

# Supercritical methanolysis of waste cooking oil for biodiesel synthesis: Experimental and simulation assessments

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## **Abstract:**

Two-step esterification/transesterification process is considered as the most widely used technology for biodiesel synthesis from waste cooking oil (WCO). However, this process has currently been explored in a single step using supercritical technology due to its higher biodiesel yield and shorter reaction time. This paper presents experimental and simulation studies on biodiesel production from high acid value WCO using supercritical methanolysis. The effect of four reaction parameters on biodiesel production including methanol to oil (M:O) molar ratio, temperature, pressure and time has been investigated. Response surface methodology (RSM) has been used to develop an empirical regression equation representing reaction variables function in response variable. Analysis of variance (ANOVA) has been used to examine the accuracy of the predicted model. Optimisation of reaction variables has been performed to maximise biodiesel production. The optimal conditions for 99.1% and 97.5% overall conversions of triglycerides and free fatty acids (FFA), respectively have been reported at 25:1 M:O molar ratio, 265 °C temperature, 110 bar pressure and 18.5 min reaction time. A commercial simulation software (Aspen HYSYS) has been used to design and simulate the production process. The reaction has been simulated using the developed kinetic data at optimal conditions. A comparative analysis has been performed for results obtained experimentally, numerically and from simulation.

## **Keywords:**

Biodiesel, Supercritical technology, Process optimisation, Response surface methodology, Process simulation.

## **1. Introduction**

The increasing demand of energy, spurred by the accelerated metropolitan growth and industrialisation, has led to extensive increase in fossil fuels consumption. Fossil fuels' prices fluctuation and instability are resulted from the huge demand and consumption. In addition, the toxic and greenhouse gasses emissions from fossil fuels have significant impacts on air pollution and global warming. These facts have enhanced the research on securing sustainable resources of energy required for transportation and energy generation [1].

Amongst the renewable energies, biofuels including biodiesel and bioethanol have been considered as potential substitute for fossil fuels. Harnessing biofuels for fossil fuels replacement provides an

ideal solution due to their compatibility with the existing engines without the need to perform any engine modifications [2]. Biodiesel is a sustainable, green and renewable fuel that is derived from animal fats, vegetable oils and microalgae. Biodiesel synthesis is very simple in terms of consumables and production time in comparison with bioethanol. Biodiesel production has been readily commercialised from edible oils. However, several obstacles have affected the expansion of biodiesel production from edible oil including the increase of crop prices, increasing the competition with food industry and water shortage. Accordingly, the research has been shifted towards non-edible and waste oils for biodiesel production [3].

WCO is considered as a substantial feedstock for biodiesel production as it significantly decreases the total production cost. On the other hand, valorisation of WCO into biodiesel has numerous advantages including lowering the cost of waste water treatment (as WCO is usually disposed) and contribute to waste utilisation. However, the main obstacles in biodiesel production from WCO is the presence of high FFAs and water content. Accordingly, extensive pre-treatment is required prior to biodiesel production from WCO using the conventional catalysed techniques [4].

Recently, supercritical technology has been implemented in biodiesel production using supercritical methanol. It has been reported that the solubility of methanol in oil is very high at its supercritical state. Hence, no requirement to catalyse the reaction as the methanol is already completely soluble in oil. Saka and Kusdiana [5] have reported the first non-catalytic supercritical production of biodiesel. They have reported that supercritical methanol has the ability to esterify the FFAs into FAMES and transesterify the triglycerides into FAMES simultaneously [6].

In his study, high acid value WCO has been used as a feedstock for biodiesel production using supercritical methanol. The effect of four reaction variables including M:O molar ratio, temperature, pressure and time on biodiesel yield have been examined. RSM using central composite design (CCD) has been employed to optimise reaction conditions. Two quadratic models have been developed representing empirical relationships between reaction variables and response.

## **2. Materials and methods**

In this section, the materials and procedures applied for experimental and simulation work were described.

### **2.1. Materials**

WCO was collected from different restaurants and industries in Egypt and mixed together to form a realistic mixture of waste oil. Methanol 99% (MeOH) was purchased from Fisher Scientific UK Ltd. The liquid CO<sub>2</sub> cylinder (99.9%) equipped with dip tube was purchased from BOC Ltd., UK.

### **2.2. Experimental procedures**

This section presents the procedures of experimental work that was performed. It is divided into four subtitles including supercritical methanolysis, experimental design, statistical analysis and reactor simulation.

#### **2.2.1. Supercritical methanolysis**

The detailed procedures for the biodiesel synthesis using supercritical methanol were reported elsewhere [7]. In summary, WCO was physically filtered using a strainer to remove any residuals resulted from the cooking process. The oil and methanol were weighted and mixed together with a specified molar ratio based on each experimental run. The mixture was then fed to a 100-mL high pressure reactor made of stainless steel (model 4590, Parr Instrument Company, USA). The reactor was fitted with a thermocouple (type J), controller (model 4848), heating mantle and a mechanical stirrer. The mixture was then heated to a targeted temperature and then pressurised CO<sub>2</sub> using a supercritical fluid pump (model SFT-10, Analytix Ltd., U.K) to a targeted pressure. Once the mixture reaches the targeted reaction temperature and pressure, it is considered as the starting time of the reaction (t=0). The reaction mixture was then quenched with an ice bath once completed the targeted

reaction time. The reaction was then depressurised and unreacted methanol was recovered using a rotary evaporator. Finally, the glycerol was separated from biodiesel using a centrifuge (1500 rpm, 3 min/cycle).

### 2.2.2. Experimental design

RSM *via* CCD method was used to design the experimental runs. The experiments were designed to investigate the influence of four independent variables. i.e. M:O molar ratio, temperature, pressure and time, on the conversion of triglycerides and FFAs. Five levels of each variable were examined and coded as -2, -1, 0, 1 and +2, as shown in Table 1. The variables levels were chosen based on our previous study on high acid value WCO [8]. Hence, thirty randomised experiments were generated using CCD.

Table 1. 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

### 2.2.3. Statistical analysis

Model development was performed using the general quadratic model as shown in Equation 1.

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

Where  $Y$  represents the process predictive response,  $b_o$  represents the model coefficient constant,  $b_i$ ,  $b_{ii}$ ,  $b_{ij}$ , represent the coefficients for intercept of linear, quadratic, interactive terms respectively, while  $X_i$ ,  $X_j$  represent independent variables ( $i \neq j$ ). Finally,  $n$  represents number of independent variables and  $\varepsilon$  represents the random error.

ANOVA was used to check the adequacy of the predicted models at 95% confidence levels. Design Expert 11 software (Stat-Ease Inc., Minneapolis, MN, USA) was used to design the experiments, model development and optimisation.

### 2.2.4. Reactor simulation

Aspen HYSYS simulation programme version 8.8 was used to design and simulate the biodiesel process (Aspen Technology Inc., USA). The procedures for process simulation based on HYSYS simulator consist of several steps including selection of chemical components, appropriate thermodynamic models, required process units and operating conditions. Triolein ( $C_{57}H_{104}O_6$ ) and Tripalmitin ( $C_{51}H_{98}O_6$ ) were used to represent the triglycerides exists in the WCO as they were reported as the major compositions (~90%) based on the chromatographic analysis of the feedstock reported elsewhere [8]. Oleic and palmitic acids have been used to represent the FFAs exist in the WCO. Hence, methyl oleate ( $C_{19}H_{36}O_2$ ) and methyl palmitate ( $C_{17}H_{34}O_2$ ) were considered as the desirable product of the reaction. Tripalmitin component was not available in the HYSYS data bank library where it has been introduced as a hypo-component using the hypo-manager tool by identifying its physicochemical properties [9].

Due to the existence of polar components in the esterification and transesterification reactions, i.e. methanol and glycerol, NRTL activity model was selected to represent the thermodynamic model of the simulation background.

### 3. Results and discussion

This section covers the results and findings of the present work. It includes the discussion of the model development and adequacy checking. This has been followed by discussing effect of process variables and their interactions of both triglycerides and FFAs conversions. Then, the optimisation of the process variables has been predicted and validated experimentally. Finally, a kinetic study has been developed and used to simulate a reactor representing the experimental results.

#### 3.1. Regression model development

The experimental results of the 30 experiments developed by Central Composite Design (CCD) have been used to develop two regression models for triglycerides and FFAs conversions, respectively. Each model has represented the reaction response function in the process variables. Different mathematical models have been used to fit the experimental data including linear, two factors interactions (2FI), quadratic and cubic polynomial models. It has been observed that the quadratic polynomial equation has the highest fitting predicted results to the experimental results. Hence, two quadratic models have been developed to represent the experimental results as shown in Equations 2 and 3.

$$Y_1 = 88.68 - 1.54 A - 1.44 B - 0.6 C + 0.037 D - 2.58 AB - 0.2 AC - 1.67 AD - 0.95 BC - 0.33 BD - 0.93 CD - 0.31 A^2 + 1.08 B^2 + 2.04 C^2 + 1.5 D^2 \quad (2)$$

$$Y_2 = 96.36 + 0.28 A + 0.37 B - 0.44 C + 0.47 D + AB - 0.2 AC - 0.17 AD - 0.12 BC + 0.07 BD - 0.06 CD + 0.02 A^2 + 0.08 B^2 + 0.5 C^2 - 0.37 D^2 \quad (3)$$

Where  $Y_1$  and  $Y_2$  represent conversion of triglycerides and FFAs, respectively. While, A, B, C and D represent the process variables including M:O molar ratio, temperature, pressure and time, respectively.

#### 3.2. Adequacy checking

The adequacy checking of the predicted models has been performed using different statistical analyses including ANOVA, coefficient of correlation ( $R^2$ ) and the lack of fit. The ANOVA results have been illustrated in Tables 2 and 3 for triglycerides and FFAs conversions, respectively. It has been reported highly significance of the both models with p-value of <0.0001 and 0.001 for triglycerides and FFAs conversions models, respectively. In addition, the  $R^2$  value has been reported for both models with 0.98 and 0.96 for triglycerides and FFAs conversions models, respectively. Finally, the lack of fit analysis has reported non-significant values for both models which demonstrate the significance of the developed models in representing the experimental data.

Table 2. Analysis of variance of the developed model for triglycerides conversion

Source	Sum of Squares	df	Mean Square	F-value	P-value	Significance
Model	483.74	14	34.55	12.63	< 0.0001	HS
A-MeOH:Oil	57.03	1	57.03	20.85	0.0004	HS
B-Temperature	49.76	1	49.76	18.19	0.0007	HS
C-Pressure	8.67	1	8.67	3.17	0.0953	NS
D-Time	0.0343	1	0.0343	0.0126	0.9123	NS
AB	106.29	1	106.29	38.85	< 0.0001	HS
AC	0.8854	1	0.8854	0.3236	0.5778	NS
AD	44.53	1	44.53	16.28	0.0011	HS
BC	14.46	1	14.46	5.28	0.0363	S
BD	1.78	1	1.78	0.6502	0.4327	NS
CD	14.03	1	14.03	5.13	0.0388	S
A <sup>2</sup>	2.67	1	2.67	0.9752	0.3390	NS
B <sup>2</sup>	32.13	1	32.13	11.74	0.0037	S
C <sup>2</sup>	114.01	1	114.01	41.68	< 0.0001	HS
D <sup>2</sup>	61.81	1	61.81	22.59	0.0003	HS
Residual	41.04	15	2.74			
Lack of Fit	40.49	10	0.654	0.03	0.765	NS
Pure Error	0.5463	5	0.1093			
Cor Total	524.77	29				

Table 3. Analysis of variance of the developed model for free fatty acids conversion

Source	Sum of Squares	df	Mean Square	F-value	P-value	Significance
Model	30.51	14	10.18	20.34	0.0014	HS
A-MeOH:Oil	1.90	1	1.90	3.02	0.1026	NS
B-Temperature	3.44	1	3.44	5.47	0.0335	S
C-Pressure	4.82	1	4.82	7.67	0.0143	S
D-Time	5.44	1	5.44	8.65	0.0101	S
AB	0.8032	1	0.8032	1.28	0.2761	NS
AC	0.6608	1	0.6608	1.05	0.3215	NS
AD	0.4731	1	0.4731	0.7526	0.3993	NS
BC	0.2298	1	0.2298	0.3656	0.5545	NS
BD	0.0977	1	0.0977	0.1555	0.6989	NS
CD	0.0734	1	0.0734	0.1168	0.7373	NS
A <sup>2</sup>	0.0109	1	0.0109	0.0174	0.8968	NS
B <sup>2</sup>	0.1867	1	0.1867	0.2970	0.5938	HS
C <sup>2</sup>	6.84	1	6.84	10.88	0.0049	HS
D <sup>2</sup>	3.88	1	3.88	6.17	0.0253	S
Residual	9.43	15	0.6286			
Lack of Fit	5.68	10	0.5680	0.7576	0.6694	NS
Pure Error	3.75	5	0.7497			
Cor Total	39.94	29				

Where HS, S and NS means highly significant, significant and non- significant, respectively.

### 3.3. Effect of process variables

The present work has investigated the effect of four reaction variables and their interaction on the conversion of triglycerides and FFAs. In addition, the interaction effects between process variables have been discussed.

#### 3.3.1. Effect of methanol to oil molar ratio

It is widely accepted that supercritical methanolysis requires huge excess of methanol during the reaction. The usage of excess of methanol is favourable for several reasons including the decrease of the critical conditions of the reactants mixture, shift the reaction equilibrium towards the product and enhance the solubility of oil and methanol [10]. In the present study, the range of the studied M:O molar was between 20:1 to 40:1 as shown in Table 1. It has been observed from the ANOVA results of the predicted models that M:O molar ratio has highly significant effect on triglycerides conversion as shown in Table 2. However, it has a non-significant effect on FFAs conversion. It is clearly observed from Figure 1 the negative effect of M:O molar ratio on triglycerides conversion where the increasing molar ratio of methanol decrease the conversion of triglycerides. Similar trend has been reported previously for the effect of M:O molar ratio on biodiesel yield on similar feedstock [8].

On the other hand, the increasing effect of M:O molar ratio has positive effect on FFAs as shown in Figure 2. However, the increasing effect is not significant as reported in Table 3. The increasing effect of FFA conversion is about 2% from 25:1 to 35:1 M:O molar ratio. This might attribute to the stoichiometry of the esterification where only one mole of methanol is required to esterify 1 mole of fatty acid. These results are in agreement to previously reported studies [10–12].

#### 3.3.2. Effect of reaction temperature

Supercritical methanolysis requires harsh conditions where the reaction should be operated at temperature higher than the critical temperature of methanol (240 °C). Increasing reaction temperature enhance the reaction rate and increase the productivity. However, high temperatures might cause thermal cracking or degradation of the chemical compounds. For instance, it has been reported that at temperatures higher than 280 °C, thermal degradation has been reported for FAME [2]. Hence, this study has investigated the effect of reaction temperature between 240 °C and 280 °C as shown in Table 1.

It has been observed that the increasing rate of temperature has increasing effect on triglycerides conversion at lower M:O molar ratio. However, negative impact of increasing temperature has been reported at higher M:O molar ratio. These results indicates that at higher M:O molar ratio, thermal degradation could occur at temperature lower than 280 °C as the excess of methanol lower the critical point of the reactants mixture.

#### 3.3.3. Interactive effect of reaction temperature and methanol to oil molar ratio

It has been reported in Table 2, a high significant interactive effect between reaction temperature and M:O molar ratio on triglycerides conversion. This highly significant effect could be demonstrated in Figure 1 where at low reaction temperature (250 °C), the increasing effect of M:O molar ratio slightly increase the conversion of triglycerides. However, at higher temperatures (270 °C), the increasing effect of M:O molar ratio has significant decreasing effect on the conversion of triglycerides.

On the other hand, the interactive effect between reaction temperature and M:O molar ratio on FFAs conversion is not significant as reported in Table 3. It is clearly demonstrated in Figure 2 that the increasing effect of M:O molar ratio on FFA conversion is the same at different reaction temperature.

#### 3.3.4. Effect of reaction pressure

The influence of the reaction pressure has been investigated between 85 and 185 bar as shown in Table 1. Increasing the reaction pressure has been performed using CO<sub>2</sub> gas, which also acts as a co-solvent for the reaction by enhancing the solubility of methanol in oil [13]. In the present study, the increasing effect of pressure has negative effect on both conversion of triglycerides and FFAs as

shown in Figures 3 and 4, respectively. These results are in agreement with previous stud that reported negative effect of increasing the reaction pressure on biodiesel production [14].


### 3.3.5. Effect of reaction time

It has been observed that reaction time has non-significant effect on triglycerides conversion as reported in Table 2. It is clearly shown in Figure 3 that the increasing effect of reaction time decreases the conversion of triglycerides until 16 min and then has positive effect at longer reaction time. A similar trend of the effect of reaction time has been observed in Figure 4 on FFAs conversion. The increasing effect of reaction time has slightly increasing effect on FFAs conversion followed by negative effect at longer reaction time.

#### Design-Expert® Software

Factor Coding: Actual

#### TG conversion (%)

82.30  99.6

X1 = A: M:O

X2 = B: Temperature

#### Actual Factors

C: Pressure = 110

D: Time = 21.6

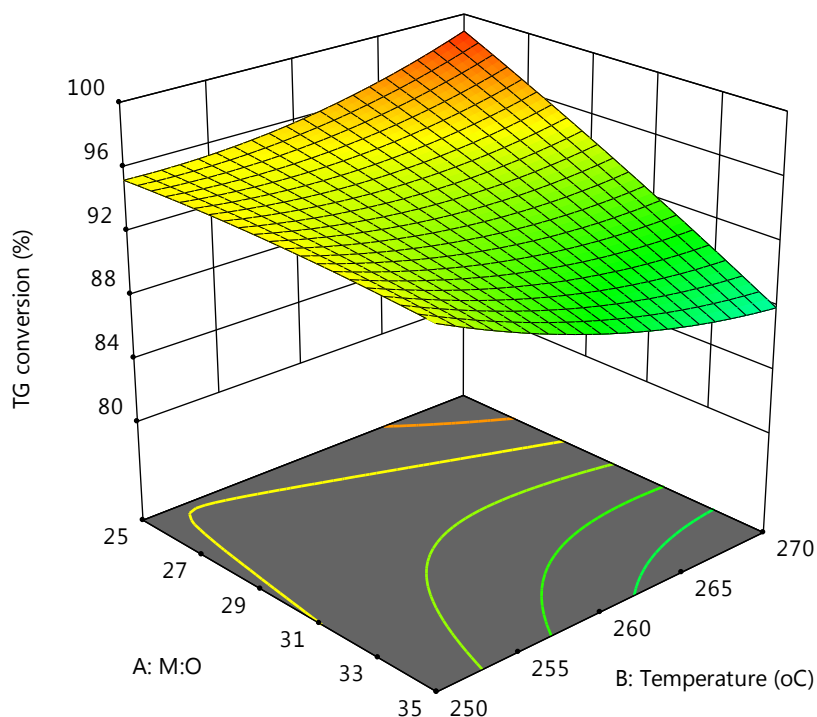


Figure 1. Response surface for M:O molar ratio and reaction temperature versus triglycerides conversion

**Design-Expert® Software**

Factor Coding: Actual

**FFA Conversion (%)**

93.1636  98.6661

X1 = A: M:O

X2 = B: Temperature

**Actual Factors**

C: Pressure = 110

D: Time = 12.4

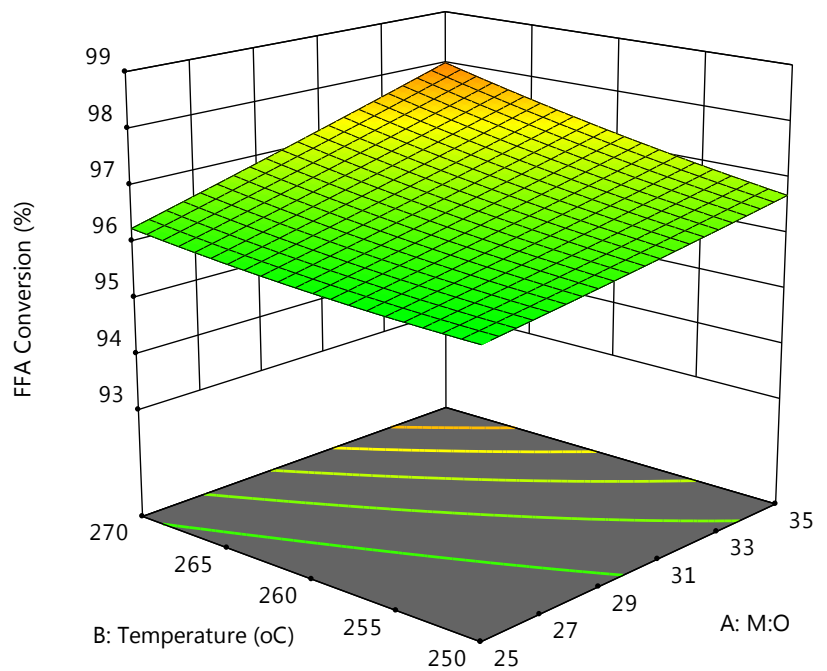


Figure 2. Response surface for M:O molar ratio and reaction temperature versus FFAs conversion

**Design-Expert® Software**

Factor Coding: Actual

**TG conversion (%)**

82.30  99.6

X1 = C: Pressure

X2 = D: Time

**Actual Factors**

A: M:O = 25.1

B: Temperature = 268.2

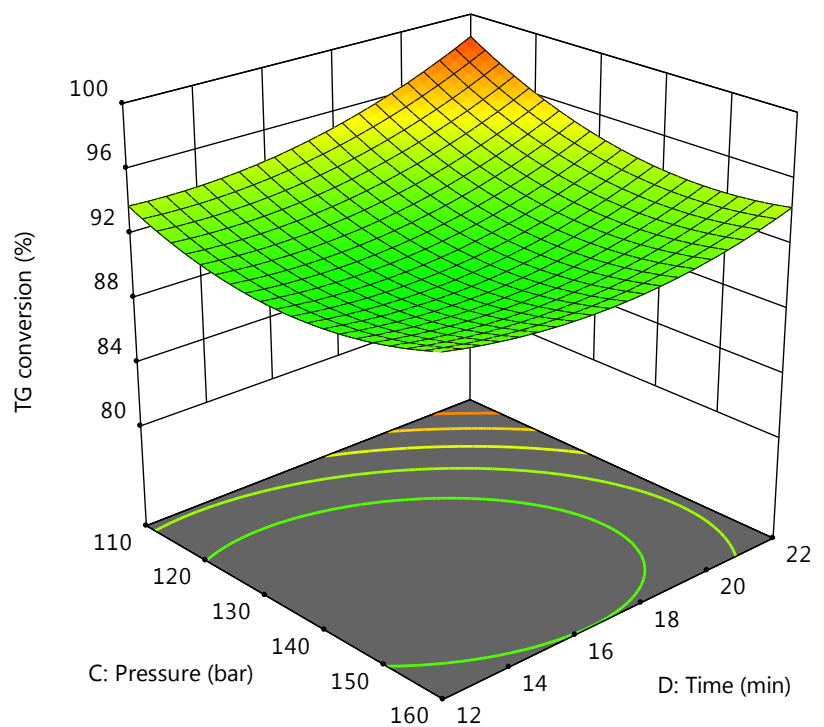



Figure 3. Response surface for reaction pressure and time versus triglycerides conversion



**FFA Conversion (%)**

93.1636  98.6661

X1 = C: Pressure

X2 = D: Time

**Actual Factors**

A: M:O = 31.8

B: Temperature = 268.8

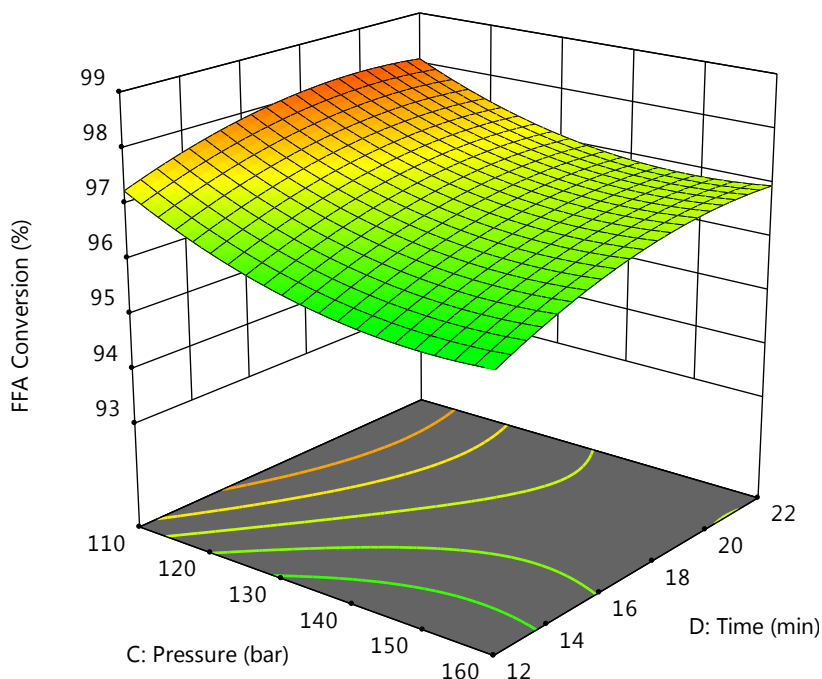


Figure 4. Response surface for reaction pressure and time versus FFAs conversion

### 3.4. Process optimisation

Numerical optimisation using RSM has been extensively used in optimising biodiesel production [1,15–18] and different applications [19]. In the present study, numerical optimisation has been employed to minimise the process variables and to maximise the process responses. The optimisation targets for process variables and responses have been presented in Table 4.

Table 4. Optimisation constraints used to predict optimum conditions for biodiesel production

Factor	Code	Goal	Limits	
			Lower	Upper
M:O (molar ratio)	A	Minimise	25	35
Temperature (°C)	B	Minimise	250	270
Pressure (bar)	C	Minimise	110	160
Time (min)	D	Minimise	12	22
Triglycerides conversion	Y <sub>1</sub>	Maximise	82.30	100
FFAs conversion	Y <sub>2</sub>	Maximise	93.16	100

Design Expert software has used the combination of the targets and developed 100 solutions where the solution with highest desirability has been selected. The highest desirability optimal conditions of 91% have been selected at M:O molar ratio, temperature, pressure and time of 25:1, 265 °C, 110 bar and 18.5 min, respectively. The predicted optimal conditions have achieved 99.1% and 97.5% for overall conversions of triglycerides and free fatty acids (FFA), respectively. An experimental validation has been performed on the predicted optimal conditions resulting in very similar conversion with 0.19% relative error.

### 3.5. Reactor Simulation

The experimental results have been used to simulate a reactor on Aspen HYSYS software to represent the reaction at the same experimental conditions. The developed kinetic data has been used to identify the kinetic simulation requirements including activation energy and frequency factor by 68.8 kJ/mol and 4.01 s<sup>-1</sup>, respectively. The reactor feed stream has been identified using the developed optimum conditions at 265 °C and 110 bar. The feed stream rate has been identified based on the M:O molar ratio with 250 kmol/h of methanol with 10 kgmol/h of oil. The volume of the reactor has been identified according to the reaction residence time and flow rate. Accordingly, the reactor has been successfully simulated and resulted in triglycerides and FFAs conversions of 99.3% and 98.5%.

### 4. Conclusions

The conversion of triglycerides and FFAs through supercritical transesterification/esterification has been analysed in this study. The effects of the controllable variables and their interactive effects on the process responses have been investigated. Two quadratic polynomial models have been developed to represent the responses function in the process variables. Numerical optimisation has been implemented to predict the optimal process parameters. The optimum conditions have been reported at 25:1 M:O molar ratio, 265 °C temperature, 110 bar pressure and 18.5 min reaction time where 99.1% and 97.5% of overall conversions of triglycerides and FFAs have been achieved, respectively. The predicted optimal conditions have been validated experimentally. Finally, a kinetic reactor has been designed and simulated at the developed optimum conditions resulting in similar outcomes to the experimental conversions.

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### Nomenclature

WCO	Waste cooking oil
M:O	Methanol to oil molar ratio
RSM	Response surface methodology
CCD	Central composite design
FFA	Free fatty acids
ANOVA	Analysis of variance

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