Enhanced biodiesel production with improved oxidation stability by water addition to supercritical methanolysis

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Abstract

Biodiesel has been established as a potential alternative fuel for petroleum diesel. However, one of the main uncertainties about biodiesel is its susceptibility to oxidation. In the present study, biodiesel has been synthesized from high acid value waste cooking oil (WCO) using supercritical methanolysis. The influence of supercritical reaction conditions on enhancing biodiesel's oxidation stability and yield has been extensively studied. Five independent reaction variables have been investigated, including methanol to oil (M:O) molar ratio (3-40), temperature (235-275°C), pressure (65-145 bar), time (5-30 min), and water content (0-8 vol%). The oxidation stability has been analyzed *via* PetroOxy commercial device based on the ASTM D7545-14 methods and compared to EN14214 standards. Response Surface Methodology (RSM) *via* Central Composite Design (CCD) has been employed to evaluate the influence of the process variables and to develop empirical models representing the reaction. Interestingly, it has been observed that water content in the feedstock would be an advantage to increase both yield and oxidation stability of biodiesel. Analysis of variance (ANOVA) has been used to investigate the adequacy of the predicted model at a 95% confidence level. The developed optimum conditions have achieved a yield of 99.8% and 26.21 min (oxidation stability) at 10:1 M:O molar ratio at 245°C, 125 bar, 6 vol% water content within 16.7 min reaction time. The predicted optimal conditions have been validated experimentally with 0.8-0.9% relative error for both responses.

Keywords

Biodiesel; Supercritical technology; RSM; Oxidation stability; PetroOxy.

1 Introduction

The population growth and the influence of accelerated metropolitan decentralization across the globe have led to a major increase in energy demand. Fossil fuels, including coal, oil, and natural gas have played a prominent dependency in the energy sector. However, these resources are finite and have been depleting for several decades. In addition, the reliance on fossil fuels contributes to toxic and greenhouse gas emissions that have considerable environmental concerns. As the world moves into a global recession and the cost of sourcing and delivering fossil fuels soar, finding an alternative sustainable bio-based energy source is crucial.[1]

Biodiesel is considered a potential alternative to petroleum diesel due to its similar properties and compatibility. Biodiesel is a mono-alkyl ester of long-chain fatty acids derived from vegetable oil and animal fats. It has advantages over petroleum diesel, including biodegradability, lower sulphur content, and higher flashpoint.[7] Presently, biodiesel is commercially produced from edible oils, i.e., rapeseed and sunflower oils. The dependency on edible oil for the biofuel industry has raised critical concerns about global security as it creates competition between the food and the energy sector. Hence, the research is currently shifting towards non-edible and waste oils as potential feedstocks for biodiesel production.[3]

Recently, the implementation of supercritical technology for biodiesel production has gained immense interest, specifically for high acidity feedstock. It has been firstly reported by Saka and Kusdiana,[4] from rapeseed oil. They have demonstrated the applicability of the simultaneous conversion of triglycerides and free fatty acids (FFA) into fatty acid methyl esters (FAMEs) through intensified transesterification/esterification reactions. The supercritical biodiesel process is a catalyst-free process that eliminates catalyst preparation and separation steps as reported in the conventional processes. It also produces a higher yield of biodiesel and shortens the reaction duration time. The technology has been reported as an ideal method for feedstock with high acidity, including WCO and non-edible crude oils.[5] Further, it has been reported that water content in the feedstock has a non-significant effect on biodiesel yield and hence a wide variety of feedstock with high water contact could be valorised into biodiesel *via* supercritical technology. [6] Several studies have been reported on the supercritical production of biodiesel including catalytic [7,8] and noncatalytic approaches [7,9]. Although methanol has been considered the dominant alcohol used for supercritical production of biodiesel, ethanol and butanol have been also reported. [3,10–12]

Optimisation of supercritical process variables, including alcohol to oil ratio, temperature, pressure and time, is a crucial step for the sustainable production of biodiesel. Response surface methodology (RSM) *via* central composite design (CCD) and box-Behnken design (BBD) has been widely used in chemical process optimisation. [13–16] RSM is a powerful tool that is used to generate a randomised set of experiments at different experimental operational conditions. These runs are used to develop a model that represents the process responses as a function of the process parameters and hence saves time, minimise material consumption by predicting a wide range of experimental data. It is also used to assess the effect of individual process parameters and their interactions together with the applicability to optimise the process variables based on set targets. [13,17] Prajapati et al [18] have studied the optimisation of biodiesel production from waste cottonseed oil *via* microwave irradiated process *via* RSM. Srivastava et al [19] have optimised the production of biodiesel from microalgae using supercritical methanol. They have achieved 98.12% fatty acid methyl ester (FAME) conversion at 285.21 ^{0}C, a methanol to oil ratio of 23.41:1 within 26.57 min.

Although the supercritical production of biodiesel requires harsh reaction conditions and high energy consumption, process optimisation/integration approaches have been developed to minimise the process waste energy. Our research group has developed an energy integrated process for biodiesel production using an efficient heat exchanger network.[20] We have also implemented a novel approach to integrate the organic Rankine cycle (ORC) process to utilize further the low temperature energy streams for electricity production as an additional revenue for the process.[21] Ziyai et al [22] have also integrated the biodiesel process with glycerol supercritical water reforming for hydrogen production. The produced hydrogen has been considered as process revenue and hence enhanced the economic viability of the process.

Despite the advantages of biodiesel as a renewable fuel, the major drawback of commercialization is the stability of alkyl esters under atmospheric conditions due to oxidation reactions. Oxidation stability is defined as the tendency of fuels to react with oxygen near ambient temperature, which describes the relative susceptibility of the fuel to degradation by oxidation. A fuel that readily goes into changes in its physicochemical properties and forms undesirable species is considered unstable. Biodiesel can be degraded by several mechanisms, including oxidation or auto-oxidation, photo-oxidation, thermal-oxidative decomposition, and hydrolysis; these are resulted in from contact with air, water, and microbial contamination.[23,24] The oxidation reaction in biodiesel leads to the formation of insoluble polymers, deposits, and corrosive compounds. Degradation by oxidation yields oxidative products that compromise fuel properties, impair fuel quality, and reduce engine performance.[25] Devi et al. [26] reported that long term storage of biodiesel promotes the formation of primary and secondary oxidation products.

Several techniques have been reported to analyze biodiesel's oxidation stability, including the Rancimat method, PetroOxy, active oxygen method, and oxygen bomb test. The induction Period (IP) is defined as the time required for biodiesel to be fully oxidized by any analysing techniques.[27] Mairizal et al.[28] have reported a different range of oxidation stability IP values for biodiesels produced from the different feedstock. They have explained that the feedstock structure and the level of unsaturation is the main reason behind this variation.

PetroOxy provides a rapid test method to analyze the oxidation stability of biodiesel. It has been recently preferable as it requires shorter analysis time is and more efficient for testing and developing new content.[29] It has been reported that the Rancimat method provides an incomplete analysis of the oxidation stability of biodiesel as it only considers high volatile oxidation products through a combination of distillation and conductivity. However, PetroOxy includes a combination of volatile and non-volatile oxidation products.[30] Araújo et al. [31] have conducted an FTIR assessment on similar samples using both Rancimat and PetroOxy methods. They have confirmed a similar oxidation pattern for both methods on a castor oil FAME.

Inhibiting the oxidation of biodiesel is very difficult to be avoided due to the presence of unsaturated fatty acids. However, the reaction can be delayed.[32] Researchers have pursued different inhibiting techniques to delay the oxidation processes, such as structural modifications, low temperature storage, removal of hydroxyl group, conversion of *cis* unsaturation to *trans*, petro-diesel blend, and antioxidants. McCormick and Westbrook,[33] have reported that a petro-diesel blend could increase the stability of biodiesel, where the presence of sulphur can act as an antioxidant. Gil-Lalaguna et al.,[34] have developed several extracted fractions of lignocellulosic bio-oil to be added to biodiesel as an antioxidant. Bharti and Singh,[35] have proposed adding green tea extracts as a renewable antioxidant for biodiesel. They have reported an enhancement of oxidation stability from 2.88 h to 7.11 h *via* green tea extracts. Our research group has also derived renewable antioxidant from kraft lignin that has significantly enhanced the oxidation stability by 340% in comparison with neat biodiesel. [36]

The previously reported studies in the literature have investigated the oxidation stability for biodiesel produced using conventional catalyzed processes. A summary of the previous studies on biodiesel oxidation stability is presented in Table 1. However, there is a lack in the literature of studies on oxidation stability for supercritical synthesized biodiesel. To the authors' knowledge, Xin et al.,[37] were the first researchers who studied the effect of oxidation stability using supercritical methanol. However, they have produced biodiesel using the conventional catalyzed method and subsequently exposed the produced biodiesel to supercritical methanol. They have reported that the feedstock with the lowest unsaturated fatty acid has the longest induction period. They have also reported that exposing biodiesel to supercritical methanol enhanced the oxidation stability of biodiesel. They have explained their findings as high temperature and pressure improve the decomposition of hydroperoxides while tocopherols remained almost unchanged. It has been reported that supercritical methanolysis may enhance oxidation stability, especially for feedstock with high peroxide values.

In the present work, an innovative study regarding the effect of supercritical reaction conditions on the oxidation stability of biodiesel has been reported. Further, this work has provided a firstly reported investigation of the influence of water content in the feedstock on oxidation stability and yield of biodiesel. Biodiesel samples were kept in an air-tight closed lid glass in a dark cupboard for a month prior to the oxidation stability test. The analysis of oxidation stability has been performed using the standard method of ASTM D7545-14(2019) *via a* PetroOxy commercial device. Five independent reaction variables have been investigated, including methanol to oil (M:O) molar ratio (3-40), temperature (235-275°C), pressure (65-145 bar), time (5-30 min), and water content (0-8 vol%). The selection of reaction parameters range was based on the supercritical conditions of methanol in addition to previous work reported in the literature.[3,5,38,39] Numerical and graphical optimization have been employed to optimize the reaction variables for biodiesel with higher productivity and stability.

TABLE 1 Oxidation stability of biodiesel from various feedstock at different conditions

Feedstock	Process	Conditions	IP	References
Vegetable oil	Base catalyst	Methanol - 100g NaOH - 2.5 g Time -30 min Temperature – 25°C	Rancimat-3.77 h PetroOxy-0.76 h	De Sousa et al.[40] De Sousa et al.[29]
Sunflower oil	Base Catalyst	M:O - 1:6 (molar ratio oil to methanol) KOH -1 wt% Temperature – 60°C Time – 3 h	PetroOxy – 13.8 min	Dueso et al.[41]
Micro algae (*Chlorella vulgaris)*	Base Catalyst	KOH - 0.5 wt% Lipid to methanol - 1:4 Temperature – 45°C-65°C Time- 5-25 min	PetroOxy- 5.0 h	Rawat et al.[42] Sharma et al.[43]
Castor Oil	Base Catalyst	NaOH Temperature – 25°C	PetroOxy- 19 min Rancimat- 183 min	Araújo et al.[31]
Soybean oil	Base catalyst	Ethanol to oil ratio (1:6) KOH – 1 wt%	Rancimat-4.34 h PetroOxy- 2.5 h	Damascenoet al.[44]
Soybean oil	Base catalyst	M:O - (1:6) NaOH - 0.6% Time - 60 min	PetroOxy-17.39 min	MacHado et al.[45]
Sunflower oil	Base catalyst	M:O - (1:6) NaOH - 0.6% Time - 60 min	PetroOxy-5.97 min	MacHado et al.[45]
Karanja oil	Base catalyst	-	PetroOxy-2.98h	Rawat et al.[46]
WCO	Supercritical methanolysis	M:O – 10:1 Pressure - 125 bar Time -16.7 min	PetroOxy-26.21 min	This work

Temperature – 25°C
Water content- 6% vol

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2. Materials and methods

2.1. Materials used

WCO was collected from different restaurants and industries in Egypt and mixed to form a realistic mixture. Methanol (99%) was purchased from Fisher Scientific UK Ltd. The liquid CO_2 and O_2 cylinder (99.9%) equipped with a dip tube was purchased from BOC Ltd., UK.

2.2. Experimental procedures

2.2.1. Supercritical synthesis of biodiesel

The detailed procedure for biodiesel synthesis using supercritical methanol was reported elsewhere.[47] In summary, WCO was heated using a hot plate for 5 min at 25°C and then filtered to remove any residuals obtained during the cooking processes. The filtered WCO was loaded to a 100 mL high-pressure reactor made of stainless steel (model 4959, Parr instrument company, USA), as shown in Figure 1. 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 based on each run molar ratio and volume, as specified in Table 3. 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 pressurizing since the vapourized methanol build-up pressure inside the reactor where the remaining pressure was obtained using pressurized 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 an ice bath to stop the reaction. The reactor was then depressurized, 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 feedstock composition are reported elsewhere.[48] The yield of the biodiesel was calculated by using Equation (1)[49]:

$$\text{Biodiesel yield (\%)} = \frac{mass\ of\ biodiesel\ obtained}{mass\ of\ WCO\ used} \text{ X } 100 \qquad (1)$$

2.2.2. Accelerated oxidation method

PetroOxy device (Anton Paar, Dahlewitz, Germany) was employed as an accelerated oxidation test method to analyze the oxidation stability of biodiesel under the standard method of ASTM D7545-14(2019). A 5 ml of biodiesel sample was placed in a sealed test chamber cell. The chamber cell was purged with O_2 twice to discharge air completely. The test cell was then closed and automatically charged with O_2 up to 700 kPa (7 bar). Once reaching the specified pressure, the test starts by gradually increasing the chamber's temperature until reaching the standardized temperature of 140°C. After maximum pressure is reached, an initial pressure drop indicates biodiesel has started to oxidize. After a 10% pressure drop, it was assumed the biodiesel has fully oxidized. IP is the elapsed time between the start of the test and the breaking point when a 10% pressure drop has been detected, which indicates the oxidation resistance. [50]

2.3. Experimental design

An experimental design using RSM *via* CCD was applied to minimize the number of experiments and provide detailed relationships between process variables and responses. In addition, the implementation of CCD in experimental design offers the possibility for process optimization, development of a numerical model, and analyzing the interactive effect of process variables.

The independent variables were M:O molar ratio, temperature, pressure, time, and water content, labelled as A, B, C, D, and E, respectively. Five levels of each variable were studied following the regulations of the CCD method, which includes axial, central, and star points. The variables levels have been set based on previous experimental reports.[6,48] The selected five levels for each variable were coded as -2, -1, 0, +1, and +2, as shown in Table 2. The studied range of M:O molar ratio was identified between 0 to 40 with an increment of 10 between each level. However, the lowest level (0) was replaced by 3 as it represents the minimum stoichiometric M:O molar ratio of 3:1. The identified variables and levels resulted in 32 randomized experiments, as shown in Table 3. The performed experimental runs were designed randomly to minimize unexplained inconsistency in the responses.[51]

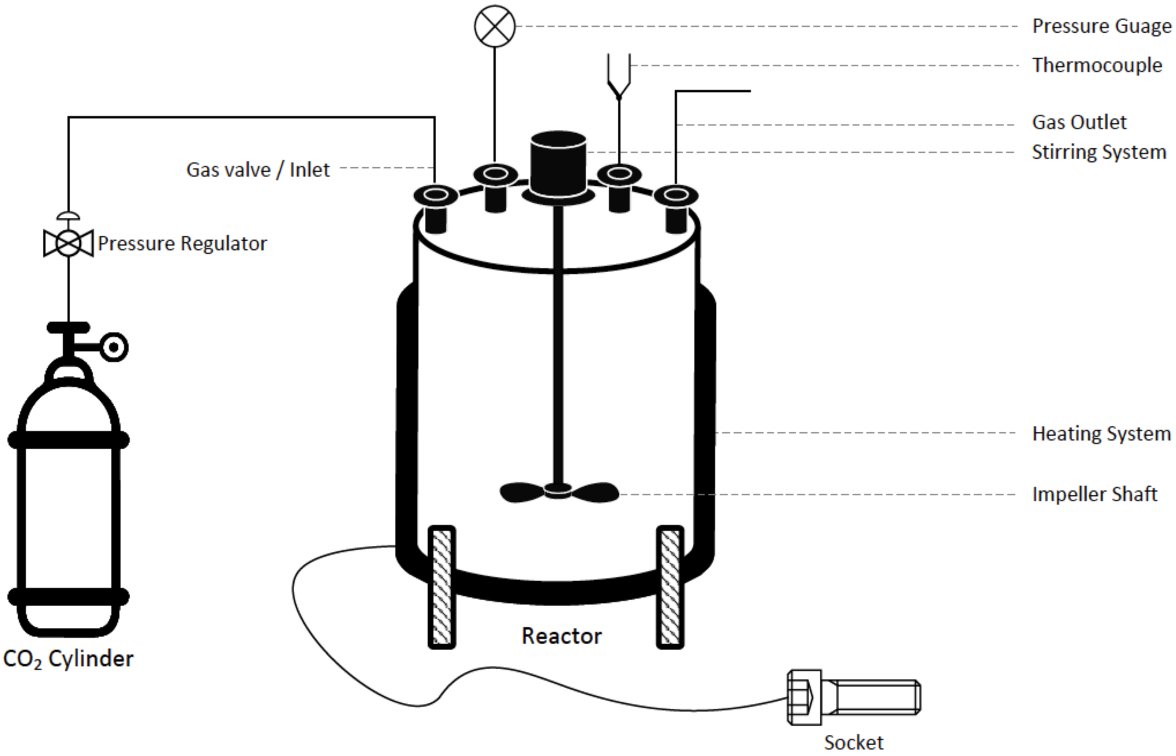

FIGURE 1 Experimental setup for biodiesel production

TABLE 2 Experimental design variables and their coded levels

Factor	Code	Levels				
		-2	-1	0	+1	+2
M:O (molar ratio)	A	3	10	20	30	40
Temperature (^oC)	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

TABLE 3 Experimental design matrix with the actual and predicted response

Run	**M:O ratio (A)**	**Temperature (ºC) (B)**	**Pressure (bar) (C)**	**Time (min) (D)**	**Water content (vol%) (E)**	**Actual PetroOxy IP (min)**	**Predicted PetroOxy IP (min)**	**Actual Yield (%)**	**Predicted Yield (%)**
1	30	245	85	10	2	19.81	19.71	99.71	99.31
2	10	245	85	20	2	15.95	16.06	99.59	98.90
3	20	255	105	25	4	15.33	15.45	95.13	95.26
4	20	255	105	15	0	17.66	17.41	86.99	87.11
5	20	255	105	5	4	17.10	17.35	85.84	88.30
6	10	265	125	20	2	16.22	16.35	82.13	81.83
7	10	245	125	10	2	19.03	19.24	84.01	82.93
8	20	255	105	15	4	16.53	17.92	89.33	89.17
9	20	255	145	15	4	17.68	17.59	82.77	83.69
10	20	235	105	15	4	16.85	16.80	78.83	80.51
11	20	255	105	15	8	18.02	18.64	67.76	70.23
12	30	245	125	20	2	14.83	14.90	69.76	70.12
13	20	255	105	15	4	18.36	17.92	88.12	89.17
14	20	275	105	15	4	13.95	14.36	88.53	89.43
15	10	265	125	10	6	14.78	14.66	79.13	77.66
16	30	265	85	20	2	19.16	18.98	91.89	92.77
17	30	245	125	10	6	17.60	17.42	75.27	74.46
18	30	265	125	10	2	17.20	17.12	98.73	98.71
19	40	255	105	15	4	19.73	20.26	89.23	88.79
20	20	255	105	15	4	18.90	17.92	89.65	89.17
21	10	245	85	10	6	20.83	20.69	68.25	66.40
22	30	265	125	20	6	16.55	16.29	90.87	90.85
23	3	255	105	15	4	21.03	20.86	84.76	87.80
24	20	255	105	15	4	17.41	17.92	86.47	89.17
25	10	265	85	20	6	17.00	16.78	90.99	89.91
26	20	255	105	15	4	18.66	17.92	92.70	89.17
27	20	255	65	15	4	19.38	19.83	91.21	92.87
28	30	245	85	20	6	17.60	17.32	85.38	84.98
29	10	265	85	10	2	17.93	17.89	96.41	95.33
30	30	265	85	10	6	20.20	19.77	77.72	76.92
31	20	255	105	15	4	18.00	17.92	91.33	89.17
32	10	245	125	20	6	22.23	22.26	91.81	90.72

2.4. Statistical analysis

The development of the regression model analysis was referred to as the general full quadratic equation as shown in Equation (2)[48]:

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

Where Y is the predicted response (i.e., PetroOxy IP and biodiesel yield), b_o is the model coefficient constant, b_i, b_{ii}, b_{ij} are coefficients for the intercept of linear, quadratic, interactive terms, respectively. At the same time, X_i, X_j are independent variables ($i \neq j$). n is the number of independent variables, and ε is the random error.

The adequacies of the predicted models were 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 models was checked using ANOVA *via* Fisher's test, i.e., F-value and p-value, at a 95% confidence interval. Further, the lack of fit analysis was employed to investigate the fitting accuracy of the predicted models to the experimental data. Design Expert 11 software (Stat-Ease Inc., Minneapolis, MN, USA) was used for designing experiments, regression analysis, graphical analysis, and numerical optimization.

3. Results and discussion

3.1. Regression model development

The developed 32 runs have been performed experimentally to report the actual PetroOxy IP and biodiesel yield results, as reported in Table 3. The range of the actual results has been observed for PetroOxy IP and biodiesel yield between 13.95-22.23 min and 67.8-99.7%, respectively. Design Expert software has been used to perform multiple regression analyses for the experimental data to fit the mathematical model. Four mathematical regression models for each response have been used to fit the experimental results, including linear, two factors interactions (2FI), quadratic and cubic polynomials. The software has suggested developing two quadratic regression models as they have been observed with high fitting to the experimental results amongst the other models.

Consequently, two quadratic models have been developed representing the empirical relationship between process responses and process variables, as shown in Equations (3) and (4), respectively.

$$Y_1 = 17.92 - 0.15\ A - 0.61\ B - 0.56\ C - 0.47\ D + 0.31\ E + 0.96\ AB - 0.96\ AC - 0.34\ AD - 0.29\ AE - 0.56\ BC + 0.34\ BD - 0.66\ BE + 0.64\ CD + 0.07\ CE + 0.48\ DE + 0.66\ A^2 + 0.58\ B^2 + 0.20\ C^2 - 0.38\ D^2 + 0.02\ E^2 \qquad (3)$$

$$Y_2 = 86.17 + 0.24\ A + 2.23\ B - 2.3\ C + 1.74\ D - 4.22\ E + 1.5\ AB - 0.12\ AC - 3.13\ AD + 0.07\ AE + 1.62\ BC - 0.96\ BD + 0.11\ BE - 1.77\ CD + 4.23\ CE + 5.88\ DE - 0.22\ A^2 - 1.05\ B^2 - 0.22\ C^2 + 0.65\ D^2 - 2.62\ E^2 \qquad (4)$$

Y_1 and Y_2 represent the response variables PetroOxy IP and Yield of biodiesel, respectively. While A, B, C, D, and E represent the independent variables, i.e., M:O molar ratio, 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 models. 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. Statistical adequacy checking

The adequacies of the predicted models have been examined to analyze the fitting accuracy of predicted results to the actual data. In this work, several statistical validations have been employed. The significance of the predicted models has been verified using ANOVA based on the p-value test, as shown in Table 4. p-value of less than <0.05 indicates the significance of the parameter. The predicted models have been observed with highly statistically significant p-values of 0.0002 and <0.0001 for PetroOxy IP and biodiesel yield, respectively.

Furthermore, the values of R^2 and R^2_{adj} have been reported as 0.96 and 0.89, respectively, for the PetroOxy IP response while 0.96 and 0.91 for biodiesel yield. The p-value for the lack of fit analysis, which examines the model fitting accuracy, has been investigated. The non-significant result for the lack of fit analysis illustrates the adequacy of the predicted models in fitting the actual data. [48] As observed from the ANOVA results in Table 4, lack of fit analysis has been reported as 0.8591 and 0.3515 (not significant) for PetroOxy and biodiesel yield, respectively. 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 results in values of 13.54 and 16.413 for PetroOxy and biodiesel yield, respectively, where a value higher than 4 is preferable. Finally, a plot representing the actual versus predicted data has been illustrated in Figure 2. The high similarity between actual and predicted results have been represented with minor deviations from the 45^o line.

TABLE 4 Analysis of variance of the developed model

	PetroOxy developed model						**Biodiesel yield developed model**					
	Sum of square	**df**	**Mean Square**	**F Value**	**p-value**	**Significance**	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	**significance**
Model	105.80	20	5.29	10.22	0.0002	HS	2138.36	20	106.92	17.45	<0.0001	S
A-M:O molar ratio	0.5460	1	0.5460	1.06	0.3264	NS	1.46	1	1.46	0.2390	0.6346	NS
B-Temperature	8.93	1	8.93	17.26	0.0016	HS	119.29	1	119.29	19.46	0.0010	HS
C-Pressure	7.53	1	7.53	14.54	0.0029	HS	126.62	1	126.62	20.66	0.0008	HS
D-Time	5.40	1	5.40	10.43	0.0080	HS	72.70	1	72.70	11.86	0.0055	HS
E-Water content	2.27	1	2.27	5.38	0.0402	S	427.28	1	427.28	69.72	< 0.0001	HS
AB	14.78	1	14.78	28.57	0.0002	HS	36.25	1	36.25	5.91	0.0333	S
AC	7.76	1	7.76	14.99	0.0026	HS	0.2322	1	0.2322	0.0379	0.8492	NS
AD	1.89	1	1.89	3.65	0.0824	NS	157.72	1	157.72	25.73	0.0004	S
AE	1.42	1	1.42	2.74	0.1263	NS	0.0749	1	0.0749	0.0122	0.9140	NS
BC	5.11	1	5.11	9.87	0.0094	HS	42.09	1	42.09	6.87	0.0238	S
BD	1.88	1	1.88	3.63	0.0833	NS	14.81	1	14.81	2.42	0.1483	NS
BE	7.05	1	7.05	13.62	0.0036	HS	0.2274	1	0.2274	0.0371	0.8508	NS
CD	6.60	1	6.60	12.76	0.0044	HS	50.21	1	50.21	8.19	0.0155	S
CE	0.0756	1	0.0756	0.1461	0.7096	NS	286.46	1	286.46	46.74	<0.0001	S
DE	3.78	1	3.78	7.31	0.0205	S	554.38	1	554.38	90.46	<0.0001	S
A^2	12.85	1	12.85	24.83	0.0004	HS	1.41	1	1.41	0.2302	0.6408	NS
B^2	9.98	1	9.98	19.28	0.0011	HS	32.29	1	32.29	5.27	0.0424	S
C^2	1.17	1	1.17	2.25	0.1616	NS	1.45	1	1.45	0.2363	0.6364	NS
D^2	4.22	1	4.22	8.16	0.0156	S	12.50	1	12.50	2.04	0.1810	NS
E^2	0.0211	1	0.0211	0.0408	0.8437	NS	202.18	1	202.18	32.99	0.0001	S
Residual	5.69	11	0.5175				67.42	11	6.13			
Lack of Fit	1.81	6	0.3020	0.3891	0.8591	NS	42.76	6	7.13	1.45	0.3515	NS
Pure Error	3.88	5	0.7762									

HS: Highly significant, S: Significant, NS: Non-significant

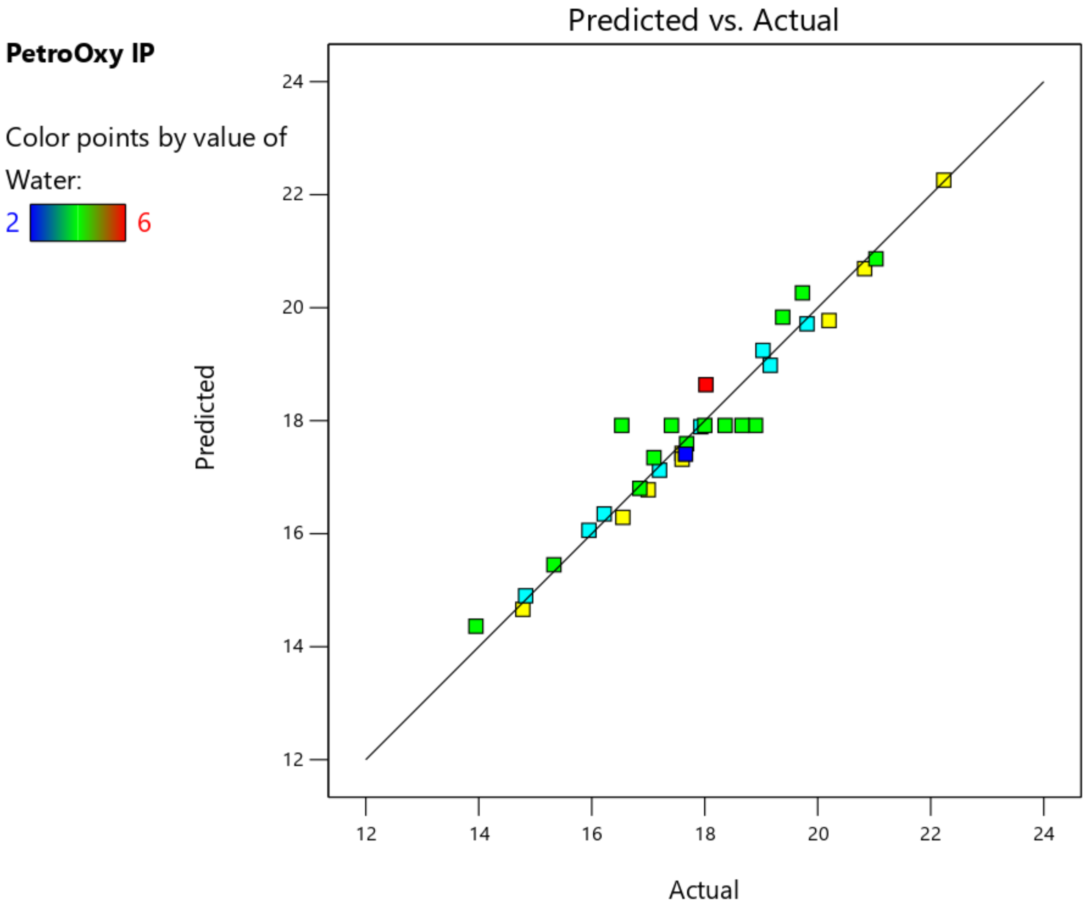

FIGURE 2 Experimental actual results *versus* predicted results from the PetroOxy model

In an additional step to ensure the validity of the predicted models and the results obtained using the ANOVA test, the three ANOVA assumptions for the residuals (difference between actual and predicted results) have been checked including the residuals normality, randomization, and homoscedasticity (equal variance).[17] The verification has only been performed on the PetroOxy model for demonstration. The externally studentized residual is the ratio between the residual of an estimate and its standard deviation.[53] The normality of the residuals has been investigated *via* the normality plot between externally studentized residuals *versus* Normal probability (%) for the PetroOxy model, as shown in Figure 3. The residuals have approximately fitted a straight line which confirms the validity of the first assumptions. The homoscedasticity of the residuals has been represented for the M:O molar ratio, where approximately equal variance at the levels of variables has been observed in the plot between externally studentized residuals *versus* the levels of the M:O molar ratio for the PetroOxy model as shown in Figure 4. Finally, the randomization of the residuals has been investigated using a plot between the externally studentized residuals *versus* predicted responses values for the PetroOxy model, as shown in Figure 5.

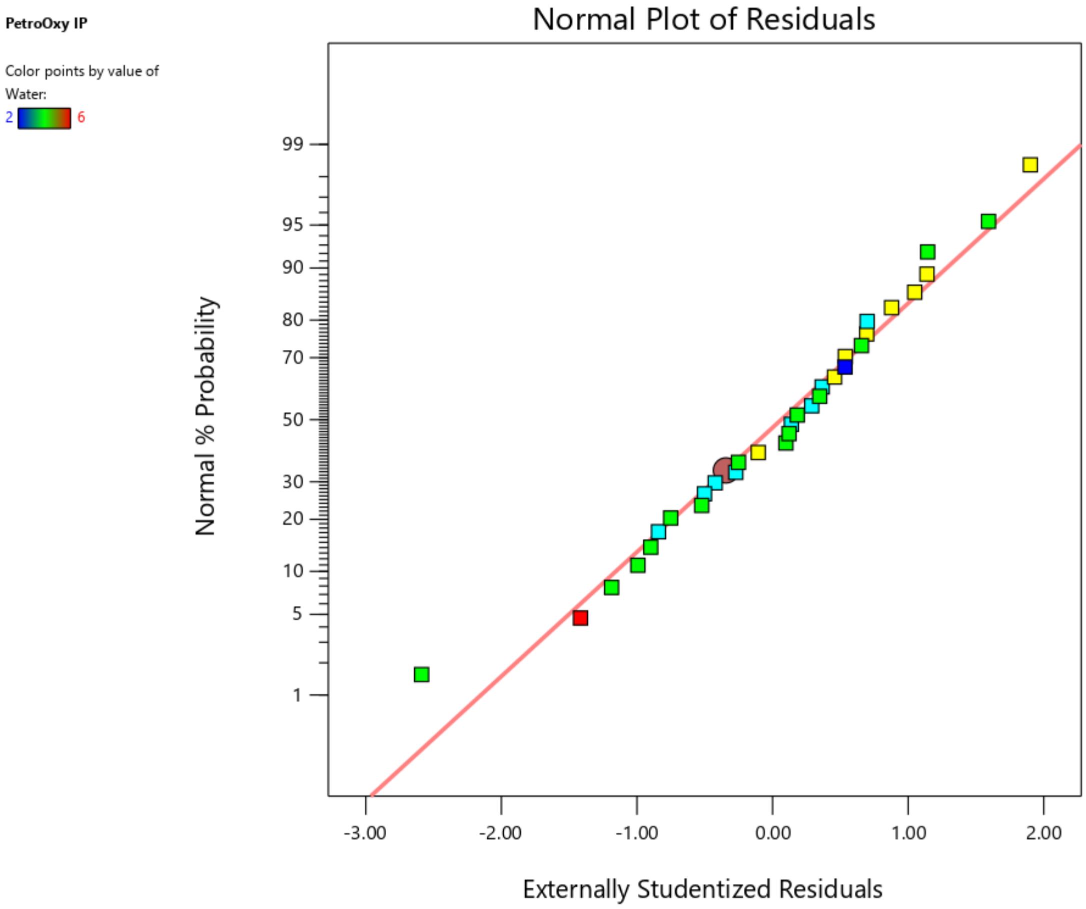

FIGURE 3 The normal plot of residuals for the predicted PetroOxy model

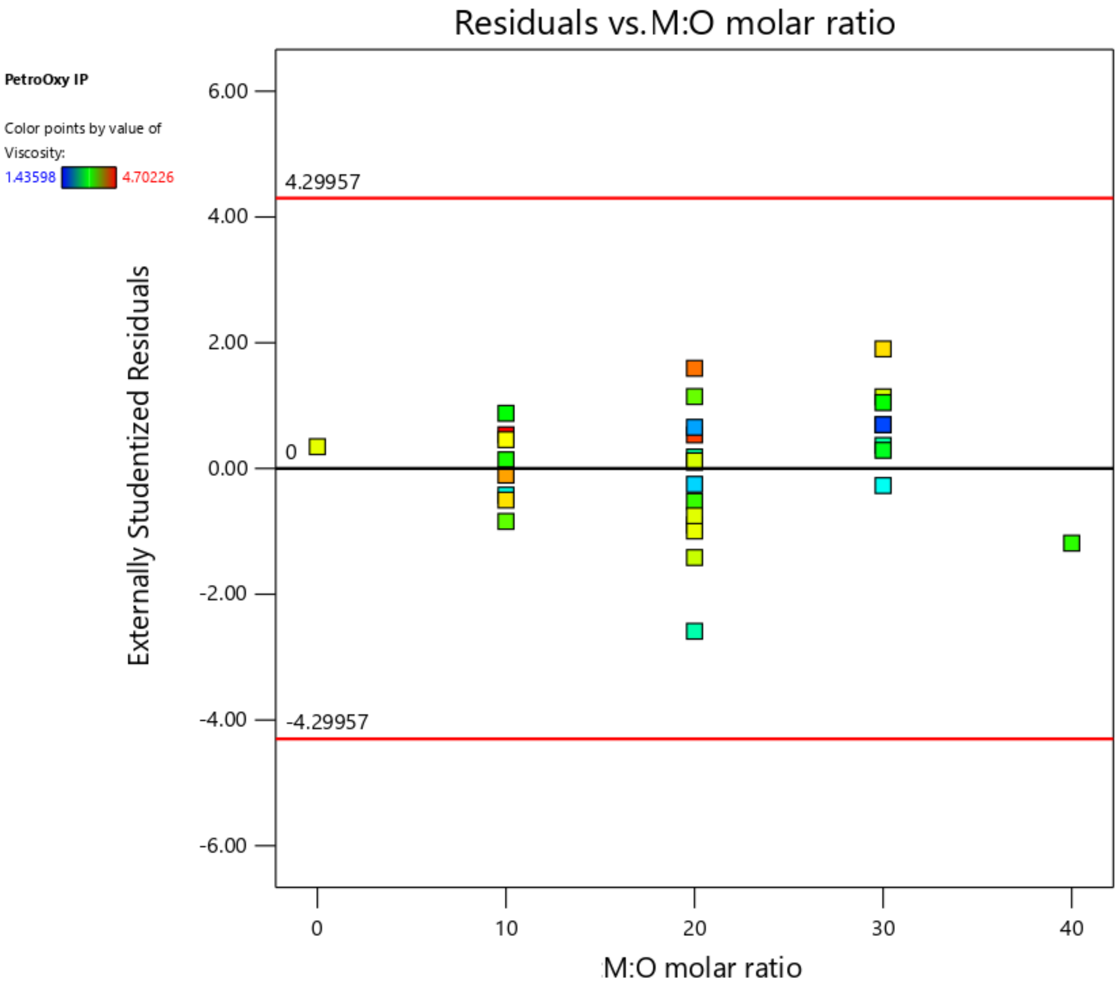

FIGURE 4 The plot of residuals *versus* predicted values of methanol to oil (M:O) molar ratio variable for the predicted PetroOxy model

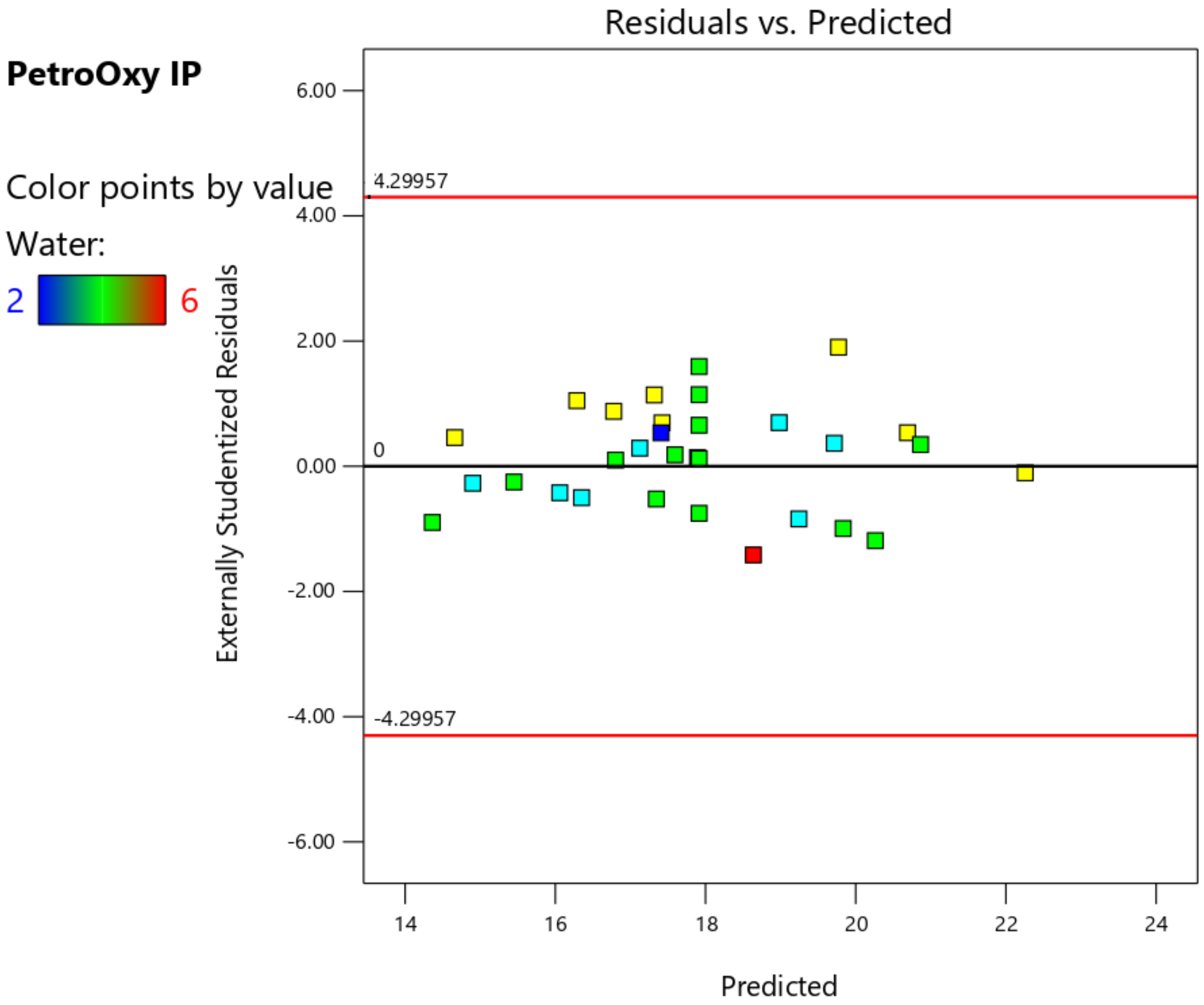

FIGURE 5 The plot of residuals *versus* predicted response for the predicted PetroOxy model

3.3. Effect of process variables and their interactions

3.3.1. Effect of reaction temperature

The effect of reaction temperature on the oxidation stability and biodiesel yield has been reported highly significant, as reported in Table 4. It has been observed that the increasing effect of reaction temperature has a negative influence on the PetroOxy IP, as shown in Figure 6. This might attribute to the high possibilities for the decomposition of the natural antioxidants (tocopherols) at higher reaction temperatures. Kumar,[54] has reported that oxidation reactions are particularly enhanced at elevated reaction temperatures between 250 and 300°C. In addition, Steel, Dobarganes and Barrera-Arellano,[55] have reported that the decomposition of tocopherols is initiated at 180°C, where the decomposition rate increases at higher temperatures. Finally, MacHado et al.,[45] have discussed the effect of different oxidation temperatures on the oxidation stability using PetroOxy. They have studied at different temperatures between 130 and 145°C. The tests have been performed on biodiesel derived from sunflower and soybean oils. They have reported that increasing the temperature between 135 and 145°C has reported a 35% and 59% decrease in the oxidation stability for sunflower and soybean biodiesel, respectively.

Reaction temperature on yield has a direct relationship between the temperature range and biodiesel yield. Biodiesel yield decreases at a very high temperature due to the decomposition of the produced FAME. This phenomenon has been reported by Ghoreishi and Moein,[38] where they have observed at a higher temperature, more than 271°C biodiesel yield starts to decrease. Further, Aboelazayem, Gadalla and Saha,[47] reported a similar observation but at a temperature of more than 270°C.

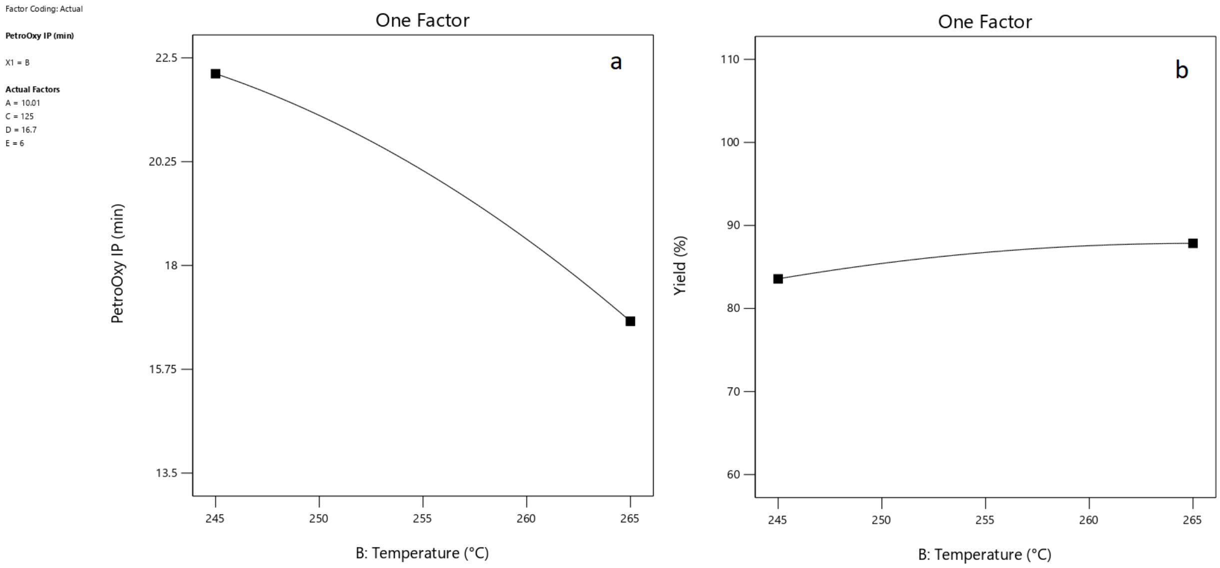

FIGURE 6 The individual effect of reaction temperature on (a) oxidation stability and (b) biodiesel yield (b)

3.3.2. Effect of reaction pressure

The reaction pressure is considered one of the main parameters that affect the supercritical production of biodiesel. The studied levels of the reaction pressure have been set between 65 and 145 bar, as shown in Table 2. The pressure range has been identified based on previously reported research on the effect of pressure on biodiesel yield.[48] Supercritical CO_2 has been used to pressurize the reaction vessel. It has been employed as a co-solvent to the reaction and also enhances the solubility between oil and methanol. The effect of reaction pressure on biodiesel production has conveyed contradictive results where several studies have reported a positive effect of increasing the pressure,[56,57] and other studies reported the decreasing effect of reaction pressure.[48,58]

In the present study, biodiesel yield slightly decreases as reaction pressure increases as shown in Figure 7b. Aboelazayem, Gadalla and Saha,[47] have reported that beyond 230 bar, the biodiesel yield starts to decrease. Similarly, Kurniawan et al.,[59] reported that the pressure effect on the supercritical transesterification using compressed nitrogen gas for Jatropha oil is directly proportional to biodiesel yield until 220 bar.

On the other hand, the reaction pressure has different effects on biodiesel oxidation stability. For instance, reaction pressure positively impacts oxidation stability at M:O molar ratio, temperature, time, and water content of 10:1, 245°C, 16.7 min, and 6 vol%, respectively, as shown in Figure 7a. The reason could be due to an increase in solubility between oil and methanol, which tends to retain high traces of tocopherols and carotenoids that do not fully decompose at low temperatures. However, the effect of reaction pressure varies under different reaction conditions. Hence, it is better to refer to the interactive effect of reaction pressure and other variables as described in section 3.3.6.

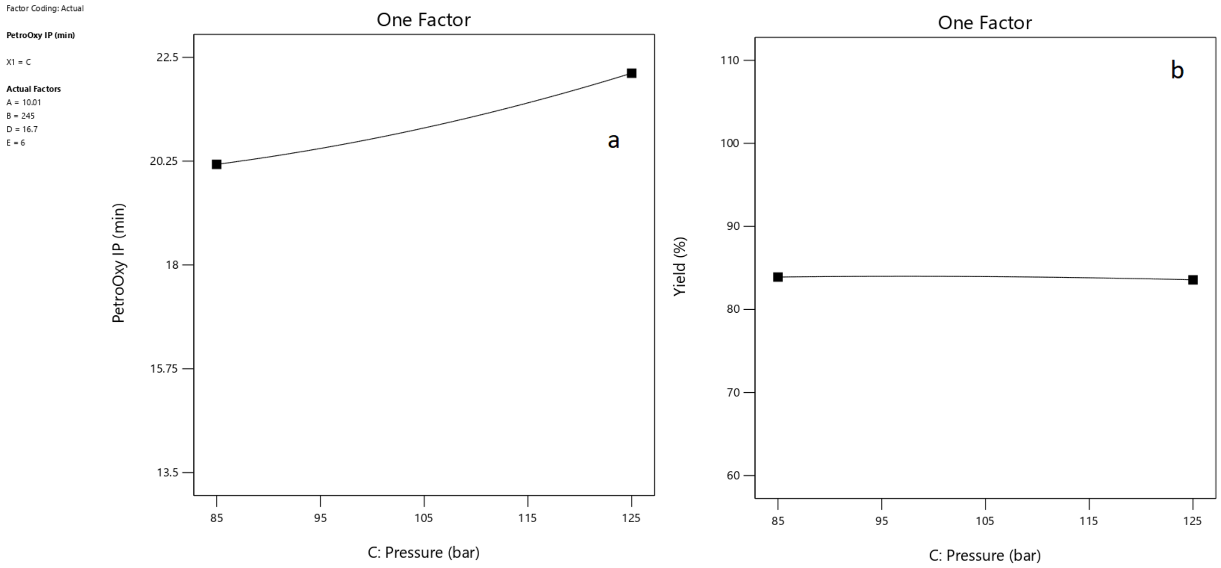

FIGURE 7 The individual effect of reaction pressure on (a) oxidation stability and (b) biodiesel yield

3.3.3. Effect of reaction time

One of the significant advantages of supercritical methanolysis is shortening the reaction time required for biodiesel production.[20] In this study, the effect of reaction time on oxidation stability has been investigated. It has been reported from the ANOVA results, as shown in Table 4, that reaction time has a significant effect on oxidation stability whereas increasing reaction time has a positive influence on PetroOxy IP, as demonstrated in Figure 8. However, the increase in reaction time should enhance the decomposition of natural antioxidants in biodiesel. These results might have referred to the limited range of reaction time investigated in this study, as the increase in reaction time increases the productivity of biodiesel. In addition, the increase of oxidation stability from 10 to 20 min has increased the PetroOxy IP from 20.8 to 22 min, which might not be considered a sharp increase in comparison with the effect of reaction temperature. Accordingly, it has been observed that increasing reaction time has enhanced the oxidation stability of biodiesel for a time range between 5 and 30 min.

On the other hand, reaction time has shown a directly proportional relationship with biodiesel yield. Similarly, Aboelazayem, Gadalla and Saha,[47] have observed a similar effect of reaction time on biodiesel yield. He, Wang and Zhu,[60] have reported similar results at temperatures lower than 300°C. However, they have explained the negative influence of reaction time on biodiesel at higher temperature reactions. They have explained that the decrease in the yield of biodiesel is due to the loss of unsaturated FAME, especially under high temperatures.

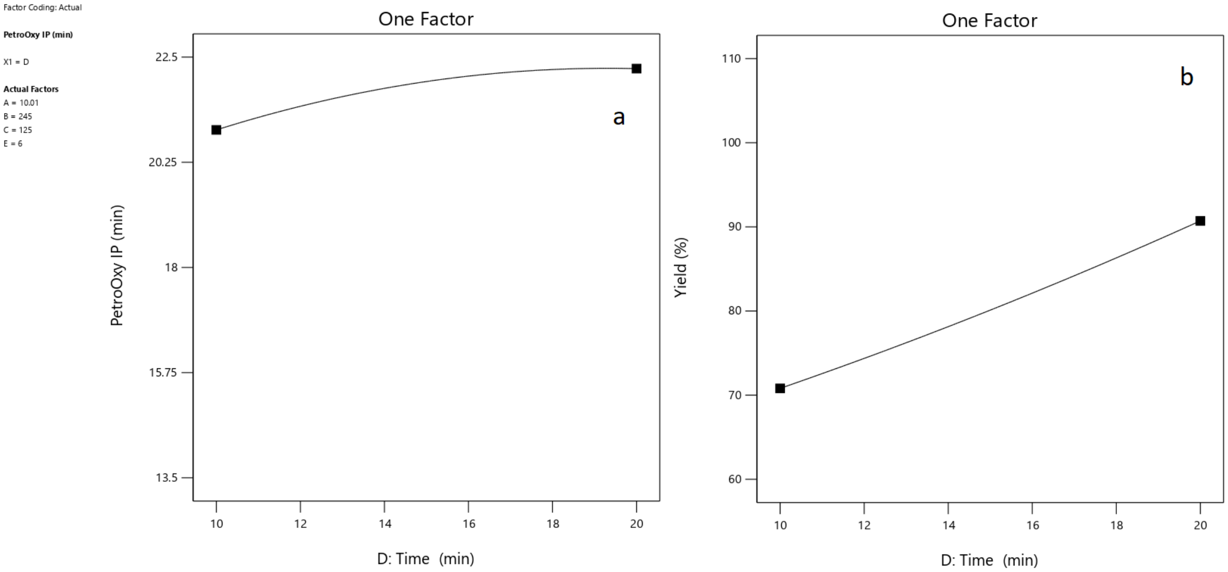

FIGURE 8 The individual effect of reaction time on (a) oxidation stability and (b) biodiesel yield

3.3.4. Effect of M:O molar ratio

It has been commonly reported that the implementation of supercritical methanolysis requires a huge excess of methanol. The increasing effect of methanol is favourable as it shifts the reaction equilibrium towards the products.[61] However, the effect of methanol excess is not always favourable, especially for feedstock with high FFAs. Aboelazayem, Gadalla and Saha,[48] have reported a negative effect of the M:O molar ratio on biodiesel yield from WCO using supercritical methanolysis. The effect of excess methanol on oxidation stability has not been reported previously in the literature.

In the present study, the increase in the M:O molar ratio has decreased the oxidation stability of and the biodiesel yield, as shown in Figure 9. Hence, the highest oxidation stability has been reported at an M:O molar ratio of 10:1. This ratio is considered very low regarding the previously reported optimal biodiesel yields [41]. Having low excess of methanol is economically favoured as it minimises the energy required to recycle the unreacted methanol from the product. As far as we are aware, there is no published correlation between the M:O molar ratio and oxidation stability.

The M:O molar ratio has shown a directly proportional relationship with biodiesel yield. However, in the present study, the relationship is inversely proportional. This might be attributed to the high dilution of water in the presence of high excess of methanol and hence hydrolysis of triglycerides is affected. Accordingly, the overall reaction might require a longer time to achieve the same conversion. Aboelazayem, Gadalla and Saha,[47] reported that a direct relationship with biodiesel yield up until M:O molar ratio value is more than 37:1. Ghoreishi and Moein,[38] 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 conditions compared to the reaction mixture components. Lowering the critical temperature of the product enhances FAME decomposition and hence reduces biodiesel yield.

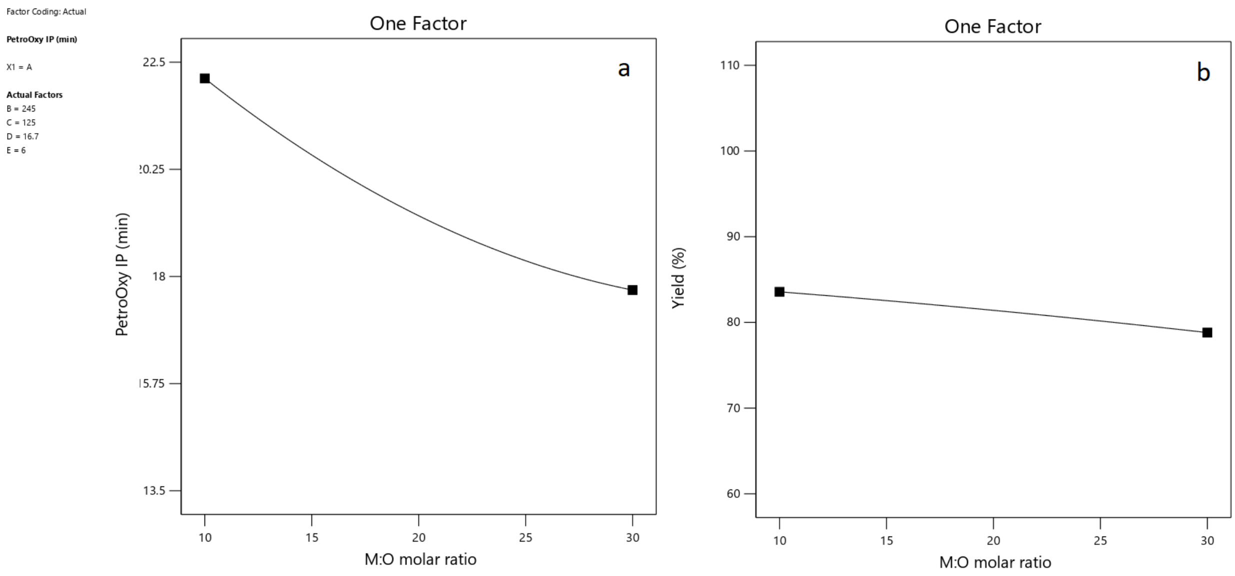

FIGURE 9 The individual effect of the M:O molar ratio on (a) oxidation stability and (b) biodiesel yield

3.3.5. Effect of water content

It is widely accepted that water in biodiesel feedstock is not favourable for the conventional production process using homogenous alkaline catalysts. It increases the rate of hydrolysis of triglycerides into FFAs. Hence, the high content of the FFAs has been considered a disadvantage for catalyzed processes. It has been reported that supercritical methanolysis tends to simultaneously operate *in-situ* transesterification and esterification.[63] Consequently, the high content of FFAs in the feedstock from hydrolysis is not considered an obstacle for supercritical methanolysis but a favoured condition. Kusdiana and Saka,[6] have reported that the existence of water does not have a significant effect on biodiesel yield.

The present study has introduced the effect of water content in supercritical methanolysis on both oxidation stability and biodiesel yield as shown in Figure 10. It has been reported that the increasing effect of the water content has an increasing influence on biodiesel yield which again attributes to the enhanced hydrolysis of triglycerides to FFAs that are easily converted to methyl esters and hence increased yield. On the other hand, the increased water content creates competition with methanol in reaction with triglycerides and it seems that hydrolysis reaction is much faster than direct transesterification of triglycerides. As a result, the presence of water provides a two-steps reactions including hydrolysis of triglycerides into FFAs followed by esterification of FFAs into methyl esters in a one-pot system.

Additionally, it has been observed that the increasing effect of water content in the supercritical methanolysis has a positive effect on the oxidation stability of produced biodiesel, as shown in Figure 10a. The reasons for the increase in oxidation stability have not yet been fully elucidated. However, a possible reason for the increase in oxidation stability is the high solubility of the natural antioxidants in water. The increase in water content prevents the decomposition of tocopherols. Xin, Imahara and Saka,[37] have reported that tocopherols have maintained high stability when exposed to supercritical methanol.

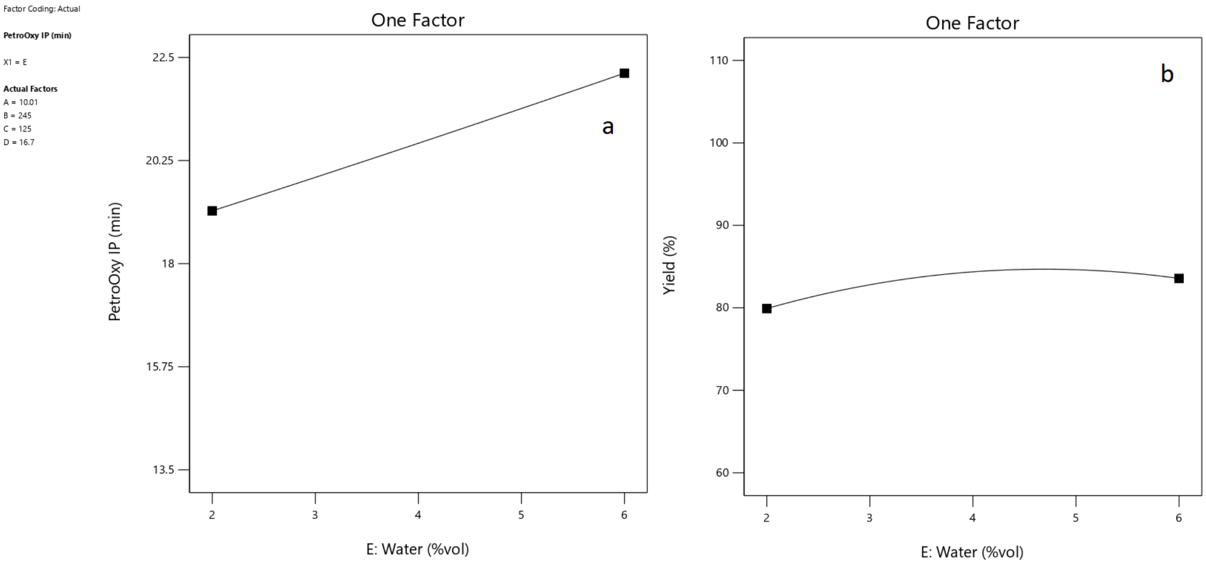

FIGURE 10 The individual effect of water content on oxidation stability

3.3.6. Interactive effects of process variables

The individual effects of variables on biodiesel oxidation stability and yield have been illustrated and discussed in the previous sub-sections. However, these effects have been demonstrated where the other variables have been kept at constant values. Aboelazayem, Gadalla and Saha,[48] have reported highly significant interactive effects between temperature and M:O molar ratio on biodiesel yield from high acid value WCO. However, the same authors, Aboelazayem, Gadalla and Saha,[47] have also reported insignificant interactive effects of temperature and M:O molar ratio on biodiesel yield from low acidity WCO. Hence, it is essential to study and analyze the interactive effects of variables as each variable might have different effects on the response at different levels of other variables.

In the present study, the interactive effect of M:O molar ratio and reaction temperature has shown a highly significant effect, as illustrated in Table 4. It is demonstrated in Figure 11 that the increasing effect of reaction temperature significantly decreases the PetroOxy IP at a low M:O molar ratio (10:1). However, at higher M:O molar ratio levels, the increasing effect of reaction temperature has a slightly decreasing effect on PetroOxy IP. The different trends of the effect of reaction temperature on the PetroOxy IP illustrate excess M:O molar ratio. The huge excess of methanol attributes to decreasing the supercritical conditions of the solution and hence increases the decomposition rate of the tocopherols at the studied temperature range. However, at a lower level of M:O molar ratio, the tocopherols showed stability at lower levels of reaction temperature. The same trend has been reported for the increasing effect of the M:O molar ratio on oxidation stability at different levels of the M:O molar ratio.

The interactive effect between reaction temperature and pressure has reported a significant value on PetroOxy IP, as shown in Table 4. It is illustrated in Figure 12 that the increasing effect of pressure is highly dependent on the value of temperature. For instance, at a low reaction temperature of (245°C), the increasing pressure rate has a positive effect on the produced biodiesel PetroOxy IP. However, at the higher reaction temperature, the pressure has a negligible effect on the PetroOxy IP. On the other hand, a significant interactive effect on reaction temperature and pressure has been demonstrated in Figure 13.

Similarly, the ANOVA results have reported a high interactive effect of reaction time and water content, as shown in Table 4. Figure 14 illustrates the interactive effect between reaction time and water content. The effect of water content on PetroOxy IP has a positive effect at all reaction times levels. This confirms the observation in section 3.3.5 for the effect of water content on PetroOxy

IP. On the other hand, water content has significantly interacted with reaction time on biodiesel yield. It has been observed in Figure 15 that at rapid reaction time (5 min), the increasing effect of the water content has a decreasing effect on biodiesel yield. However, at longer reactions, the yield of biodiesel has improved by increasing water content. This explained the advantage of the presence of water content in the feedstock in supercritical methanolysis. Triglyceride conversion to FFAs has been enhanced through hydrolysis by increasing water content to FAMEs *via* esterification with methanol.

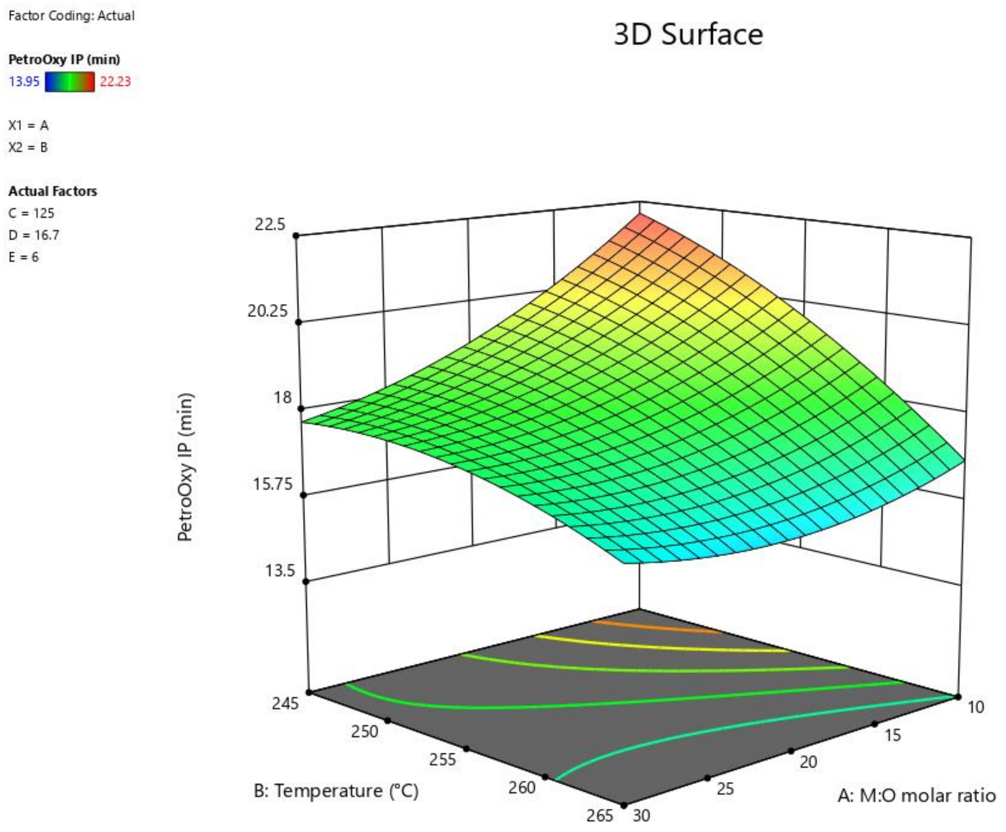

FIGURE 11 Response surface plot for reaction temperature and M:O molar ratio *versus* PetroOxy IP

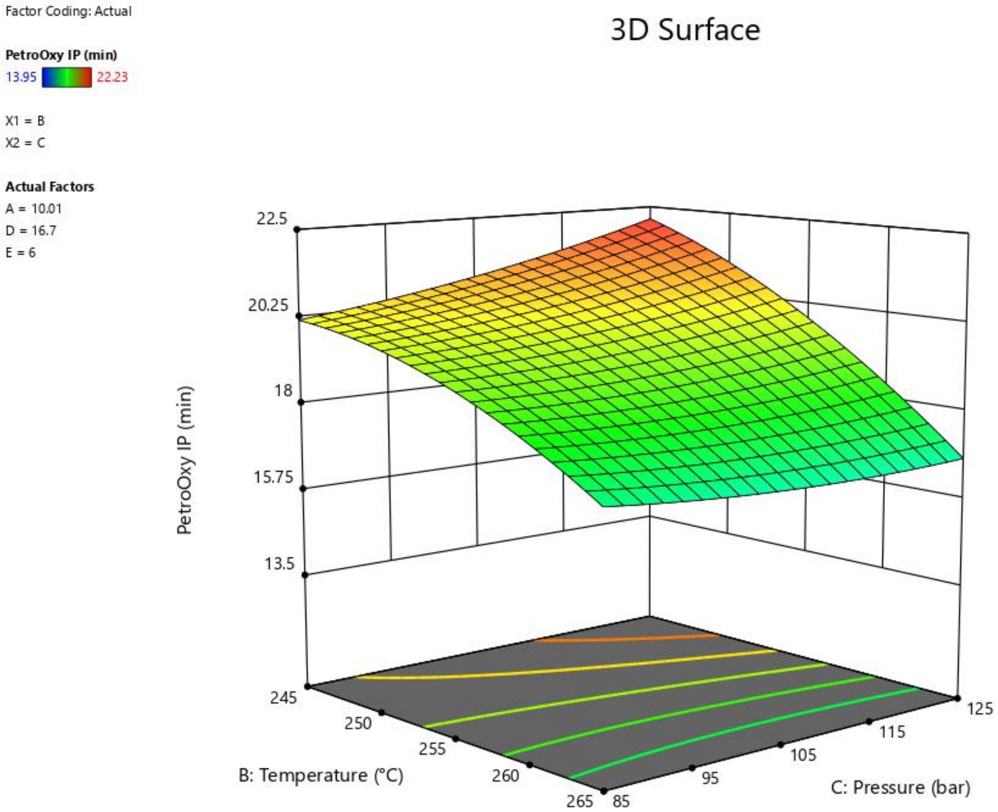

FIGURE 12 Response surface plot for reaction temperature and pressure *versus* PetroOxy IP

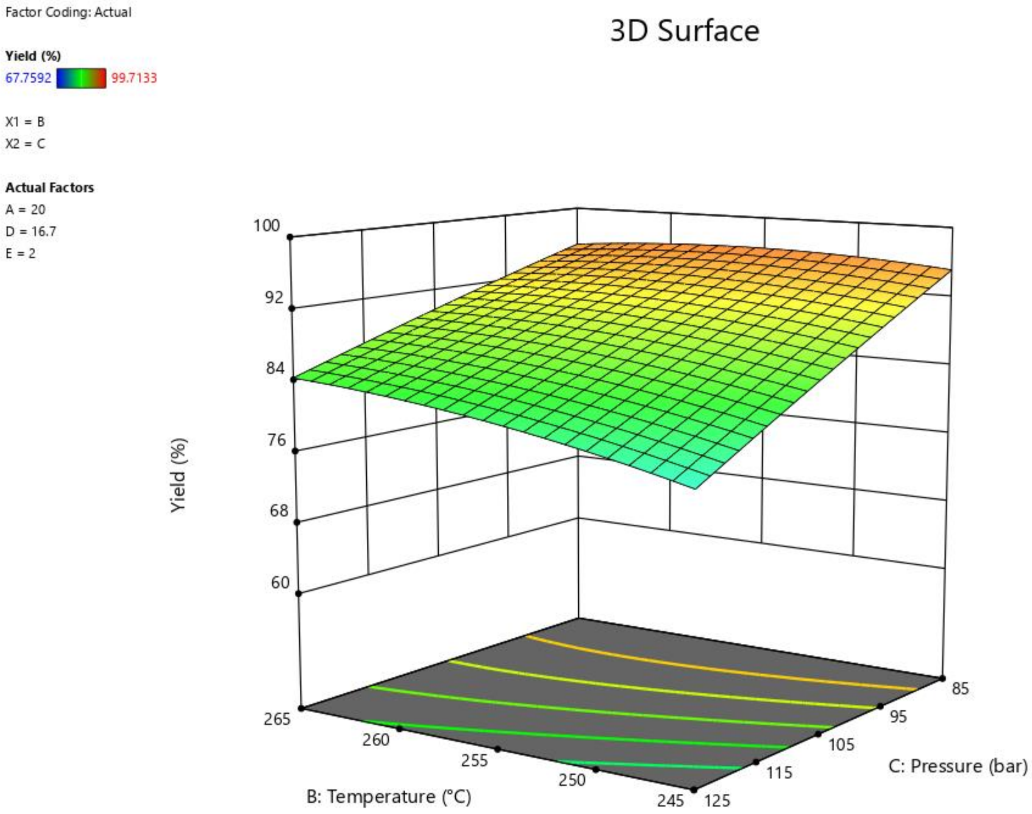

FIGURE 13 Response surface plot for reaction temperature and pressure *versus* biodiesel yield

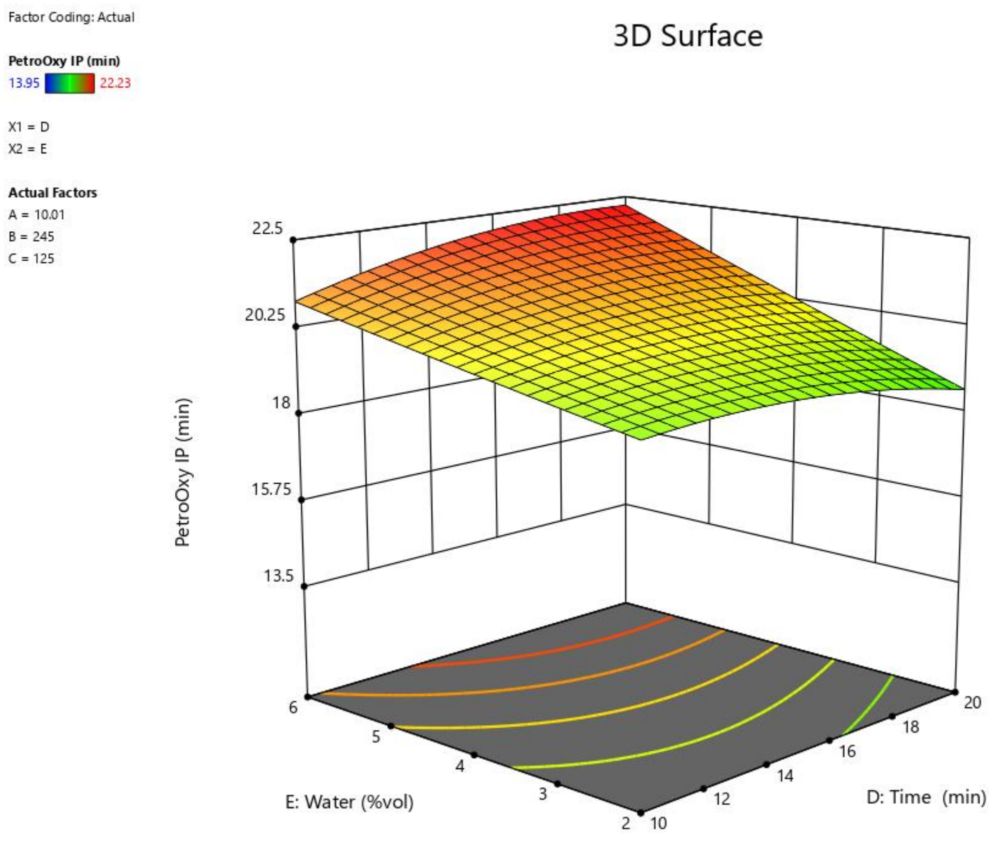

FIGURE 14 Response surface plot for reaction time and water content *versus* PetroOxy IP

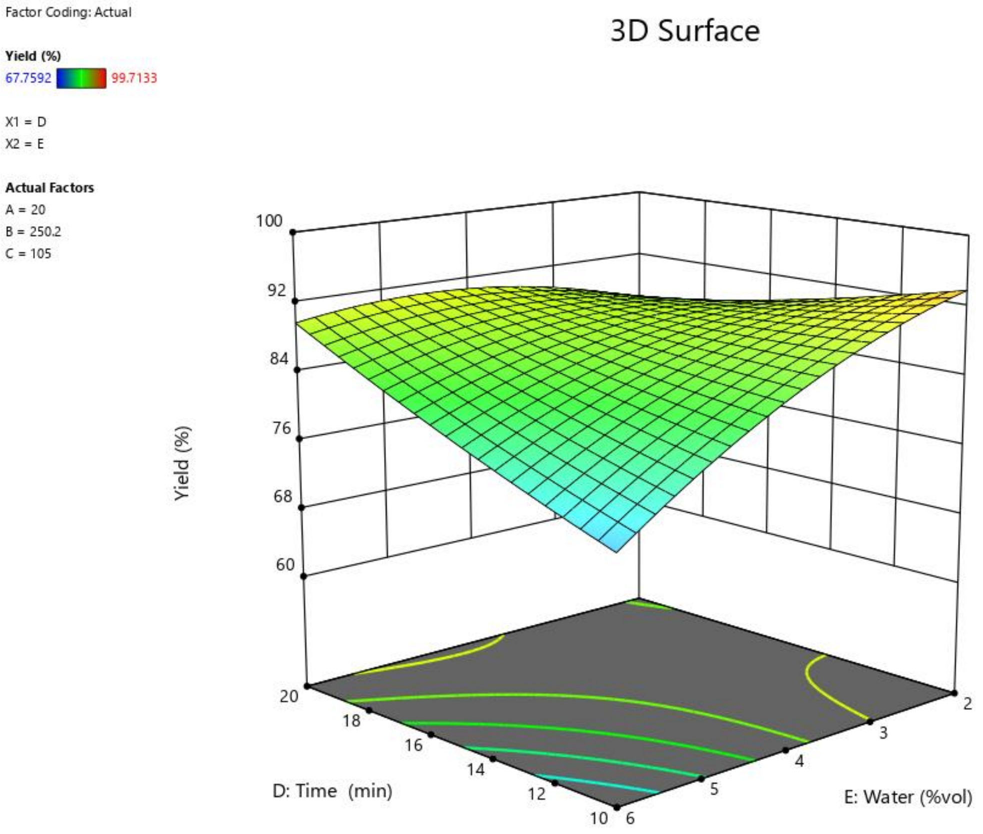

FIGURE 15 Response surface plot for reaction time and water content *versus* biodiesel yield

3.4. Process optimization

The application of RSM in experimental design has several advantages, including implementing the developed regression model to predict the optimal conditions as per the desired targets. The optimization target has been set to maximize the process responses, i.e., PetroOxy IP and biodiesel yield. However, the process variables have been set to reduce the huge consumption of energy that is not economically favourable. The software has used RSM to integrate the process variables *via* the developed models to achieve the optimization targets. A summary of the optimization targets for independent variables and responses is given in Table 5.

Table 5 Optimization constraints used to predict optimum conditions

Factor	Code	Goal	Importance	Limits	
			Scale 1-5	Lower	Upper
M:O (molar ratio)	A	Minimize	2	10	30
Temperature (^{o}C)	B	Minimize	4	245	265
Pressure (bar)	C	Minimize	2	125	185
Time (min)	D	Minimize	2	10	20
Water content (%vol)	E	In range	-	2	6
PetroOxy IP (min)	Y_1	Maximize	5	21	26
Biodiesel yield (%)	Y_2	Maximize	5	66.7	100

The numerical optimization feature in Design Expert software has generated 69 solutions for the desired targets. The solution with the highest desirability has been chosen as the process optimal condition. The developed optimal condition has reported a yield of 99.8% and 22.6 min of PetroOxy IP (higher than all the experimental results) at 10:1 M:O molar ratio, 245°C, 125 bar, 6 vol% within 16.7 min reaction time as shown in Figure 16. In addition, graphical optimization 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 the desirability, as shown in Figure 17.

The predicted optimal conditions have been performed experimentally with a relative error of 0.8-0.9% for both responses. The experimental results of PetroOxy IP at the predicted optimal conditions have reported a similar trend to the predicted results (high oxidation stability). Additionally, the experimental results at the predicted optimal conditions have reported PetroOxy IP of 26.2 min, which is considered higher than all of the previous experimental runs. Finally, the PetroOxy IP result obtained experimentally has been correlated to the Rancimat method using two correlations, including a suggested correlation recommended by the instrument manufacturer and an empirical correlation reported by LucÃ-a Botella et al., [64], as shown in Table 6. The correlated results Rancimat have resulted in 8.6 and 10.35 h, which compiles within the EN14214 specifications. Hence, a process for enhancing the oxidation stability of produced biodiesel *via* supercritical methanolysis might be considered.

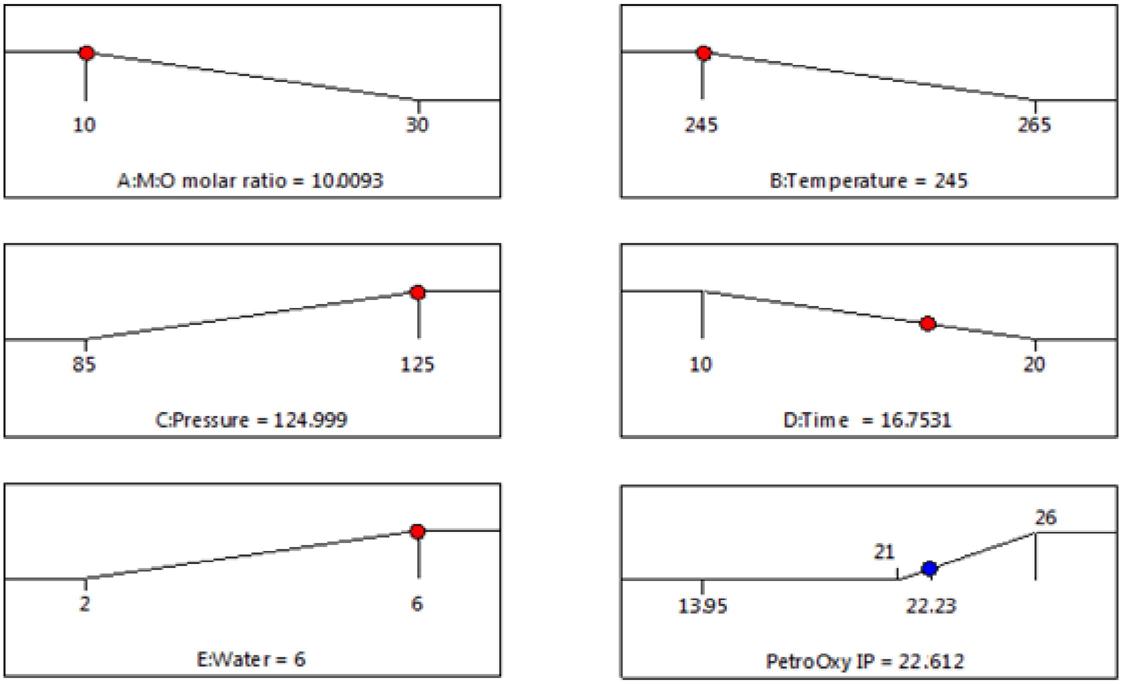

FIGURE 16 Optimization ramps

Table 6 Oxidation stability of biodiesel produced at the optimal conditions

M:O	**Temperature (°C)**	**Pressure (bar)**	**Time (min)**	**Water content (vol%)**	**PetroOxy (min)**	**Biodiesel Yield (%)**	**R_1 (h)**	**R_2 (h)**
10	245	125	16.7	6	26.21	99.8	8.6	10.35

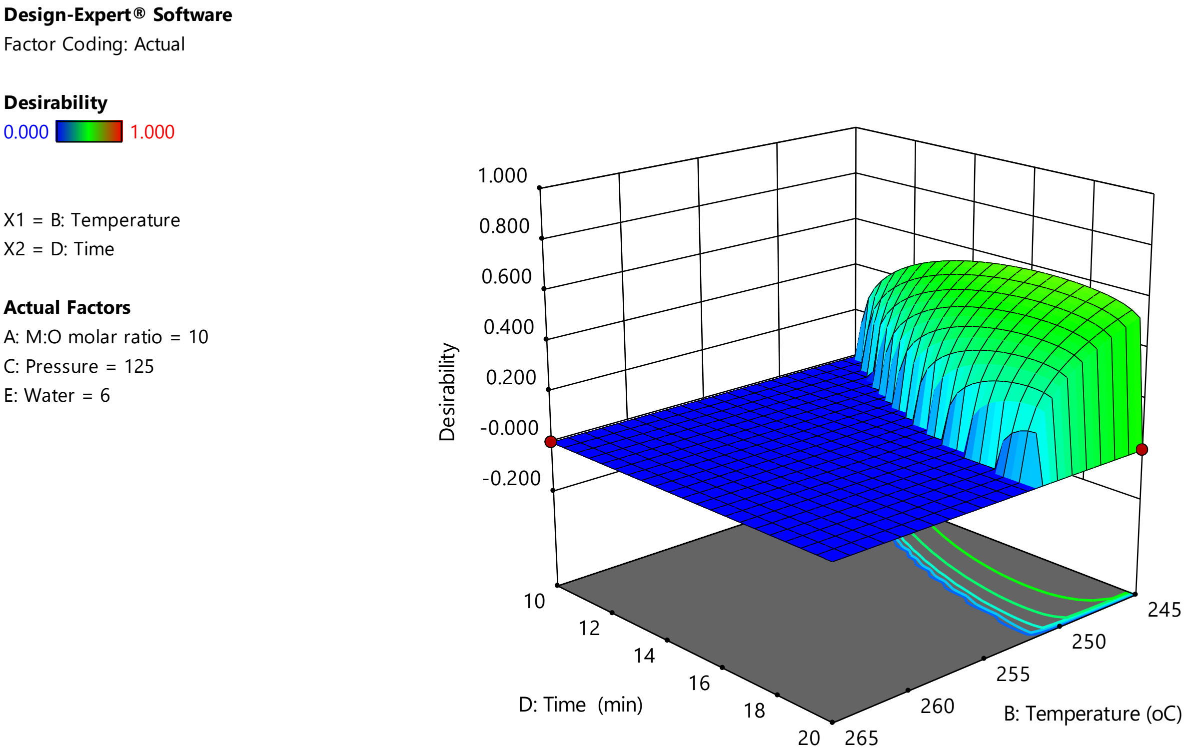

FIGURE 17 Surface plot showing the interactive effect of reaction temperature and time on optimization desirability

4. CONCLUSIONS

The influences of supercritical methanolysis process variables on biodiesel's oxidation stability and yield have been investigated in this study. Five independent variables have been studied, including M:O molar ratio, temperature, pressure, time, and water content. The analysis of oxidation stability has been conducted using PetroOxy, and the optimum results have been correlated to the Rancimat method. It has been observed that increasing water content in the feedstock positively influences both oxidation stability and biodiesel yield. In addition, interactive effects of reaction variables on oxidation stability have been discussed. The study has confirmed that supercritical methanolysis would enhance the oxidation stability of biodiesel. Further, it has reported the favourability of high-water content feedstock for stable biodiesel production. The optimum conditions have been achieved for 26.2 min for PetroOxy IP (oxidation stability) and 99.8% biodiesel yield at 10:1 M:O molar ratio, 245°C, 125 bar, 6 %vol of water content within 16.7 min of reaction time. The optimal conditions reveal a new pathway to minimise the usual huge excess of methanol required for supercritical production of biodiesel at a relatively lower temperature (similar to the critical temperature of methanol) compared to previous studies. These promising results should significantly affect the techno-economic viability of the process as much lower methanol is required to be recycled and the process operated under milder conditions and hence saving energy and operational costs.

Future work should be directed towards studying the detailed kinetics of both esterification/transesterification reactions at the supercritical state of methanol and superheated water. The utilisation of waste energy and side products *via* energy and process integration techniques is a promising pathway to further enhance process profitability. Additionally, the utilisation of waste CO_2 (used as a co-solvent) *via* either carbon capture or valorisation would also enhance the process sustainability and offer a possible negative-carbon process for biodiesel production.

CRediT authorship contribution statement

Yusuf Umar: Investigation, Methodology, Software, Formal analysis, Validation, Data Curation, Writing - original draft, Visualization. **Omar Aboelazayem:** Conceptualization, Methodology, Software, Formal analysis, Writing - review & editing, Project administration. **Mamdouh Gadalla:** Writing - review & editing, Funding acquisition, Project administration. **Basudeb Saha:** Resources, Inputs for improving the quality of the manuscript, Writing - review & editing, Supervision of the PhD student (YU), Funding acquisition, Project administration.

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