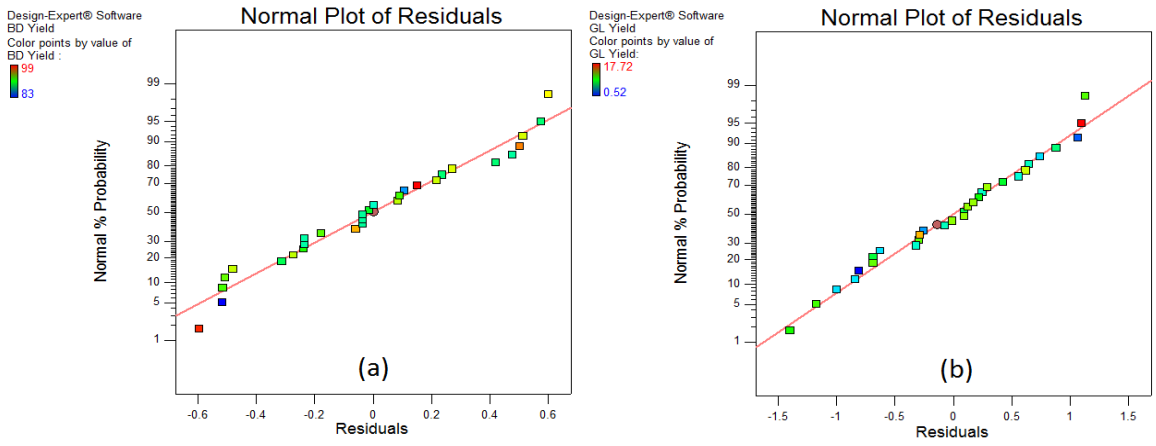

Figure 3. Normal plot of residuals for (a) biodiesel yield model and (b) glycerol yield model

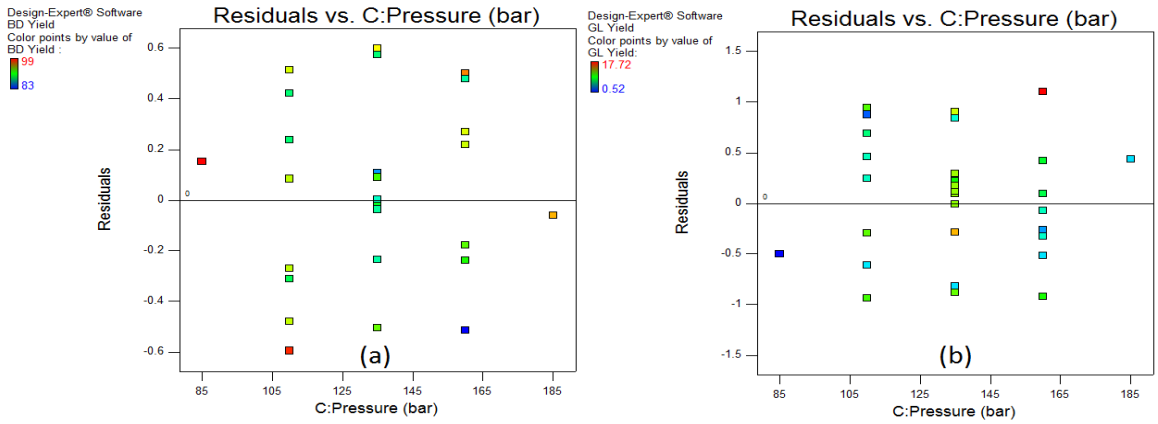

Figure 4. Plot of residuals *versus* predicted values of pressure variable for (a) biodiesel yield model and (b) glycerol yield model

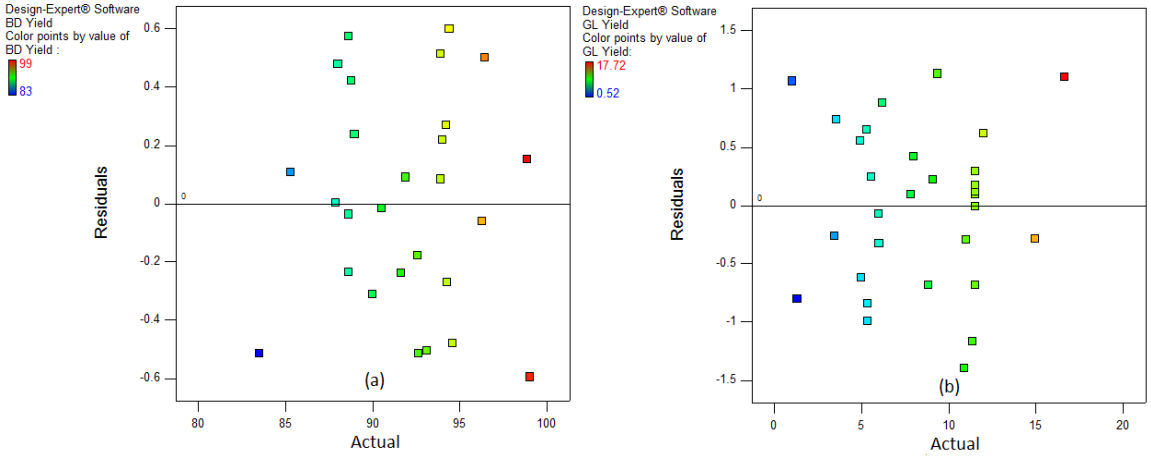

Figure 5. Plot of residuals *versus* actual response for (a) biodiesel yield model and (b) glycerol yield model

3.3. Effect of process variables and their interactions

The effects of individual parameters and their interactions have been studied to analyse and investigate the influence of parameters variation on the responses.

3.3.1. Effect of individual variables on responses

Perturbation plot is used to compare the influence of reaction variables at particular point in space. In this study, centre point of all variables has been selected as a constant point of comparison between variables. The influence of individual reaction variables on biodiesel and glycerol yields have been presented in Figures 6a and 6b, respectively.

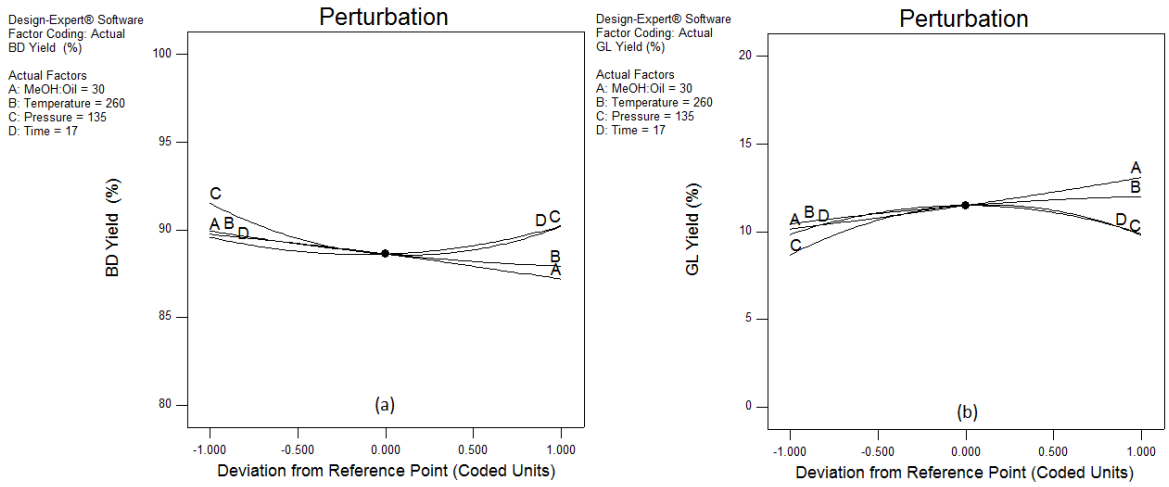

Figure 6. Perturbation plot showing the effect of individual variables on (a) biodiesel yield and (b) glycerol yield

One of the drawbacks of using supercritical methanol technique for biodiesel production is the usage of large excess of methanol, where it is very important to investigate its effect on the biodiesel yield for optimisation considerations. It is clearly shown in Figure 6a that M:O molar ratio (A) has negative effect on biodiesel yield, where increasing M:O molar ratio has decreasing effect on biodiesel yield. These findings are in agreement with previous study by Rade et al. [34] on high acidity soybean oil, where they have reported a negative influence of alcohol to oil molar ratio on biodiesel yield. Varma et al. [25] have reported that increasing M:O molar ratio for supercritical synthesis of biodiesel does not have significant effect on biodiesel yield. They have explained these results as the formation of homogenous reaction phase only requires lower molar ratios. Accordingly, increasing methanol to oil ratio does not have a significant effect on the homogeneity of the solution. However, these results contradicts previous studies for biodiesel production from

WCO using supercritical methanol [29,30]. The different properties of the utilised feedstocks (acid value) is considered as the main reason for these contradicting results. It also attributes to the esterification reaction rate of FFA that exists in the feedstock where it has been reported that increasing M:O molar ratio has negatively effect on FFA conversion for high acidity feedstock [35]. On the other hand, M:O molar ratio has positive effect on glycerol yield as shown in Figure 6b. This is an expected result as it has been reported previously that M:O ratio enhance transesterification reaction of which glycerol is produced [29].

Reaction temperature is an important parameter for supercritical production of biodiesel. It has been reported that at reaction temperature higher than 280^{o}C, thermal degradation of FAME occurs [36]. Since the critical temperature of methanol is 240^{o}C, the studied temperatures ranges have been chosen between 240^{o}C and 280^{o}C. In the present study, reaction temperature has negative effect on biodiesel yield as shown in Figure 6a. This result contradicts previous studies where it has been reported positive impact of increasing temperature on biodiesel yield [37,38]. The effect of temperature varies at different levels of M:O molar ratio. Hence, this is comprehensively discussed in section 3.3.2.1. However, glycerol yield has been positively affected by increasing reaction temperature as shown in Figure 6b.

Reaction pressure is one of the most important factors for supercritical transesterification reactions. It has a very high impact on the properties of the solution including density and hydrogen bond intensity [39]. It has been reported that the effect of reaction pressure on biodiesel yield is not highly significant. In the present study, reaction pressure showed significant effect on biodiesel yield. However, the variation in biodiesel yield reported 6% while varying pressure from 85-185 bar. Moreover, slightly negative impact is shown at Equation 4 with very small coefficient. These results are in agreement with Ting et al. [40] who have reported about 7% variation in biodiesel yield when varying pressure from 10-25 MPa. Hence, they have considered constant pressure for their optimisation procedures. Nevertheless, reaction pressure showed insignificant effect on glycerol yield as shown in Table 6. Increasing reaction pressure from 110 to 140 bar, resulted in 4% increase in glycerol yield. However, higher values of pressure have slightly decreasing effect on glycerol yield.

Reaction time is one of the advantageous factors for supercritical transesterification over catalysed processes as it recorded much shorter reaction time. The studied time interval has been chosen between 12 and 22 min as it has been recommended previously [30]. In this study, reaction time has been reported to have very limited effect on biodiesel yield.

Biodiesel variation has been reported to be 3% by varying time from 12-22 min. On the other hand, reaction time has been found to be insignificant on glycerol yield.

3.3.2. Effect of variables interactions on responses

The interaction effect of each pair of variables has been observed from both interaction plots and ANOVA results. Moreover, 3D-surface and contour plots for biodiesel and glycerol yields *versus* interaction of two independent variables have been used to illustrate the effect of interaction. In each plot the two remaining independent variables have been kept constant at their centre points. For simplicity, this analysis only includes biodiesel yield response.

3.3.2.1 Interactive effect of methanol:oil molar ratio and temperature

As reported in ANOVA results shown in Table 5, interactive effect of M:O molar ratio and temperature has recorded a significant effect on biodiesel yield. Figure 7 illustrates an interaction plot between M:O molar ratio and temperature where antagonistic interaction is clearly observed which confirms ANOVA results. Figure 8 represents a response surface and contour plots for M:O molar ratio and temperature interactive effect on biodiesel yield. It can be seen from Figure 8 that at low temperature the effect of M:O molar ratio is approximately neglected, however at higher temperatures, M:O molar ratio has negative effect on biodiesel yield. Additionally, at low M:O molar ratio, increasing reaction temperature shows positive influence on biodiesel yield. However, at high levels of M:O molar ratio, biodiesel yield decreases with an increase in temperature. These results showed the importance of studying the variables interactive effect. Figueroa et al. [37] have studied the individual yields of different FAMEs from high acidity raw castor oil using supercritical methanol. They have reported decreasing effect of methyl oleate and methyl palmitate (which are the main components of the WCO used in the present study) yields while increasing temperature starting from 250^{o}C at a constant M:O molar ratio of 1:40. They explained this phenomenon to the increasing rate of thermal degradation of both FAMEs and FFAs. Interaction effect of M:O molar ratio and temperature for high acidity feedstock was not reported widely. Aboelazayem et al. [32] have reported insignificant interaction effect between M:O molar ratio and temperature for low acidity WCO. Hence, FFA content attributes strongly to the effect of both M:O molar ratio and temperature.

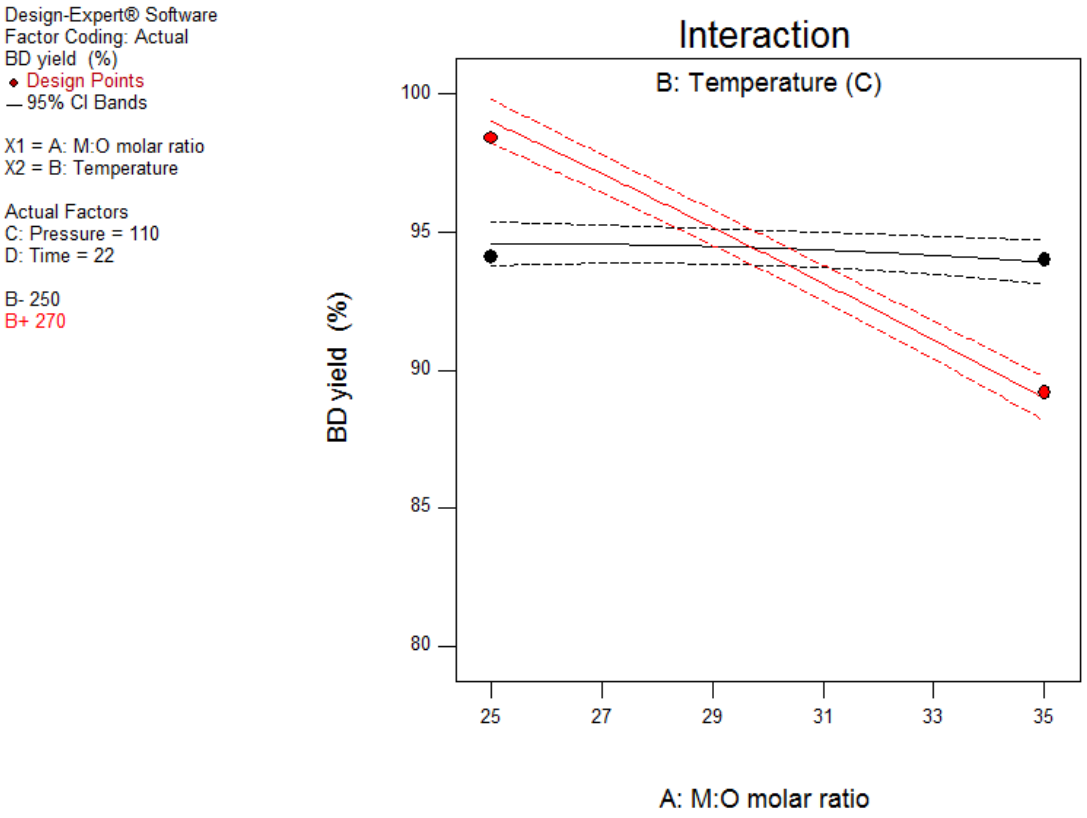

Figure 7. Interaction plot showing interactive effect of methanol ratio and temperature on biodiesel yield

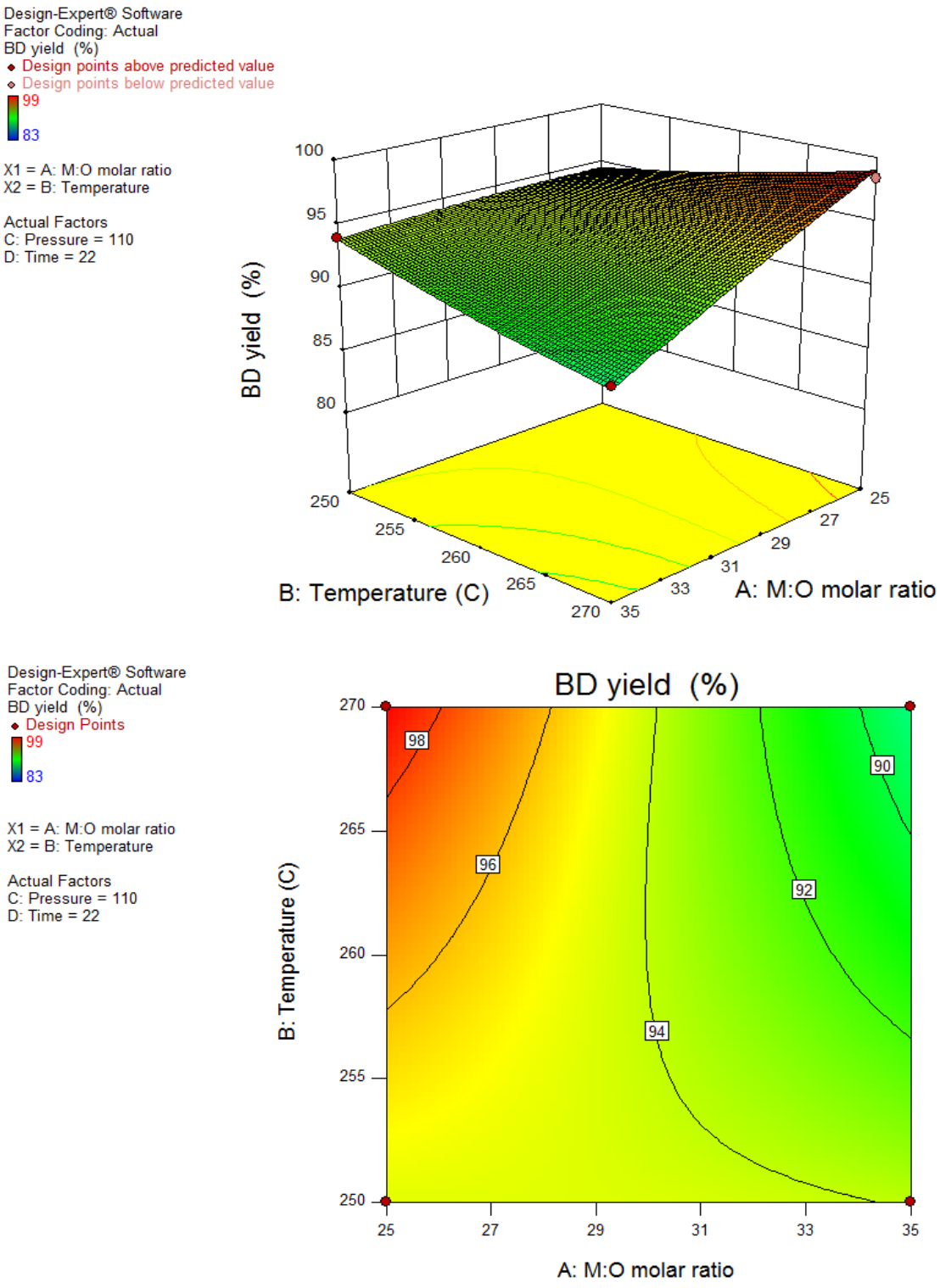

Figure 8. 3D response surface and contour plot for M:O molar ratio and reaction temperature *versus* biodiesel yield

3.3.2.2 Interactive effect of reaction pressure and time

Carbon dioxide (CO_2) gas has been used to pressurise the reaction to the desired pressure using a high-pressure pump. In addition, carbon dioxide acts as a co-solvent, where it enhances the solubility of methanol in oil [41]. The exponential interactive effect of reaction pressure and time on biodiesel yield is shown in Figure 9, which confirms the significant effect of their interaction as reported in ANOVA in Table 5. As shown in Figure 10, reaction pressure showed negligible effect on biodiesel yield at shorter reaction times. However, slightly negative effect of reaction pressure observed at longer reaction times. It has been reported by Ong et al. [42] that the increasing effect of pressure is not crucial as it exceeds the critical pressure of methanol. They have explained that both transesterification and esterification have the same number of moles of reactants and products. Hence, change in pressure would not affect the chemical equilibrium of reaction according to Le Chatelier's principle. While the negative effect of increasing pressure might be resulted from FAME degradation as addition the CO_2 decrease the critical point of the system and hence requires milder temperature [41].

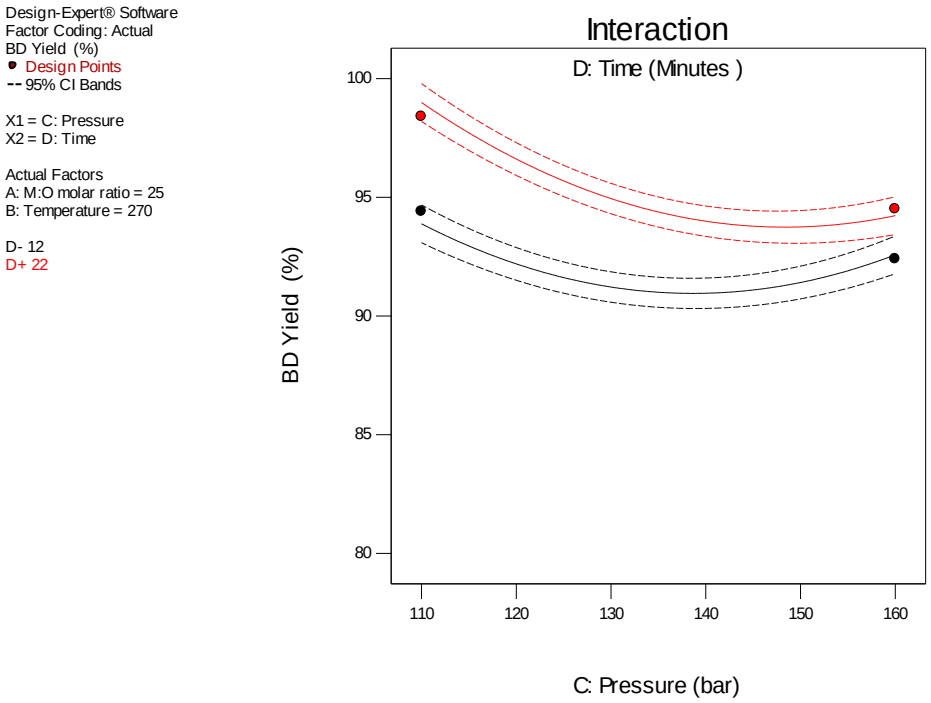

Figure 9. Interaction plot showing interactive effect of reaction pressure and time on biodiesel yield

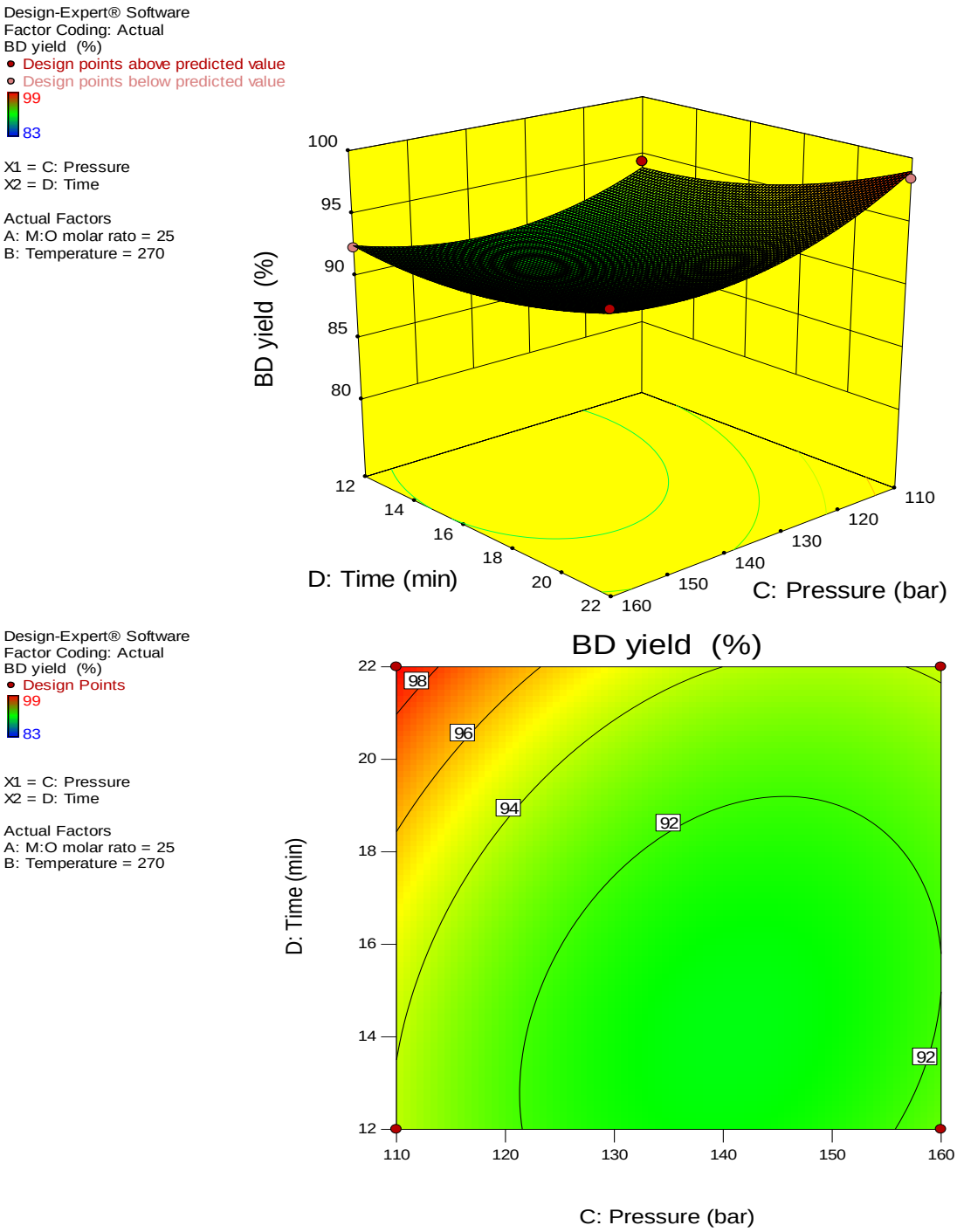

Figure 10. 3D response surface and contour plot for reaction pressure and time *versus* biodiesel yield

3.4. Process optimisation and experimental validation

The application of RSM to optimise the reaction variables affecting biodiesel production have been reported in previous studies [38,43–45]. In order to optimise both reaction responses (i.e. biodiesel and glycerol yields), numerical feature using Design Expert 10 software has been implemented to evaluate the best combination of conditions for achieving the desired target. Biodiesel yield response has been set to a maximum target while minimum target of glycerol has been adjusted. The independent variables have been set to a minimum level as shown in Table 7. Subsequently, 40 solutions for optimum conditions have been generated by the software where the solution with highest desirability has been selected. The resulting optimum conditions achieved 98% and 2.05% for biodiesel and glycerol yield, respectively at 25:1 M:O molar ratio, 265^{o}C, 110 bar pressure in 20 minutes reaction time.

In order to validate the predicted optimum conditions, three experiments have been conducted at these conditions, where the average result has been considered as the experimental outcome. The experimental validation has resulted biodiesel yield of 98.82%, which shows the adequacy of the predicted optimum conditions within 0.83% relative error from the experimental results.

Table 7. Optimisation constrains used to predict optimum conditions for biodiesel production

Factor	Code	Goal	Limits	
			Lower	Upper
M:O (molar ratio)	A	Minimise	25	35
Temperature (^{o}C)	B	Minimise	250	270
Pressure (bar)	C	Minimise	110	160
Time (min)	D	Minimise	12	22
Biodiesel yield	Y_1	Maximise	95	99
Glycerol yield	Y_2	Minimise	0.52	17.72

The purified biodiesel produced at the optimum condition has been analysed and compared with the European Biodiesel Standard, EN14214. All the main measured physicochemical properties are within the range of the European standard as shown in Table 8.

Table 8. Comparison between produced biodiesel properties and European biodiesel standard EN14214

Test	Unit	Produced biodiesel	Biodiesel (EN14214)
Density at 15^{o}C	kg/m^3	884	860 - 900
Kinematic viscosity at 40^{o}C	cSt	4.6	3.5 - 5
TAN	mg KOH/ g oil	0.3	< 0.5

It is recommended to perform techno-economic study for supercritical production of biodiesel from very low quality WCO. FFA conversion and intermediate conversions of triglycerides could be considered as dependant responses for future studies. Exergy analysis is also recommended to be studied for such a typical process. Finally, integrated process simulation could be designed as a first step for scaling-up the process for industrial scale.

4. CONCLUSIONS

Valorisation of a typical Egyptian WCO with high acid value into biodiesel at very high yield has been achieved. Both esterification and transesterification reactions have taken place simultaneously throughout the reaction. High acidity feedstock behaves differently with different reaction variables. Highly significant interactive effect of M:O molar ratio and temperature has been observed. The optimum biodiesel yield has been predicted with 98% at M:O molar ratio of 25:1, reaction temperature of 265^{o}C and reaction pressure of 110 bar in 20 minutes. The optimal conditions have been validated experimentally resulting in biodiesel yield of 98.82%, which shows the adequacy of the predicted optimum conditions within 0.83% relative error from the experimental results. The quality of the produced biodiesel has been compared with the European biodiesel standard (EN14214) showing excellent agreement with the standard biodiesel properties. This study has provided an appropriate pathway for solving a real world problem for sustainable production of biofuel from typically very low quality feedstock in Egypt.

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