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Effect of Factor Interaction in Esterification of High FFA Oil

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Abstract:

An efficient methyl ester production process from high free fatty acid (FFA) waste cooking oils (WCO) was explored via esterification of free fatty acids, an alternative to mineral acids and other common catalysts was tested, Response surface methodology (RSM) based on factorial design was employed to study the effect of independent factor interaction on the process to simultaneously optimize the responses of the reaction (free fatty acid conversion). A quadratic-polynomial mathematical model for the reaction of waste cooking oil (WCO) was developed in terms of catalyst concentration, methanol to oil ratio and reaction time. Analysis of the waste cooking oil indicates that the free fatty acid (FFA) of the oil was 71.4% having composition of 42.5%, 0.86% and 27.71% of palmitic, myristic and stearic acids, respectively. %FFA Conversion determined the extent of esterification. The experimental results showed linear coefficient of catalyst load was the most significant model term affecting FFA reduction at 95% confidence level. coefficient of determination ($R_2 = 0.9511$) and F -value = 14.58 proved the model equation to be significant.

Keywords: Esterification, waste cooking oil, factor interaction, fatty acid

1. Introduction

The quest for alternative fuel has become necessary owing to the reduction in oil field reserves and the increasingly high amount of emissions produced in the combustion reaction of its derivatives, also due to the fact that the supply of fossil fuel is limited while energy demand continues to rise, Industrialization processes continue to grow globally in par with human population which leads to the growing worldwide demand for energy as well as for petrochemical resources, coal and natural gases. This phenomenon has caused the depletion rate of fossil energy resources to increase exponentially and caused alarming environmental problems to the society. Recently, many fuel developers have showed interests in alternative renewable fuels to substitute or blend with petroleum-based fuels. An alternative fuel shall be easily available, environment friendly and techno-economically competitive (Abdullah et al. 2009, and Sharma et al. 2008). Biodiesel plays a major role in energy sector due to its similar combustion properties with petroleum. Furthermore, biodiesel is sometimes more superior than petroleum diesel with improved physical and chemical properties, such as higher flash point, higher cetane number, ultralow sulfur content, better lubricity, improved biodegradability, and smaller carbon footprint (Sharm et al. 2010, Benjumea P et al. 2008, Jha et al. 2008). Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids and is typically made from transesterification reaction of biological triglyceride sources such as vegetable oil and animal fats with alcohol in the presence of catalyst. This process reduces the viscosity to a value comparable to that of diesel and hence improves combustion (Leung et al. 2010). It is also known as oxygenated fuel, meaning that it emit low amount of carbon to the environment because it contains higher hydrogen and oxygen than carbon (Lapuerta et al.. 2008).

According to Meng et al.. (2009), biological feedstock supply for biodiesel production covers more than 75% of the overall production cost (Meng et al. 2009). The favorable properties in selecting the best biodiesel feedstock include lowest oil price, high oil content, and favorable fatty acid composition (saturated or unsaturated acid). The International Energy Outlook, an annual forecast by the U.S. Energy Information Administration forecasted due to the growing population and economic growth in developing countries that the world in 2035 would be more dependent on fossil fuels than ever, it finds. Countries overall would be consuming 49% more energy and spewing 43% more carbon dioxide into the atmosphere in 2035 than in 2007. To get rid of this problem biodiesel plays an essential role in manner to reduce the emissions of carbon dioxide and reduce the consumption of fossil fuel. Vegetable oil use as alternative fuel has been on since 1990 when the inventor of the diesel engine Rudolph Diesel first tested them, in his compression engine (Foglia et al.. 2004). biodisel production projects numerous problems especially with used or waste cooking oils, hence the process esterification is needed in processing these oils Since Free fatty acids (FFA) in reaction, poisonhomogeneous catalysts such as NaOH and KOH, forming soaps and some mineral acids which are difficult to separate from the products of the reaction, recycle and may be poisonous. (Mbaraka et al.. 2003). Sulfated tin oxide ($\text{SO}_4^{2-}/\text{SnO}_2$) is an interesting candidate in a sulfated metal oxides family

for esterification reactions owing to its very high acidity, which is called superacidity (Matsuhashi et al.. 2001). Numerous papers have suggested that the superacidity is responsible for its unique catalytic activities (Sejidov et al.. 2005). $\text{SO}_4^{2-}/\text{SnO}_2$ has been reported to have stronger acid strength than sulfated zirconia, $\text{SO}_4^{2-}/\text{SnO}_2$ (Matsuhashi H et al.. 2001)., which well catalyzes esterification reactions of carboxylic acids (Furuta et al.. 2004), (Juan j c et al.. 2005). Therefore, the activity of $\text{SO}_4^{2-}/\text{SnO}_2$ is expected to be higher than $\text{SO}_4^{2-}/\text{ZrO}_2$ Khder and coworkers (Khder et al. 2008) and Moreno and coworkers (Moreno et al. 2011) have conducted intensive studies in the synthesis and characterization of $\text{SO}_4^{2-}/\text{SnO}_2$ as well as its activity for esterification reactions. The catalytic activity of $\text{SO}_4^{2-}/\text{SnO}_2$ strongly depends on its acidity, which is greatly affected by the sulfate concentration and calcination temperature However, the modification of $\text{SO}_4^{2-}/\text{SnO}_2$ with other metal oxides is hardly found in the literature. The introduction of Al_2O_3 onto $\text{SO}_4^{2-}/\text{SnO}_2$ and its application for benzoylation have been reported by Guo and coworkers (Guo et al.. 2008). For the purpose of this work, we intend to try it on high FFA waste cooking oil. "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may in the course of time be as important as petroleum and the coal tar products of the present time" (Meher et al. 2006). Many studies have reported the production of biodiesel from waste oil feedstock with a few cited here to summarize the advantages and challenges of using waste oils, Most of the waste oil is spent cooking oil from restaurants that has been thermally degraded by sustained high temperatures. It further degrades when in contact with water in the grease trap through a process known as hydrolysis (Montefrio et al.. 2010).

2. Materials and Method

Waste cooking oil was also collected from eateries in Zaria, while reagents($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, AlCl_3 , $\text{CH}_3\text{COONH}_4$ and H_2SO_4) were of analytical grades from chemical stores.

2.1. Preparation of $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$

The preparation of $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ was adapted from the procedure of Furuta and coworkers [10]. A mixture of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (20 g) and aluminum precursor, AlCl_3 (corresponding to 2, 4, 10 and 20 mol% Al) was dissolved in 600 ml of distilled water. An ammonia solution (30 wt%) was added under vigorous stirring until the pH was 8. The precipitate was separated, suspended in $\text{CH}_3\text{COONH}_4$ solution (4 wt%), filtered and dried at 100°C for 24h, yielding aluminum-tin compound. The compound then was immersed in H_2SO_4 solution (30 wt% sulfates) to form gels. The gels were further stirred for 1h, filtered, dried at 100°C for 2h and calcined at 500°C for 3h to give alumina-doped sulfated tin oxide. In this study, the designations of $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-SnO}_2$ are used.

2.2. Fourier Transform Infra-Red (FTIR) Analysis

To determine whether a chemical reaction took place between organic compounds and the clay samples and also to investigate the position and presence of characteristic organic groups in the sample's structure, FTIR Analysis was carried out using KBr. The FTIR spectra were recorded on a Shimatzu Fourier Transform Infrared Spectrometer (FTIR) at the National Research Institute for Chemical Technology (NARICT) Zaria.

2.3. Gas chromatography-mass spectra(GC-MS) analysis

Fatty acid content was determined by using a gas chromatograph (GC) equipped with a flame ionization detector (FID) (Perkin Elmer, USA). The analysis was conducted using a DB-Wax column (30 m x 0.53 mm, 0.5 μm), where 1 μl of sample was injected into the GC for each run. The injector temperature was set to 250°C , while the detector temperature was kept at 270°C . The oven temperature was maintained at 60°C for 1 min, and then increased to 220°C in 10 min as the final oven temperature. Nitrogen was used as the carrier gas for the GC.fatty acid content was expressed as a relative percentage of the total peak area. The methyl ester was identified by comparing its retention time to the retention time of their standard.

2.4. Determination of acid value

Acid values of the various vegetable oils were also determined by ASTM method (ASTM – D 974(00)). 0.2 – 0.5g of sample were weighed into 250ml conical flask. 50ml of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solution was titrated against 0.1M KOH using phenolphthalein as indicator. The acid value was determined after which the free fatty acid was calculated respectively as follows;

$$\text{Acidvalue} = \frac{AMM56.1}{W} \quad (1)$$

Where, A = ml of 0.1M KOH consumed by sample
M = Molarity of KOH
W = weight in grams of the sample

$$\text{Therefore} \quad \text{FreeFattyAcid} = \frac{\text{Acidvalue}}{2} \quad (2)$$

2.5. Viscosity

The Brookfield DV II + Pro viscometer was used to estimate the viscosity of samples at 40 °C according to ASTM D455. Exactly 16 ml of each sample was used. A spindle size of 16 was selected for the analysis because of the rheology of the oil samples.

2.6. Determination of Density

The densities of the oils were determined by ASTM method D – 1298 – (99) The sample was brought to a specified temperature and a test portion was transferred to a hydrometer cylinder that had been brought to approximately the same temperature. The appropriate hydrometer, also at a similar temperature, was lowered into the test portion and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale reading and the temperature of the test portion were taken. The observed hydrometer reading was reduced to the reference temperature by means of a petroleum measurement table. Any hydrometer correction was applied to the observed reading and the corrected hydrometer scale reading recorded to the nearest 0.1kg/m³ as dens.

2.7. Determination of Basic Sediment and Water

50ml of the oil sample and 50ml of toluene were mixed in a 100ml centrifuge tube with the tube tip having graduation of 0.01ml over the range of 0 to 0.2ml. The tube and its content were stoppered and allowed to attain the laboratory temperature (28°C). The tube was placed in a trunnion cup opposite another filled tube to establish a balanced condition of a mechanical shaker. The samples were whirled for agitation at a speed of 1800rpm for 10 minutes to ensure homogeneity. The combined water and sediment at the bottom of the tube was reported to the nearest 0.005ml (ASTM D2709 – 96).

2.8. Esterification Reaction

The process was carried out in a 100 ml three-necked flask attached with reflux condenser, thermometer and stopper and a magnetic stirring hot plate is used. In a typical reaction, 50g (WCO) oil sample was heated to temperature while a mixture of methanol (wt%) and SO₄²⁻/Al₂O₃-SnO₂ catalyst were charged into the flask. Experiments were conducted at 55°C for 2.5–4hrs. while reaction mixture was stirred vigorously at constant stirring rate for all runs. Methanol to oil molar ratio, catalyst loading and reaction time were varied according to the experimental design for each run. After the designated time for the reaction has been reached, the flask was removed from the oil bath and the reaction was stopped by quickly submerging the flask in a water bath to cool the mixture to room temperature. Then, the reaction mixture was transferred to a separating funnel to allow separation of products from by products, and left to settle overnight. When the mixture became biphasic, the upper and the lower layers could be isolated by decantation further solvent removal was done by rotary evaporator. On the other hand, the acid conversion % was obtained by determining the acid number of acid before and the process by Potassium hydroxide (KOH) titration. % FFA is calculated using the equation:

$$FFA\text{Conversion} = \frac{\text{InitialFFA} - \text{FinalFFA}}{\text{InitialFFA}} \times 100 \quad (3)$$

2.9. Statistical Analysis

Experimental data generated using Design Expert 7.0 statistical software (Stat-Ease Inc. USA) is analyzed via RSM in order to fit the polynomial order equation. The response (FFA Conversion) is initially fitted to the factors via multiple regressions. The quality of the fit is determined using the coefficient of determination and analysis of variance (ANOVA). The sum of squares for main and interaction effects is calculated. The significant factors (main and interaction) are identified by ANOVA technique (Aigbodion et al. 2010). And the quadratic response surface model is fitted to the Equation (Jeong et al., 2009).

3. Results and Discussion

3.1. Physico-Chemical Properties

The physico-chemical properties of both waste cooking oil and catalyst were determined and reported in the table below. Table 1: Physico-chemical properties of waste cooking oil (WCO)

Test	WCO	Method
Colour	Dark brown	
Moisture content	4.3%	ASTM D2709-96)
Viscosity(cst) at 40°C	36.4	ASTM D445
Density at 25°C	0.914	ASTM D 1298
Sediment	<1%	ASTM D2709-96).
Acid value(KOH/g oil)	2.80	
%Free fatty acid(FFA)	1.40	ASTM – D 974(00)
Iodine value(mgIodine/g)	103.10	AOCS (16-87)
Saturated fatty acids	71.07%	
Unsaturated fatty acids	21.14%	

Table 1

The analysis of waste cookingoil presented in Table 1 represents mean of triplicate analysis of each parameter. It is evident that the properties of waste cooking oil used in this study compared favourably with literature values (El-Diwani et al., 2010). The high value of FFA (3.42%) in the oil sample indicates that the oil contained more saturated fatty acids (palmitic and stearic acids) than the unsaturated fatty acids which does not require esterification before trans-esterification. High value of FFA > 1% adversely affect the transesterification reaction in which the FFA in the oil reacts with the alkali catalyst to produce soap (saponification) hence, decreasing the catalyst amount needed for the transesterification reaction (El-Diwani et al., 2010). The high value of water content (4.3%) in the oil suggests that the oil requires pretreatment by reducing the water content to < 0.5% before the reaction. The presence of water in oil feeds for biodiesel production normally cause soap formation and frothing which usually results in increase in viscosity. According to (Demirbas, 2009), foam and gel formation caused by water hinders the separation of glycerol from biodiesel. However, these saturated fatty acids give biodiesel fuel advantages in terms of a higher cetane number and better oxidation stability. In contrast, saturated fatty acids show disadvantages such as the fuel having higher cloud point and pour points. (Mohammed et al. 2012).

3.2. Compositional Analysis of Waste Cooking Oil

Analysis of free fatty acid(FFA) composition (Table 2) of the waste cooking oil indicates the oil to be predominantly (C16:0) palmitic acid followed by stearic acid (C18:3) oleic acid (C14:0) myristic and others. with compositions of 42.5%, 27.71%, 21.14%, 0.86%, and (7.79%) respectively indicating a high level of saturation in the oil. In comparison to (Adeeb et al., 2011) which reported the fatty acid compositions of sludge palm oil (SPO) with the highest fatty acids been oleic, palmitic, linoleic and stearic acid. Saturated fatty acids in SPO were 47.17 wt.% while unsaturated fatty acids were 52.83 wt.%.

Fatty acid profile	Relative weight %
Palmitic acid methyl ester C16:0	42.5%
Myristic acid methyl acid ester C14:0	0.86%
Stearic acid methyl ester C18:0	27.71%
Oleic acid methyl ester C18:3	21.14%
Others	7.79%

Table 2: Profile of fatty acid methyl ester from waste cooking oil

3.3. FT-IR Monitoring of Methyl Ester Conversion

FTIR spectroscopic analysis for monitoring transesterification reactions of waste cooking oil(WCO) showed FTIR spectra of WCO it's derived biodiesel were recorded. The presence of IR bands in the region 1425–1447 cm⁻¹ for CH₃ asymmetric bending and 1188–1200 for O–CH₃ stretching in all biodiesels. IR spectra clearly depicted the conversion of WCO (i.e., triglycerides) to fatty acid methyl esters, as these IR bands were not present in the parent oil (waste cooking oil WCO)

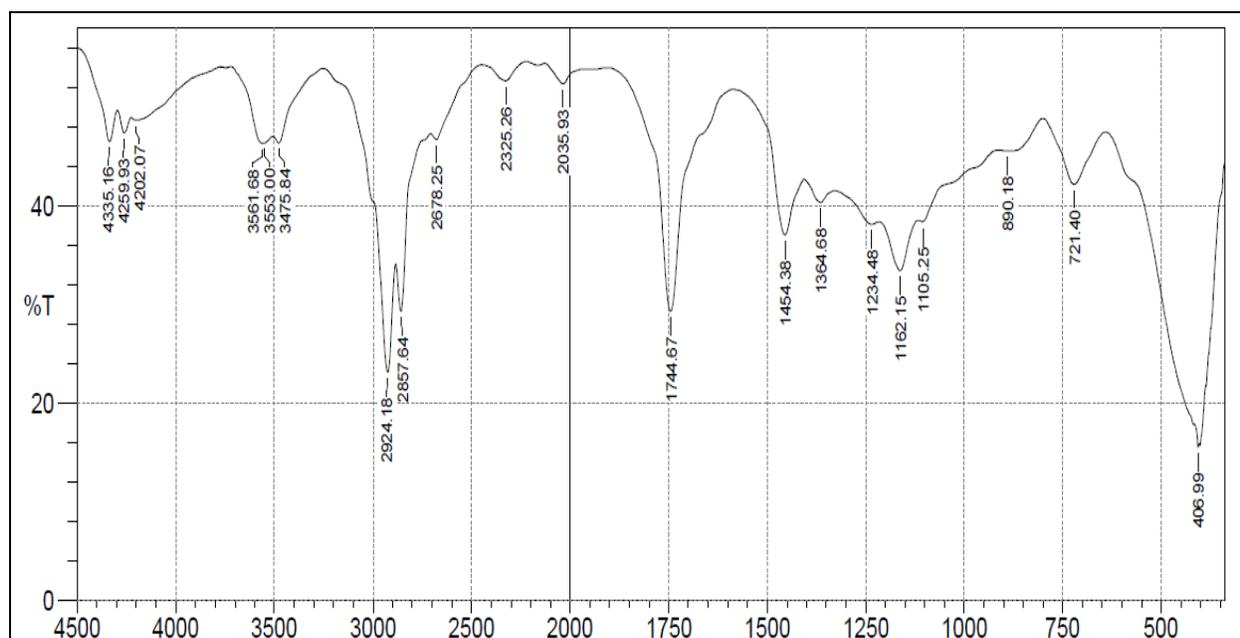


Figure 1: FT-IR spectra of methyl ester from waste cooking oil

3.4. Experimental Design

The study was performed using an experimental design method. The effect of three process variables (methanol to oleic acid molar ratio, catalyst loading, and reaction time) on the responses of the process was studied using response surface methodology(RSM)

based on a factorial design. Factorial design allows the estimation of all the regression parameters required to fit a second order model to a given response. Table 3 represents the experimental range and factor level for the esterification process. Eight runs were required, which included full 2^3 factorial designs (three factors each at two levels).

Factors		Range			
		Coded		Uncoded	
Methanol/oil Catalyst load(%) Time(hrs)	X1	-1	+1	-1	+1
	X2	-1	+1	3:1	6:1
	X3	-1	+1	2.5	5.0
	X3	-1	+1	1.0	3.0

Table 3: Experimental range and factor level of process variables.

Run	Alcohol/Oil ratio (w/w)%	Catalyst load (%)	Time (hrs)	% conversion
1	3	2.50	3.00	64.8
2	3	5.00	2.00	74.2
3	3	2.50	2.00	67.3
4	3	5.00	3.00	86.4
5	6	2.50	3.00	55.3
6	6	5.00	3.00	92.1
7	6	5.00	2.00	78.7
8	6	2.50	2.00	47.5

Table 4: Experimental factorial design and response values

3.5. Response Surface Model Equation of Reaction and Plots

The model equation that predicted the relationship between free fatty acid conversion (Y) and independent variables is represented below

- Final equation in terms of coded factors

$$Y = +70.79 - 2.39 * A + 12.06 * B + 3.86 * C + 4.94 * A * B \quad (4)$$

- Final equation in terms of actual factors

$$Y = +66.8875 - 11.46667 * A - 2.20000 * B + 7.72500 * C + 2.63333 * A * B \quad (5)$$

Where

A=Alcohol/Oil ratio

B= Catalyst load

C= Time

Source	Sum of squares	df	Mean Square	F-value	P-value Prob>F
Model	1524.01	4	381.00	14.58	0.0263
A-methanol-oil ratio	45.60	1	45.60	1.75	0.2782
B-Catalyst load	1164.03	1	1164.03	44.55	0.0069
C-Time	119.35	1	119.35	4.57	0.1222
AB	195.03	1	195.03	7.46	0.0718
Residual	78.39	3	26.13		
Cor Total	1602.41	7			

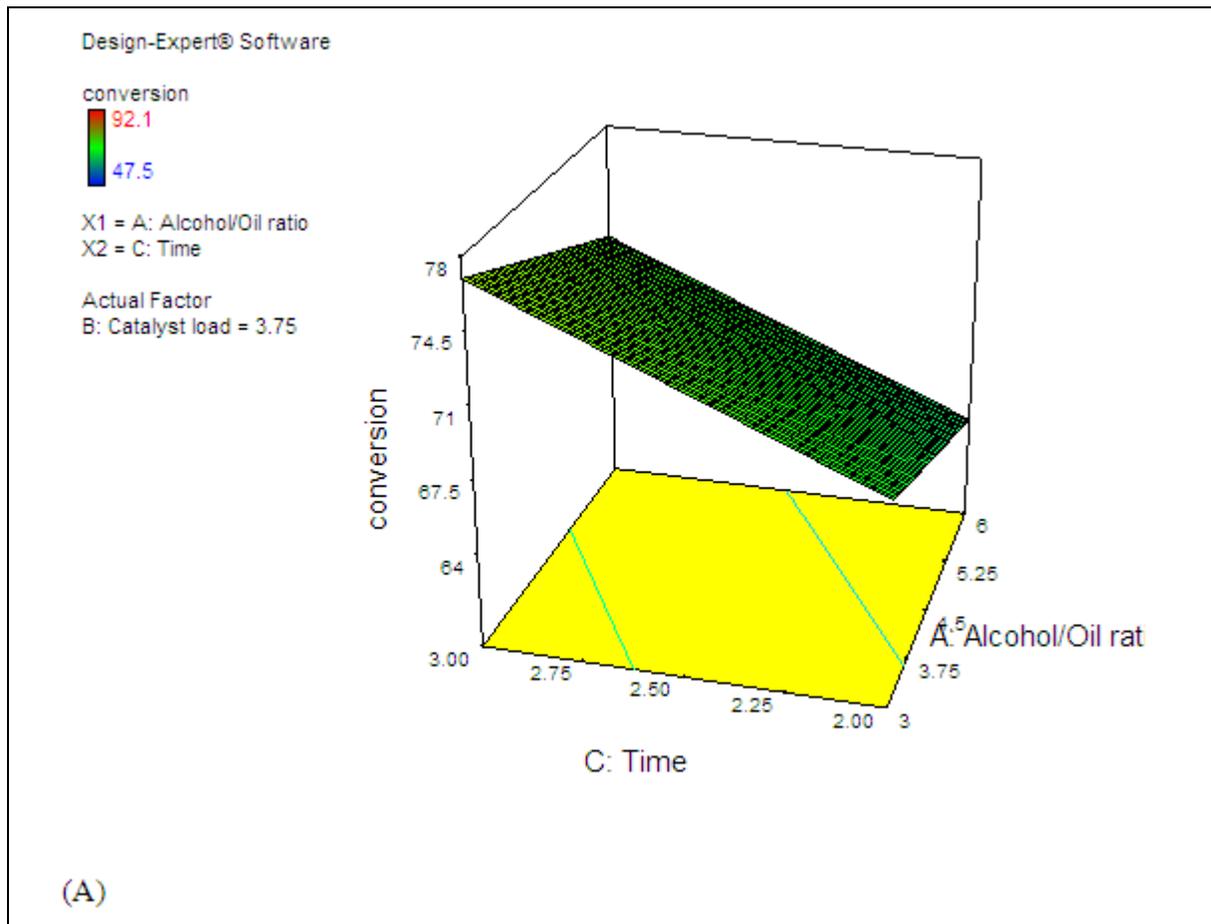
Table 5: ANOVA Result

The coefficient of determination (R_2) for Eq. (5) is 0.9511, as given from data analysis of experimental results using DESIGN EXPERT 7.0 only a lesser percentage of the total variation in the response did not fit the model, which highlighted that the model is adequate to cover over 90% of the variability in the experiments. Furthermore, the model can predict the response with greater accuracy based on the high value of R_2 . The model was then tested for its adequateness by analysis of variance (ANOVA), and the statistical analysis is represented in Table 4. The mathematical model was tested with 95% confidence level. From the calculation, it was found that the calculated F-value (14.58) model for oleic acid conversion was higher than the F-value from the distribution table which confirmed that the model was significant, could not have been due to noise and can give good predictions of free fatty acid conversion at high confidence level (95%)

3.6. Response Surface Plots

The graphical representation of interaction between independent variables and free fatty acid conversion are presented as response surface plots in Fig.1. Fig1a. depicts interaction of methanol–oil ratio and reaction time. conversion increased significantly with increasing time but however decreased as higher methanol–oil ratio were reached. There was considerable interaction between the variables with fatty acid conversion due to the elliptical nature of the contour plot (Wan and Saidina 2011). The same trend was also reported by (Elsheikh, 2011) in esterification of crude palm oil using [BMIM][HSO₄] to catalyze the reaction, as the conversion of FFAs remained virtually unchanged after reaction time of 2 h. However, there was slight decrease in the conversion after 6 h of reaction in this study, (Leung and Guo 2006) mentioned that it was related to the reaction time, where prolonged time favored the backward reaction (i.e. hydrolysis of esters), which reduced the conversion.

Response surface plot for interaction between catalyst loading and molar ratio of alcohol/oil with fatty acid conversion is illustrated in Fig 1b. Conversion can be seen to increase more rapidly with increasing molar ratio and catalyst load, conversion was highest at 6:1 and 5wt% molar ratio and catalyst load respectively. This was also the case in reaction time and reaction catalyst load interaction with respect to fatty acid conversion as shown in Fig. 5c. conversion increased rapidly with increasing reaction time and catalyst load up to 87% conversion.



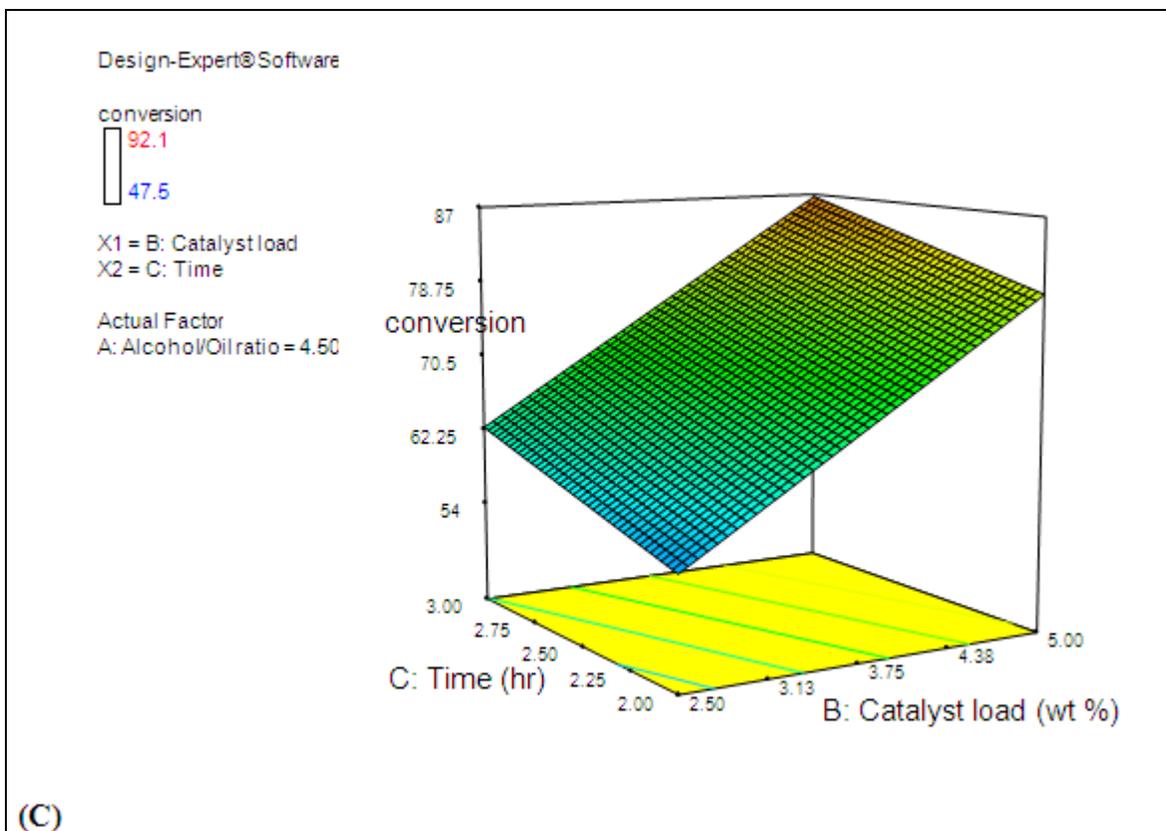
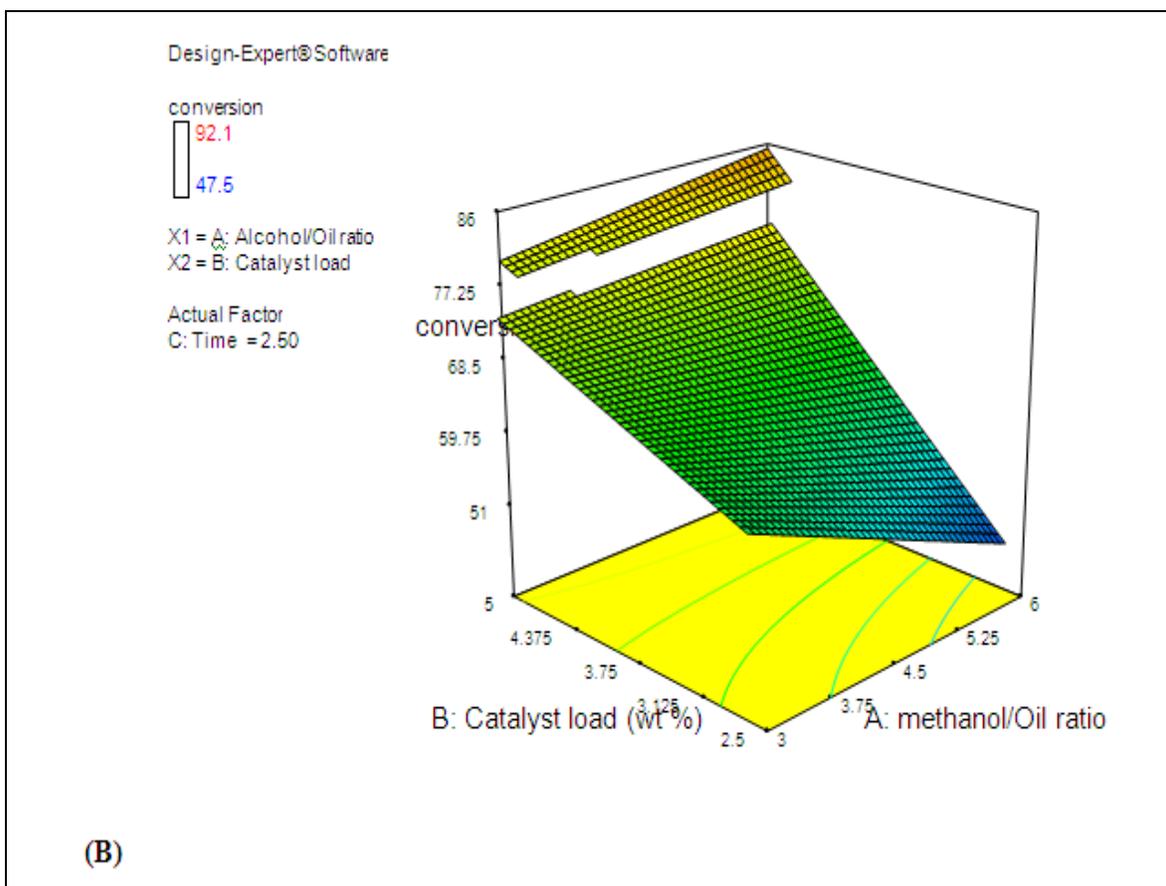


Figure 1: Response surface plots of fatty acid conversion as a function of (a) methanol–oil ratio and reaction time, (b) methanol–oil ratio and catalyst load (c) catalyst loading and reaction time.

4. Conclusion

The efficiency of the process depends on interaction of the factors, valid responses were obtained for waste cooking oil esterification with catalyst, the coefficient of determination R_2 showed 95% interaction among factors and the quadratic mathematical models produced was significant at $F= 14.58$, and $P < 0.05$. Linear coefficient of catalyst load for the mathematical model was the most influential variable for the responses.

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