# SYSTEMATIC MULTIVARIATE OPTIMIZATION OF BIODIESEL SYNTHESIS FROM HIGH ACID VALUE WASTE COOKING OIL: A RESPONSE SURFACE METHODOLOGY APPROACH

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

*[1] Centre for Energy and Environment Research, School of Engineering, London South Bank University, 103 Borough Road, London, SE1 0AA, UK.*
*[2] Department of Chemical Engineering, The British University in Egypt, Misr-Ismailia Road, El-Shourouk City 11837, Cairo, Egypt.*
*[3] Department of Chemical Engineering, Port Said University, 42526, Port Said, Egypt.*

ABSTRACT: Biodiesel has received increasing attention as a green alternative fuel for petroleum diesel. It is synthesized from renewable resources including vegetable oils, animal fats and microalgal cells. Recently, biodiesel production using supercritical technology has been considered as a viable production technique for different feedstocks with potential industrial application. Supercritical production of biodiesel has many advantages over conventional catalyzed methods e.g. it neither requires catalyst nor washing water, requires shorter time, provides higher biodiesel yield and produces purer glycerol and purer methanol without dehydration process. However, the high process energy consumption due to harsh operating conditions is the main obstacle for industrial scale-up of the process. In the present study, a multivariate optimization technique has been employed for minimizing the operational conditions of supercritical production of biodiesel from high acid value waste cooking oil (WCO). The feedstock has been selected based on its wide availability from various food industries. The following process variables have been analyzed for optimization e.g. methanol to oil (M:O) molar ratio, temperature, pressure and reaction time. Response surface methodology (RSM) using central composite design (CCD) has been employed to design the experiment and to optimize the process. A quadratic mathematical regression model has been developed for each response function in the reaction variables. The influence of the reaction variables and their interactions on the reaction responses have been extensively investigated. The significant process variables have been identified using analysis of variance (ANOVA). Highly significant influences of reaction temperature, pressure and time have been observed. In addition, the interactions between different reaction variables have shown significant effect on reaction responses. The optimum conditions have been identified at M:O molar ratio of 25:1, 536 K reaction temperature and 110 bar pressure within 16.7 min of reaction time.

*Keywords: Biodiesel, waste cooking oil, supercritical technology, optimization, response surface methodology.*

## 1. INTRODUCTION

It is widely accepted that the reserves of crude oil, natural gas and coal are running out. In addition, the concerns of over-exploitation and environmental degradation of natural resources have boosted the search for alternative renewable energy resource. Further, environmental concerns for the increasingly anthropogenic effect on climate changes due to the emission the greenhouse gases, require essential reduction of fossil fuels consumption. In this regard, biodiesel is considered as one of the renewable and sustainable fuels that could effectively replace petroleum diesel fuel. Biodiesel combustion emission has reported a significant carbon dioxide ($CO_2$) reduction between 50% and 80% in comparison to petroleum diesel fuel (Suresh et al., 2018).

Biodiesel is defined as mono alkyl esters of long chain fatty acids derived from lipids feedstock including vegetable oils, animal fats and microalgal cells. Similar to diesel fuel, biodiesel is composed of long chain fatty acids between C14:0 and C24:3. Accordingly, biodiesel has been used to fuel compression ignition engines. Additionally, biodiesel is superior to petroleum diesel as it biodegradable, non-toxic, sulphur free and produce less smoke (Aboelazayem et al., 2018).

Biodiesel production has been established using different techniques, however transesterification reaction considers the most commonly employed technique. Several processes of transesterification have been reported for biodiesel production including homogenous catalyzed, heterogenous catalyzed, enzymatic and non-catalytic processes. Recently, some other processes have been reported for biodiesel production i.e. microwave-assisted, ultrasonic-assisted, high-shear mixing and micro-reactors. Among all the aforementioned processes the non-catalytic supercritical process has reported robust developments. Supercritical technology provides numerous advantages over the catalytic methods where it is a catalyst free process, produce biodiesel with higher yield, can be applied on a variety of feedstocks with less restrictions and it requires no pretreatment steps. Additionally, as the process is catalyst free, the product separation is much easier than the catalytic processes and is more environmentally benign by eliminating the usage of water for washing and hence, reduce the wastewater volume. However, the harsh reaction conditions are the main disadvantage of the supercritical process (Farobie & Matsumura, 2017).

In an attempt to mitigate the main disadvantage of supercritical transesterification, the aim of this paper is to minimize different reaction parameters for biodiesel production i.e. M:O molar ratio, temperature, pressure and reaction time. The percentage yield of different fatty acids i.e. palmitic, oleic ad linoleic acids have been considered as the responses of the process. Process optimization has been proceeded using RSM. Three quadratic models have been developed to represent the response variables function in the reaction parameters. Finally, the predicted optimum conditions have been validated and checked for an adequacy statistically using ANOVA and experimentally.

## 2. MATERIALS AND METHODS

This section describes the materials that was used during the experimental work. The experimental procedures were also clarified. Further, the methodologies used for experimental design, chemical and physical analysis, reaction parameters selection and the levels of each parameters were clearly stated for reproducibility reasons.

### 2.1 Chemicals used

WCO was collected from different local restaurants and food industries in Egypt. Methanol 99% (MeOH) was purchased from Fisher Scientific UK Ltd. Toluene 99.8%, 2-propanol 99.7%, 0.1 M volumetric standard hydrochloric acid, 0.1 M standardized solution of potassium hydroxide in 2-propanol, *p*-naphtholbenzein and methyl orange were purchased from Merck, UK. The standard methyl esters used for preparing calibration curves and heptadecanoic acid methyl ester used as an internal standard were

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

### 2.2 WCO characterization

Physicochemical properties were analyzed for WCO i.e. kinematic viscosity, density and TAN (total acid number) based on the standard testing procedures by ASTM D-445, ASTM D-4052 and ASTM D-974, respectively. The composition of the fatty acids of the oil was analyzed using the derivatization of triglycerides to fatty acids methyl esters (FAME). The standard methylation method (BS-EN-ISO-12966-2:2011) was employed for the conversion. The composition of the esters was determined using gas chromatograph (GC) equipped with a capillary column (TR-BD 30 m × 0.25 mm × 0.25 µm) and flame ionization detector (FID). Both injector and detector temperatures were adjusted at 250$^{o}$C. Helium was used as the carrier gas. The temperature program was started from 60°C and held for 2 min. Then it ramped with 10°C/min to 200°C and directly ramped with 1°C/min to 210°C. Finally, the temperature was increased to 240°C with a ramp rate of 20°C/min and remained for 7 minutes. Tables 1 illustrates the composition of WCO.

Table 1. Fatty acids composition of the waste cooking oil

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

### 2.3 Experimental setup

WCO was filtered using a conventional kitchen mesh strainer to remove the cooking residuals. The oil was heated to 30$^{o}$C for liquefaction. A 100 mL stainless steel high pressure reactor (model 4590, Parr Instrument Company, Moline, IL, USA) which was fitted with a thermocouple (type J), heating mantle, controller (model 4848) and a mechanical stirrer was used to perform the experiments. Oil and methanol were added to the reactor at a specific molar ratio and heated to the target temperature with constant stirring rate of 300 rpm using a mechanical stirrer. The reaction pressure was then controlled using a supercritical fluid pump (model SFT-10, Analytix Ltd., UK), which compress $CO_2$ to the reactor up to the targeted pressure. Once the reaction reaches the required temperature and pressure, the reaction time starts counting. An ice bath was used to quench the reactor in order to stop the reaction after finishing the reaction time. The reactor was then depressurized to remove $CO_2$ and the product was separated using a centrifuge (1500 rpm, 3 min per cycle), which formed two separate layers. The upper layer which represent the biodiesel was then separated and heated to 80 °C for 30 min to recover the unreacted methanol. The physicochemical properties of the produced biodiesel were then analyzed and compared to the European biodiesel standard (EN14214).

The main response of this experiments is the percentage yield which represent a ratio between the amount of produced methyl esters of each runs to the amount of produced methyl esters using standard

methylation as shown in Equation 1 (Liu et al., 2008). The standard methylation was used as a reference of the total amount of esters that could be produced from a WCO sample. The percentage yield of methyl oleate, palmitate and linoleate have been selected as the responses of the experiments as they represent the majority of fatty acids composition of the WCO.

$$Percentage\ yield = \frac{Actual\ Yield}{Theoritical\ Yield} \times 100\ (\%) \quad (1)$$

## 2.4 Experimental design

The design of the experiments was done using RSM *via* CCD to investigate the effect of specific reaction parameters on the reaction responses. Four independent reaction parameters were varied within the experimental design including M:O molar ratio, temperature, pressure and time, which were labelled as A, B, C, and D, respectively. Three levels were considered for each parameter including the centre point and two maximum and minimum ranges. Table 2 illustrates the reaction parameters and their levels.

Table 2. Actual and coded levels of the reaction parameters

| Fatty acid | Composition (wt%) | Code | Levels | | |
|---|---|---|---|---|---|
| | | | -1 | 0 | +1 |
| M:O molar ratio | 48.2 | A | 20 | 30 | 40 |
| Temperature (K) | 41.6 | B | 523 | 533 | 543 |
| Pressure (bar) | 9.3 | C | 85 | 135 | 185 |
| Time (min) | 0.8 | D | 7 | 22 | 27 |

RSM is a multivariate method, which can be used to develop an empirical mathematical model representing the reaction response function in the reaction parameters. The general quadratic equation representing four variables was used to define the model as shown in Equation 2.

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

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

ANOVA was used to check the statistical adequacy of the predicted model using *p*-value and *F*-test at 95% confidence level. Design Expert 10 software (Stat-Ease Inc., Minneapolis, MN, USA) was used for experimental design and statistical analysis.

## 3. RESULTS AND DISCUSSION

This section represents the results that have been obtained from this experimental work. The results could be summarized in three sections i.e. development and validation of statistical model, studying the effect of reaction parameters and numerical process optimization.

### 3.1 Model development

The experimental design performed using CCD has been used to design thirty experiments in a randomized order to avoid any unexplained inconsistency. The experiments have been performed where the responses have been reported for each run. A regression model has been developed for each response function in the reaction parameters as shown in Equations 3-5.

$$Y_1 = 99.37 - 0.032\,A + 0.089\,B - 0.0084\,C + 0.036\,D + 0.061\,AB + 0.024\,AC - 0.05\,AD + 0.052\,BC - 0.066\,BD + 0.077\,CD - 0.069\,A^2 - 0.12\,B^2 - 0.056\,C^2 - 0.16\,D^2 \quad (3)$$

$$Y_2 = 99.19 - 0.022\,A + 0.023\,B - 0.0045\,C + 0.01\,D + 0.044\,AB + 0.017\,AC - 0.029\,AD + 0.061\,BC - 0.047\,BD + 0.065\,CD - 0.053\,A^2 - 0.086\,B^2 - 0.026\,C^2 - 0.092\,D^2 \quad (4)$$

$$Y_3 = 99.10 - 0.038\,A + 0.038\,B - 0.010\,C + 0.042\,D + 0.054\,AB + 0.027\,AC - 0.031\,AD + 0.036\,BC - 0.049\,BD + 0.036\,CD - 0.016\,A^2 - 0.045\,B^2 - 0.019\,C^2 - 0.099\,D^2 \quad (5)$$

where $Y_1$, $Y_2$ and $Y_3$ represent percentage yield of methyl oleate, methyl palmitate and methyl linoleate, respectively. While, A, B, C and D represent the process variables including M:O molar ratio, temperature, pressure and time, respectively.

### 3.1 Model validation and adequacy checking

The predicted models' adequacies have been checked using different techniques including ANOVA, plots of actual *versus* predicted values for each response and the lack of fit analysis. For simplicity, the adequacy checking of only one response (methyl oleate) has been reported in this paper.

The ANOVA results for the methyl oleate predicted model (Equation 3) has been illustrated in Table 3. The ANOVA results showed that the model is highly statistically significant with *p*-value less than 0.0001. In addition, it has been observed that M:O molar ratio, temperature and reaction pressure are significant parameters affecting the percentage yield of methyl oleate. Among all parameters, reaction temperature has shown the most significant variable affecting the yield with *F*-value of 41.68. In addition, reaction pressure has been observed as a non-significant variable in the reaction with *p*- value of 0.54 (higher than 0.05). Further, the interaction effect of all the variables have shown a significant effect on reaction response except the interaction between M:O molar ratio and pressure. On the other hand, lack of fit analysis, which measures the accuracy of the model in predicting the experimental results, has been reported as non-significance. This result illustrates the high accuracy and precision of the predicted model. Finally, a plot of actual *versus* predicted values have shown high similarity between both experimental results and predicted results by the model as shown in Figure 1.

Table 3. ANOVA results of the predicted model

| Source | Sum of Squares | df | Mean Square | F- Value | p-value |
|---|---|---|---|---|---|
| Model | 0.649 | 14 | 0.046357 | 36.39757 | $5.18*10^{-09}$ |
| A-M:O molar ratio | 0.011154 | 1 | 0.011154 | 8.757851 | 0.009746 |
| B-Temperature | 0.013216 | 1 | 0.013216 | 10.37696 | 0.005709 |
| C-Pressure | 0.000506 | 1 | 0.000506 | 0.39729 | 0.537977 |
| D-Time | 0.002554 | 1 | 0.002554 | 2.005608 | 0.177149 |
| AB | 0.03066 | 1 | 0.03066 | 24.07289 | 0.00019 |
| AC | 0.004651 | 1 | 0.004651 | 3.651949 | 0.075306 |
| AD | 0.013748 | 1 | 0.013748 | 10.79398 | 0.005006 |
| BC | 0.058709 | 1 | 0.058709 | 46.09595 | $6.1*10^{-06}$ |
| BD | 0.0351 | 1 | 0.0351 | 27.55899 | $9.8*10^{-05}$ |
| CD | 0.067522 | 1 | 0.067522 | 53.01532 | $2.69*10^{-06}$ |
| A^2 | 0.078233 | 1 | 0.078233 | 61.42473 | $1.11*10^{-06}$ |
| B^2 | 0.20354 | 1 | 0.20354 | 159.811 | $2.11*10^{-09}$ |
| C^2 | 0.014867 | 1 | 0.014867 | 11.67271 | 0.003826 |
| D^2 | 0.234591 | 1 | 0.234591 | 184.1902 | $7.9*10^{-10}$ |
| Residual | 0.019104 | 15 | 0.001274 | | |
| Lack of Fit | 0.01459 | 10 | 0.001459 | 1.616075 | 0.310851 |
| Pure Error | 0.004514 | 5 | 0.000903 | | |
| Cor Total | 0.668104 | 29 | | | |

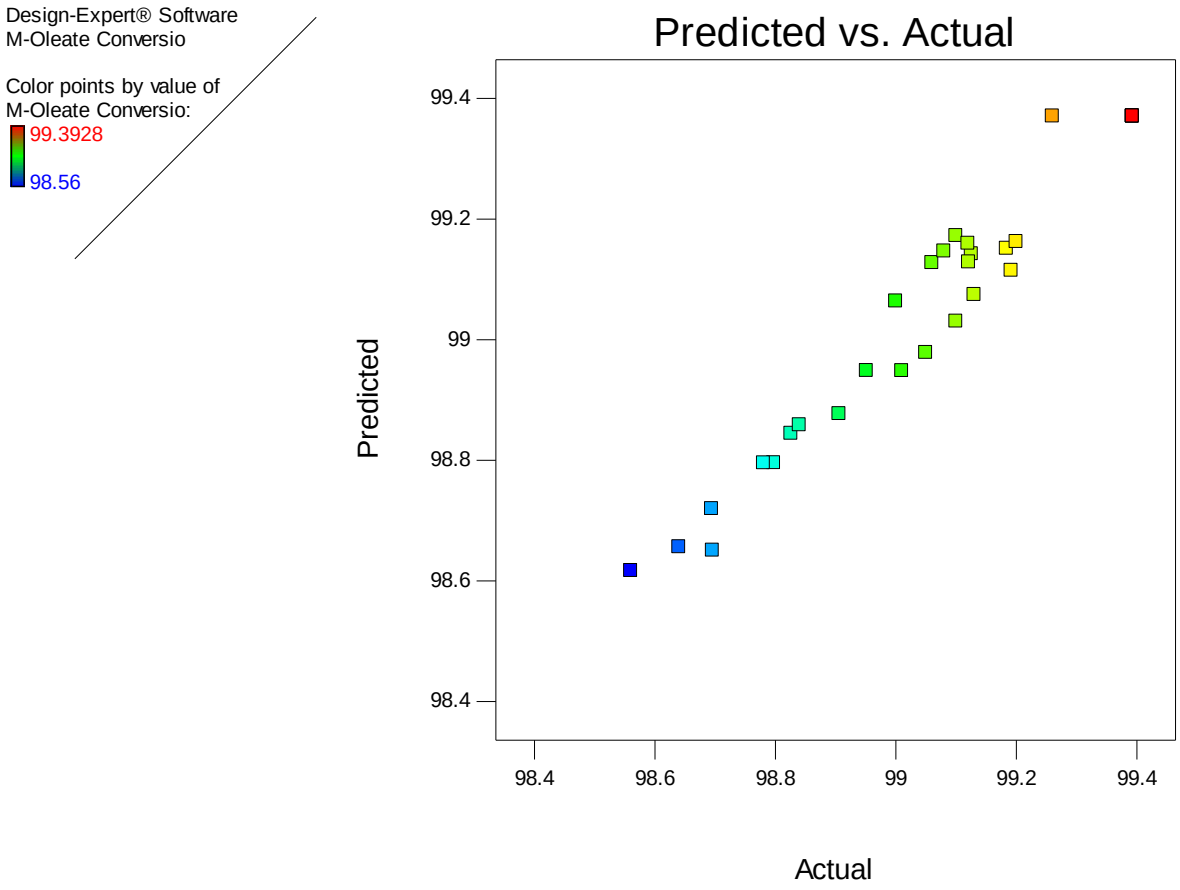


Figure 1. Predicted *versus* actual values for methyl oleate model

### 3.2 Effect of reaction variables

The effect of each reaction variable and their interactions have been illustrated using 3D surface plots as shown in Figures 2 and 3. The effect of reaction variables on the percentage yield of methyl palmitate has been discussed.

Supercritical methanolysis requires large excess of methanol in order to decrease the oil and methanol mixture critical point. Hence, it is important to study the effect of M:O molar ratio on the reaction in order to be able to optimize the excess of methanol used in the reaction. In this study, the effect of M:O molar ratio has shown a significant effect on the methyl oleate yield as illustrated in Table 3. It can be seen in Figure 2 that the increasing effect of M:O molar ratio has negative effect on methyl oleate yield at lower temperature (523 K). However, the same increasing effect of M:O molar ratio has increasingly affected methyl oleate yield at higher temperature (543 K). This illustrates highly significant interaction between M:O molar ratio and temperature on the reaction response, where the effect of M:O molar ratio is dependent on reaction temperature. Previous reports have conveyed similar results for the effect of M:O molar ratio on the overall biodiesel yield (Aboelazayem et al., 2018b). Additionally, Ghoreishi and Moien have reported highly significant effect of M:O molar ratio on biodiesel yield (Ghoreishi & Moein, 2013).

Reaction temperature is an important parameter that affects the biodiesel production using supercritical methanolysis. The minimum temperature for such technique should exceed the critical point of methanol (513 K). Due to the high energy consumption of such harsh reaction conditions, it is essential to minimize the reaction temperature as much as possible, while maintaining the high yield of biodiesel production. In this study, the range of temperature applied for the reactions did not exceed 543 K to avoid any thermal degradation of the methyl esters. It has been observed that the increasing effect of

temperature has positive influence for the methyl oleate yield. However, the increasing rate of the response by increasing the reaction temperature depends on the selected M:O molar ratio of the reaction. At higher M:O molar ratio, the increasing effect of temperature has highly significant effect on reaction response. Similar results have been reported previously for the effect of reaction temperature on biodiesel yield (Aboelazayem et al., 2018).

One of the most significant advantages of supercritical methanolysis is the short reaction time in comparison with the conventional catalyzed processes. In this paper, reaction time has been reported as a significant variable affecting the yield of methyl oleate as shown in Table 3. The effect of reaction time is illustrated in Figure 3, where the yield increases by increasing the reaction time up to 19 min. However, at longer duration of reaction, the yield decreases. This attributes to the possibilities of thermal degradation of methyl esters within longer reaction at such harsh conditions (Saluja et al., 2016).

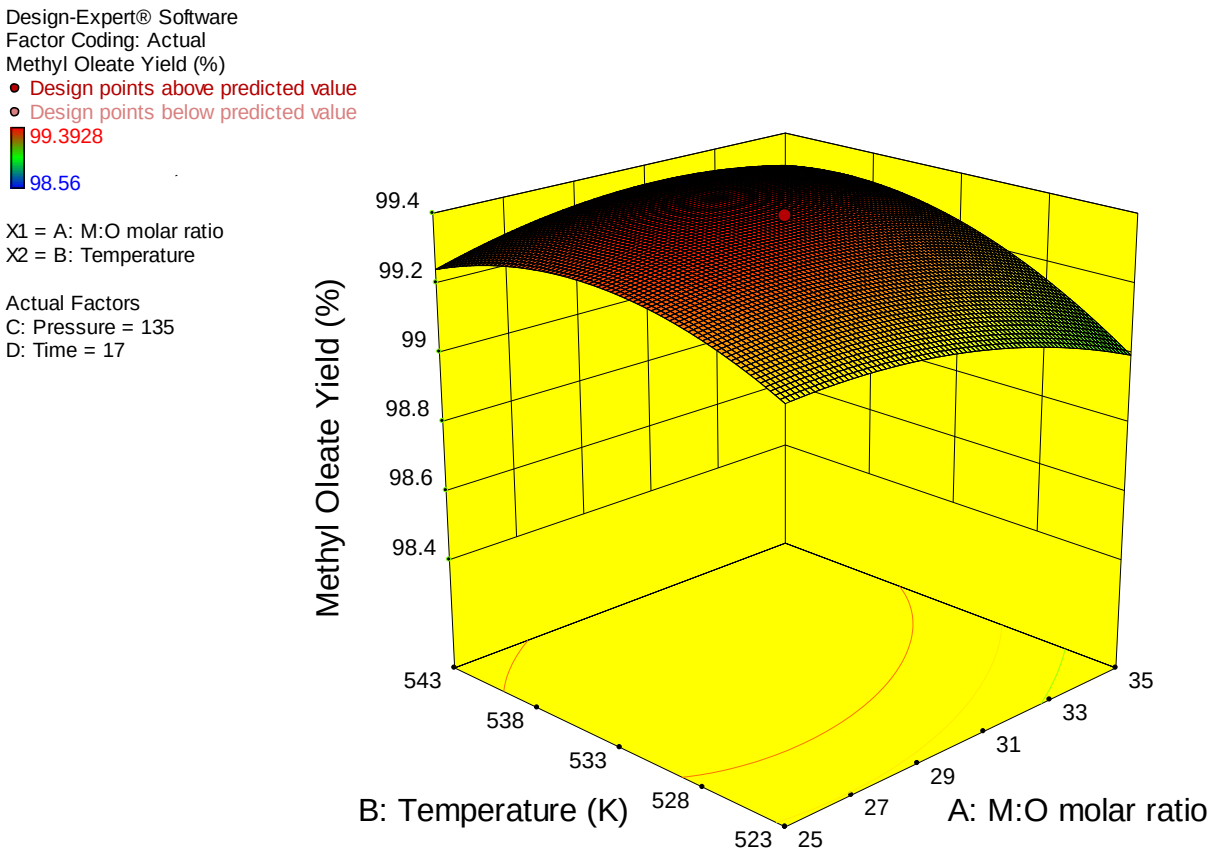


Figure 2. 3D Surface plot of M:O molar ratio and reaction temperature *versus* methyl oleate yield

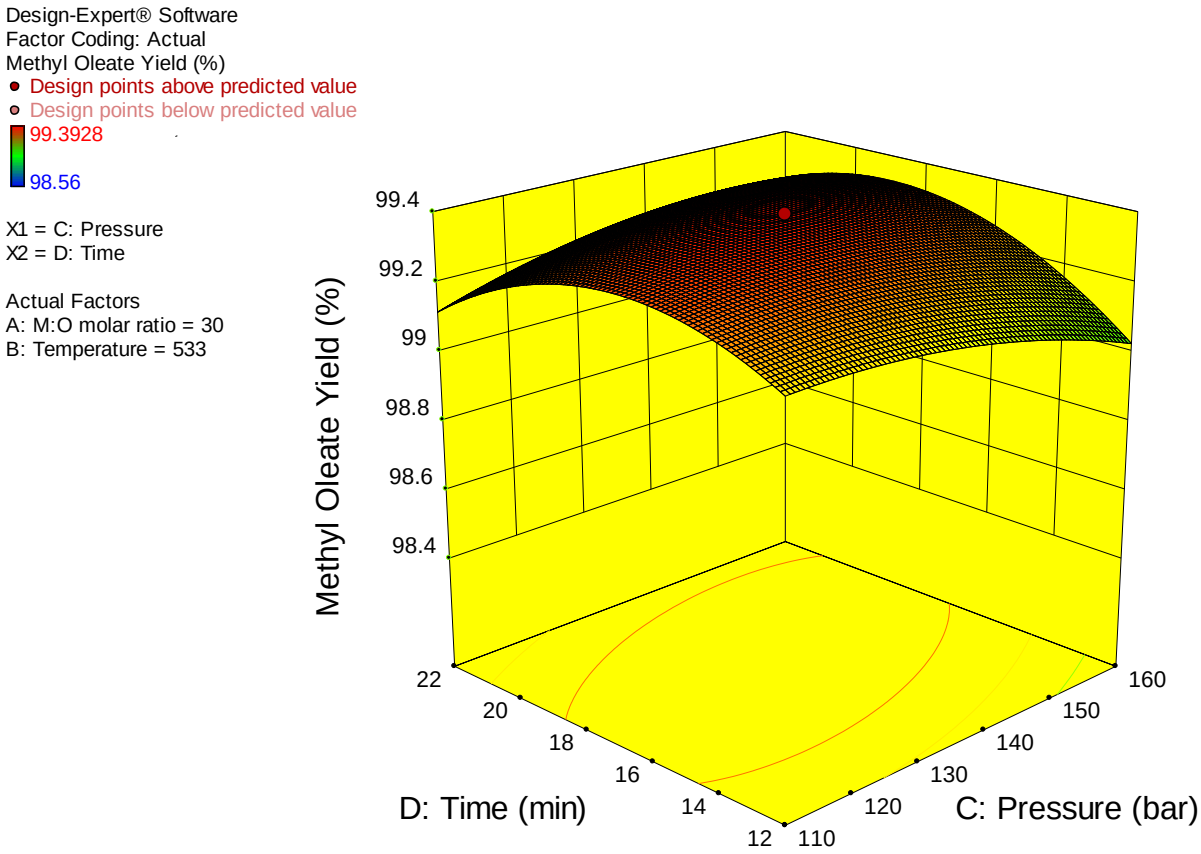


Figure 3. 3D Surface plot of reaction pressure and time *versus* methyl oleate yield

### 3.3 Process optimization

In an attempt to minimize the process energy consumption, numerical optimization for the reaction has been applied to minimize the reaction variables. The reaction variables including M:O molar ratio, temperature, pressure and time have targeted to be minimized while maximizing the yields of methyl oleate, palmitate and linoleate. Design Expert software using RSM has been used to search for the optimum combination of reaction variables that could achieve the required optimization goals. Accordingly, fifty-three solutions have been developed using the software, where the solution with the highest desirability has been chosen. The optimum conditions for 99.2%, 99.3% and 99.13% of methyl oleate, methyl palmitate and methyl linoleate yields, respectively, have been identified at M:O molar ratio of 25:1, 536 K reaction temperature and 110 bar pressure within 16.7 min of reaction time. The predicted optimum conditions have been validated experimentally, where the relative errors between the experimental and the predicted values were between 0.5 and 0.85%.

## 4. CONCLUSIONS

Non-catalytic production of biodiesel using supercritical methanol has proved to be an efficient biodiesel production method from high acid value WCO. The percentage yields of the main WCO fatty acids have been investigated under different reaction conditions. Three mathematical regression models have been developed to represent the reaction responses function in the reaction variables. The influence of four reaction variables have been analyzed including M:O molar ratio, reaction temperature, pressure and time. In addition, the interaction effects between the reaction variables have been discussed. The optimum conditions for maximum methyl esters yields have been developed at molar ratio of 25:1, 536 K

reaction temperature and 110 bar pressure within 16.7 min of reaction time. At the developed reaction conditions, the esters yields have reported 99.2%, 99.3% and 99.13% of methyl oleate, methyl palmitate and methyl linoleate yields, respectively. The predicted optimum conditions have been validated experimentally with very low relative error between experimental and predicted results.

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