Effects of Process Parameters on Biodiesel Production from Refined Soy Oil.

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ABSTRACT

In this study, the effects of process variables such as methanol-to-oil molar ratio, catalyst amount, and reaction temperature on the transesterification of the refined soy oil to biodiesel were investigated. Methanol with potassium hydroxide (KOH) as a homogenous catalyst was used for the transesterification process at a time of 1hr and 250rpm stirring speed. Factorial design was applied at two levels of methanol-to-oil molar ratio of (1:1-6:1), catalyst % of (0.5-1.0) and reaction temperature of (35-50oC) as independent variables and refined soy oil biodiesel yield as dependent variable (response). A statistically significant (P<0.0001) linear regression model was obtained for biodiesel production (using Design-Expert® statistical program (v.8.0.2) and verification experiment confirmed the validity of the predicted model. In addition the fuel properties of the produced biodiesel were investigated and compared with the standards. The optimum combinations for transesterification to achieve a maximum biodiesel yield of 97% were found to be methanol-to-oil molar ratio, 6:1; catalyst amount of 1.0% and a reaction temperature of 35^{o}C

(Keywords**:** ANOVA, biodiesel, factorial design, refined soy oil, transesterification)

INTRODUCTION

Centuries ago the world's energy supply relied on non-renewable crude oil derived (fossil) liquid fuels out of which 90% is estimated to be consumed for energy generation, transportation and industrial applications. It is also known that gaseous emissions from the combustion of these fuels such as carbondioxide (CO_2), carbonmonoxide (CO), nitrogen-oxides (NO_x), and sulphur containing residues are the principal causes of global warming and many countries have passed legislation to arrest their adverse environmental consequences [1].

Biodiesel, which consists of long chain fatty acid alkyl esters (FAAE) obtained from renewable lipids such as those in vegetable oils or animal fat, can be both as an alternative fuel and as an additive for petroleum diesel ([2], [3], and [4]). The advantages of biodiesel fuel over conventional diesel are lower emission pollutants, higher cetane number, no aromatics, no sulphur and contains 10-11% oxygen by weight ([5] and [6]).

One popular process for producing biodiesel from (fats/oils) is transesterification of triglycerides by methanol (methanolysis) to make methylesters of the straight chain fatty acid and the purpose of this transesterification process is to lower the viscosity of the oil. Transesterification is the reaction of a lipid with an alcohol in the presence of a catalyst to form esters and a by- product, glycerol. The reaction is reversible and thus an excess of alcohol is usually used to force the equilibrium towards the production of fatty acid esters and glycerol ([1], [5]).The transesterification is represented as:

$$\underset{Ester}{RCOOR^1} + \underset{Alcohol}{R^1OH} \rightleftharpoons \underset{Ester}{R^1COOR^1} + \underset{Alcohol}{ROH}$$

Biodiesel production from soybean oil is very popular. Researchers have focused on different catalyst systems, different solvents, and different acetyl acceptors. Soybean oil have five fatty acids: approximately equal amounts of palmitic acid, oleic acid and linolenic acid (about 13% each), linolenic acid, (approximately 55%), and stearic acid (approximately 4%). A useful industrial application of soybean oil is in biodiesel blends. According to Kinney and Clemente [7], soybean oil-derived biodiesel possess enhanced biodegradation, increased flashpoint, reduced toxicity, lower emissions, and increased lubricity.

The main objective of this work is to explore the relationships between the relevant reaction variables (i.e., catalyst amount, molar ratio of methanol to oil, and reaction temperature) and the product characteristics (i.e., ester content and yield). The optimal conditions for biodiesel production from refined soy oil were also obtained.

MATERIALS AND METHODS

Materials

Refined Soya cooking oil was obtained from a shop in Ogbete main market Enugu state Nigeria. Methanol (CH_3OH), potassium hydroxide (KOH), and other chemicals in pellet form were obtained from Pymotech Research Laboratory Abakpa Enugu, Nigeria, and they are of analytical reagent grade.

The molecular weight of the oil was determined from the saponification and acid values using Eq. (1-3) according to [9,12]

$$\text{Saponification Value} = \frac{56.1\,(B - S) \times M\ of\ HCl}{Weight\ of\ Sample} \quad \textbf{(1)}$$

$$\text{Acid Value} = \frac{A \times M \times 56.1}{W} \quad \textbf{(2)}$$

$$\text{Molecular weight} = \frac{56.1 \times 1000 \times 3}{SV - AV} \quad \textbf{(3)}$$

Where SV and AV are the saponification and acid values (mg KOH/g), respectively. Density and viscosity measurements were measured according to ASTM standards D1298 and D445 respectively. The pour point and flash points were determined following ASTM standards D97 and D93 respectively. Kinematic viscosity was estimated at 40^{o}C. The properties of the refined soy oil are summarized in Table 1 below. It is seen also that the refined soy oil has an acid value of 0.1mg KOH/g and this corresponds to a free fatty acid of 0.05**%.**

Preparation of Potassium Methoxide

An appropriate volume of alcohol was measured and poured into a 250ml conical flask. The catalyst in pellet form was weighed and mixed with alcohol. The mixture was then shaken for about 1 hr until all the catalyst dissolved. Since alcohols would vaporize easily, the flask was covered with aluminum foil during shaken to reduce the loss of alcohol by evaporation. The covering can also avoid the methoxide from absorbing water from the air [11].

Biodiesel Production by Transesterification Process

To produce a test quantity of biodiesel, the refined soy oil was first filtered to remove any form of impurity in the oil. Potassium hydroxide (KOH) catalyst was added in methanol (CH_3OH) and shaken well so that the catalyst is completely dissolved in the alcohol. The alcohol-catalyst mixture was then charged in a conical flask, containing the soy oil. The whole mixture was stirred well at a fixed speed of 250rpm. After the reaction was completed, the product of the reaction was exposed to open air to evaporate excess methanol for 30mins.

The mixture was poured into a separating funnel and allowed to settle overnight. Two distinct immiscible liquid phases were observed: crude ester layer on top and glycerol layer at the bottom. Glycerol was flowed out by means of a separating funnel and the remaining ester layer was washed with distilled warm water to remove all the residual by-products including the excess alcohol, the catalyst, soap, and the untreated glycerides ([9], and [10]). The biodiesel sample produced was stored for analysis at a room temperature of 28^{o}C as shown in Table 1 below.

$$\text{Biodiesel Yield (\%)} = \frac{weight\ of\ fatty\ acid\ methylester}{weight\ of\ oil\ used} \times 100\% \quad \textbf{(4)}$$

Table 1: Physico-Chemical Properties of Produced Biodiesel from (RSO).

Parameters	Value
Free fatty acid (%)	0.05
Acid value (mg KOH/g)	0.1
Ash content (%)	Nil
Specific gravity	0.8869
Kinematic viscosity (cst)	4.3
Refractive index	1.460
Flash point (^oC)	130
Cloud point (^oC)	5.0
Fire point (^oC)	140
Water content(%)	Nil
Heating value (Cal)	150.96
Pour point (^oC)	-0.1

Table 2: Properties of the Biodiesel Produced in Comparison with Standards.

Properties	Refined Soy Oil	EN14214	ASTMD-6751
Free Fatty Acide %	0.05	≤ 0.25	≤ 0.4
Acid Value (mg KOH/g)	0.1	≤ 0.5	≤ 0.8
Ash Content %	Nil	--	--
Specific Gravity	0.8869	--	--
Kinematic Viscosity (CST)	4.3	3.5-5.0	1.9-6.0
Refractive Index	1.460	--	--
Flash Point (^oC)	130	≥130	≥120
Cloud Point	5.0	--	--
Fire Point	140	--	--
Water Content	Nil	≤ 500	--
Heating Value	150.96	--	--
Pour Point (^oC)	-0.1	--	--

Statistical Experimental Design for Optimization of Biodiesel Production

The experimental design selected is the yield of fatty acid methyl ester (FAME). Factorial design was used to investigate the effect of methanol-to-oil molar ratio, catalyst amount and reaction temperature on the conversion of RSO to biodiesel. A two level three factor factorial design was employed in the optimization study, requiring eight experiments. The methanol-to-oil molar ratio, catalyst concentration and reaction temperature were the independent variables selected to optimize the conditions for biodiesel (fatty acid methyl ester) production of base catalyzed transesterification.

Table 3 gives factors and their values. Table 4 gives the experimental design and the eight experiments that were carried out. Experimental runs were randomized to act as insurance against the effects of lurking time related variables and also to satisfy the statistical requirements of independence of observations. The conversion to biodiesel was analyzed using design Expert software program (v 8.0.2) to fit the following Equation (5):

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{123} ABC \quad (5)$$

Where Y is the predicted response, β_0 is the value of the fixed response or intercept; $\beta_1, \beta_2, \beta_3$ are the linear coefficients for the input factors A, B, C; $\beta_{12}, \beta_{13}, \beta_{23}$ are the interaction effect coefficients regression terms, respectively; A, B, C are the levels of independent variables. Using the above model in equation (5), the Design-Expert program (version 8.0.2) software was used for the regression analysis of experimental data and to plot response surface.

Table 3: Range and Levels of the Independent Parameters.

Factor Coding	Low Level	High Level
Methanol-to-Oil Molar Ratio (A)	1	6
Catalyst wt % (B)	0.5	1.0
Reaction Temperature (^oC) (C)	35	50

Table 4: Factorial Design for Optimizing Biodiesel Yield.

Std. Order	Run	Coded factor A B C	OH to Oil ratio	Catalyst %	Rxn. Temp. ^oC	Biodiesel yield %
1	7	- -1 -1	1:1	0.50	35	95
2	6	+1 -1 -1	1:6	0.50	35	94
3	4	-1 +1 -1	1:1	1.00	35	94
4	2	+1 +1 -1	1:6	1.00	35	97
5	3	-1 -1 +1	1:1	0.50	50	95
6	5	+1 -1 +1	1:6	0.50	50	96
7	1	-1 +1 +1	1:1	1.00	50	95
8	8	+1 +1 +1	1:6	1.00	50	95

Table 5: Complete Matrix Including Interaction with Effects

Std.	Main Effects A	B	C	Interaction Effects AB	AC	BC	ABC	Response Y_2 (refined soy oil)
1	-	-	-	+	+	+	-	95
2	+	-	-	-	-	+	+	94
3	-	+	-	-	+	-	+	94
4	+	+	-	+	-	-	-	97
5	-	-	+	+	-	-	+	95
6	+	-	+	-	+	-	-	96
7	-	+	+	-	-	+	-	95
8	+	+	+	+	+	+	+	95
Effect Y_2	1.0	0.0	0.0	1.0	0.0	-1.0	-1.0	95

Table 6: Half Normal Plot of Effects for Refined Soy Oil.

Point	Effect	Absolute Value of Effect	Cumulative Probability (%)
1	B	0.00	7.14
2	C	0.00	21.43
3	AC	0.00	35.71
4	BC	-1.00	50.00
5	ABC	-1.00	64.29
6	A	1.00	78.57
7	AB	1.00	92.86

Analysis of Variance (ANOVA)

To protect against spurious outcomes, it is absolutely vital that one verifies the conclusions drawn from the half normal plots by doing analysis of variance (ANOVA) and associated diagnostics of residual error [8]. The ANOVA result is shown in Table 7. The F-value of 6.366E+007 implies the model was significant. There is only 0.01% chance that a "model F-value" as large this could due to noise.

Table 7: Analysis of Variance (ANOVA) for Selected Factorial Model.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	Prob >F
Model	8.00	4	2.00	6.366E+007	<0.0001
A-Alcohol/oil	2.00	1	2.00	6.366E+007	<0.0001
AB	2.00	1	2.00	6.366E+007	<0.0001
BC	2.00	1	2.00	6.366E+007	<0.0001
ABC	2.00	1	2.00	6.366E+007	<0.0001
Residual	0.000	3	0.000		
Cor Total	8.00	7	0.000		

The Model F- value of 63660000.00 implies the model is significant. There is only a 0.001% chance that a "Model F- value" this large could occur due to noise. Values of "Prob $> F$ " less than 0.0500 indicate model terms are significant. In this case A, B, C, and BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Validation to Model

It is necessary to diagnose residuals to validate statistical assumptions. For statistical purpose it is assumed that residuals are normally distributed and independent with constant variance. Two plots are recommended for checking the statistical assumptions:

- Normal plot of residuals
- Residuals versus Predicted level

RESULTS AND DISCUSSION

The independent variables considered for this experiment were Alcohol/Oil ratio (A), Catalyst wt. (B), and reaction temperature (C). The experimental runs were randomized to satisfy the statistical requirement of independences of observations. Randomization acts as insurance against the effects of working time-related variable.

The half normal probability plot was used to select the statistically significant effects that were included in the model [8].

From Figure1, it is noticed how the three effects (B, C and AC) fall in a line near zero. These effects evidently vary only due to normal causes. Presumably as a result of experimental error (noise in the system), so they are probably insignificant.

The effects of A, AB, BC and ABC are very big relative to other effects. They obviously do not fall on the zero line. In statistical sense, each of these standout effects should be considered significant populations in their own right.

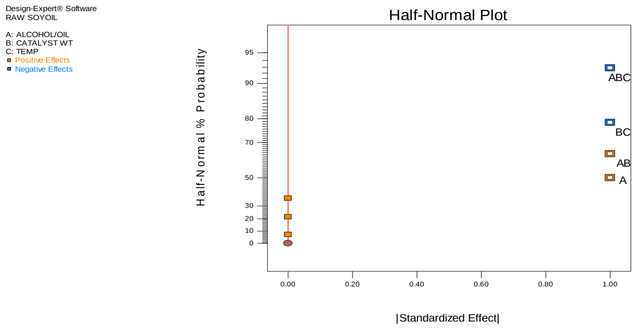

Figure 1: Half Normal Probability Plot.

Effect of Transesterification Process Variables

Based on the ANOVA, the transeseterifcation reaction was significantly affected by interaction of the three process variables A (Alcohol/Oil ratio), B (Catalyst wt.), and C (Reaction temperature). On the other hand, significant individual process variables that affect the transesterification reaction are methanol-to-oil molar ratio (A), Catalyst wt. (B) and reaction temperature (C). The ratio of methanol-to-oil is one of the important factors that affect the conversion of triglyceride to fatty acid methyl ester (FAME).

The result obtained from this study as shown in Figure 2 showed that biodiesel yield increased as methanol to oil ratio increased also. Higher ratio of methanol used could also lead to the increase in the purity of the FAME layer which would also be responsible for the observed increase in the FAME yield.

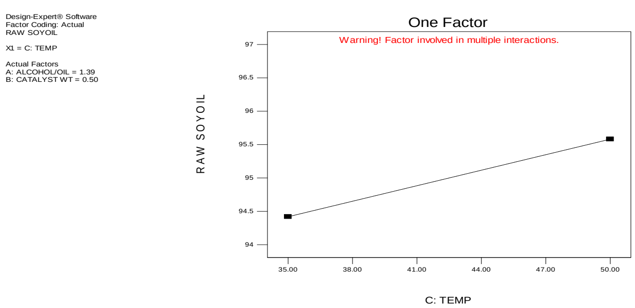

Figure 2: Effect of Methanol-to-Oil Ratio on Refined Biodiesel Yield.

Figure 3 illustrates the effect of the amount (mass) of KOH catalyst on biodiesel yield. When the mass ratio of catalyst to oil was increased from 0.5% to 1.00%, the transesterification reaction was accelerated thereby increasing biodiesel yield. The figure below showed a1.38% increase in yield of biodiesel as the catalyst amount is increased from (B-) to (B+).

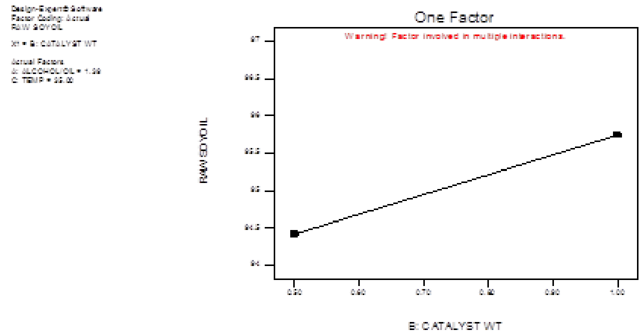

Figure 3: Effect of Catalyst amount on Refined Biodiesel Yield.

The figure 4 below shows the effect of reaction temperature on biodiesel yield. It can be observed from the plot that biodiesel yield increases with increase in reaction temperature from (C-) to (C+). The increase in the yield of FAME at higher reaction temperature is due to higher rate of reaction. The transesterification reaction is basically diffusion controlled. At lower reaction temperature, the lower viscosity of soy oil might cause poor diffusion between the phases that will lead to slower rate of reaction. Figure 4 below showed a 1.27% increase in FAME yield as temperature is increased from (C-) to (C+).

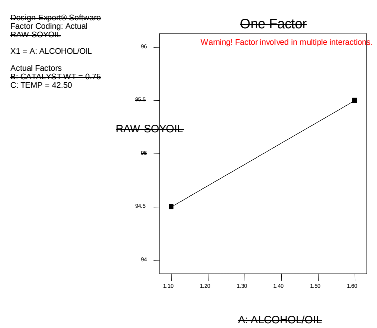

Figure 4: Effect of Reaction Temperature on Refined Biodiesel Yield.

Effect of Interaction between Process Variables

Figures 5, 6, and 7 show the interaction between methanol to oil molar ratio & catalyst wt. , catalyst wt. & temperature, and alcohol vs. temperature respectively on the yield of FAME. Figures 8, 9, and 10 show the three dimensional surface plot, plotted on the basis of the model equation to investigate the interaction among the variables and to determine the optimum condition of each factor for biodiesel production.

Figure 5 shows the interaction of factors A and B. From the figure below at high methanol to oil ratio and high catalyst amount gave a biodiesel yield of 97% which depicts a positive movement of the red line (A+). But when the catalyst amount is lowered at 0.5% as the methanol to oil molar ratio is increased there is a decline in the yield of biodiesel as can be seen from the negative movement of the black line.

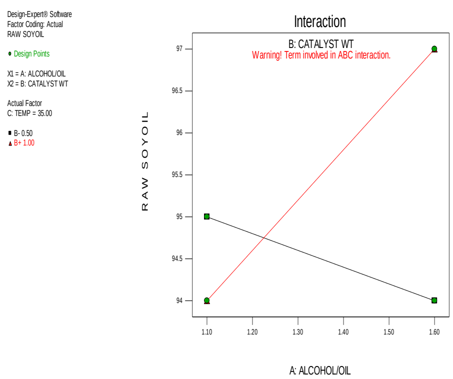

Figure 5: Effect of Methanol to Oil Ratio vs. Catalyst Amount.

Figure 6 shows effect of interaction of catalyst wt. and temperature. From the figure it shows that when the temperature is low (C-) at 35^{o}C the black line grew in the positive direction linearly indicating a strong positive effect due to increase in catalyst concentration. When the temperature is high (C+) at 50^{o}C the red line steeps negatively downward indicating a decline in the yield of biodiesel as the catalyst amount is increased.

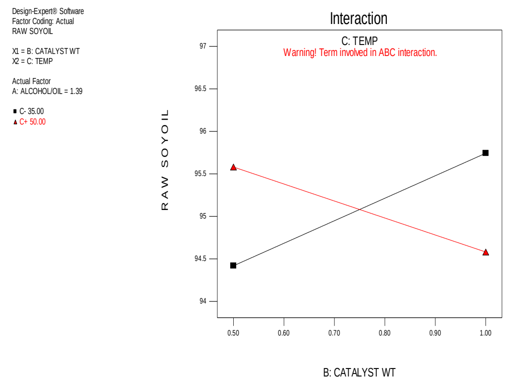

Figure 6: Effect of Interaction of Catalyst Amount vs. Temperature.

Figure 7 shows the interaction between alcohol/oil ratio and temperature. It can be observed that when the reaction temperature is high (C+) there is a clear positive movement indicating strong yield of biodiesel as the alcohol/oil ratio is increased. But when the temperature is low (C-) no yield of biodiesel is observed from the plot below

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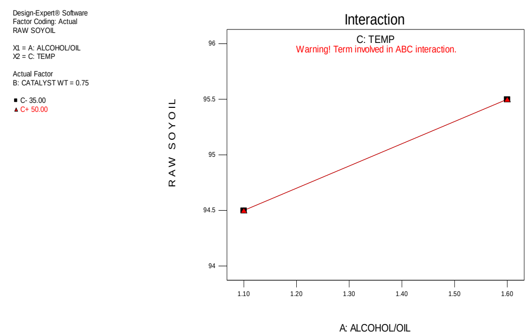

Figure 7: Effect of Methanol-to-Oil Molar Ratio vs. Temperature.

The three dimensional surface plot shows the interaction between methanol to oil molar ratio and catalyst wt%, catalyst wt. and reaction temperature, and methanol to oil molar ratio vs. temperature respectively on the yield of FAME. Generally, an increase in reaction temperature favors the yield of FAME in all three cases.

The effect of methanol-to-oil molar ratio and temperature on biodiesel production at a constant reaction time of 60min is presented in Figure 8 below. It can be deduced from the plot below that as the methanol-to-oil molar ratio is increased and at a temperature of 35^{o}C, there is a positive linear movement of the yield of biodiesel. But when the Alcohol/oil ratio is increased at a temperature of 50^{o}C (red line), the line steeply downward indicating a decline in the yield of biodiesel.

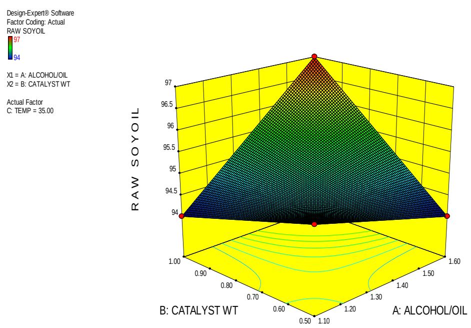

Figure 8: 3D Surface Plot of Methanol-to-Oil Ratio vs. Catalyst.

Figure 9 shows the interaction of catalyst amount and reaction temperature on conversion of refined soy oil to biodiesel. It can be deduced from the plot below that as catalyst concentration is increased from 0.5-1.00% and at a temperature of 35^{o}C (C-) the black line, there is a linear movement of the line which depicts increase in the yield of biodiesel. When the catalyst concentration is increased at a higher temperature of 50^{o}C the red line (C+) there is a clear visible decline in the conversion of RSO to biodiesel.

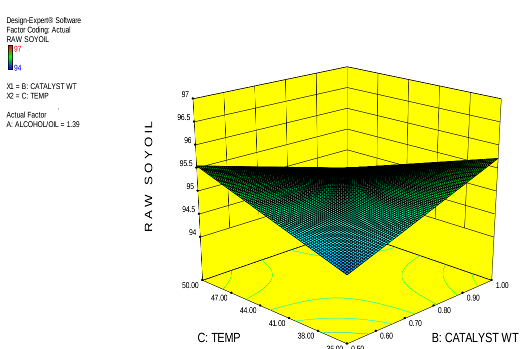

Figure 9: 3D Surface Plot of Catalyst wt. vs. Temperature.

The 3D surface interaction plot of methanol-to-oil ratio vs. catalyst wt. can be seen from Fig. 10 below. As the methanol-to-oil molar ratio is increased from 1:1(A-) to 6:1(A+) and at a catalyst concentration of 1.00% (B+) there is a clear visible increase in the conversion of RSO to FAME. But when the Alcohol/oil ratio is increased at a low temperature of 35^{o}C, it is observed from the plot that the line steeply downward indicating a decline in the yield of biodiesel.

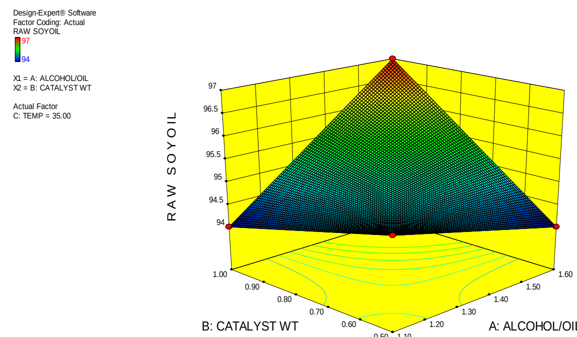

Figure 10: 3D Surface Plot of Alcohol/oil ratio vs. Catalyst wt.

Figures 11, 12 and 13 shown below reveals the contour plots of the three process variables that was studied in the course of this work and their interactive effects in the production of biodiesel.

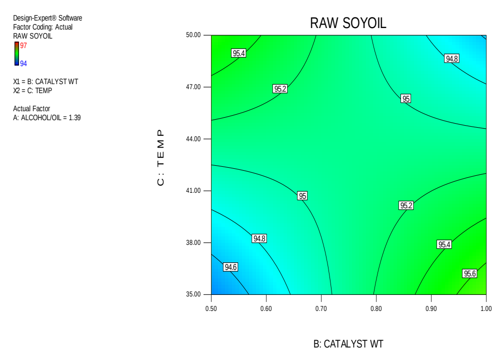

Figure 11: Contour Plot of Catalyst wt. vs. Temperature.

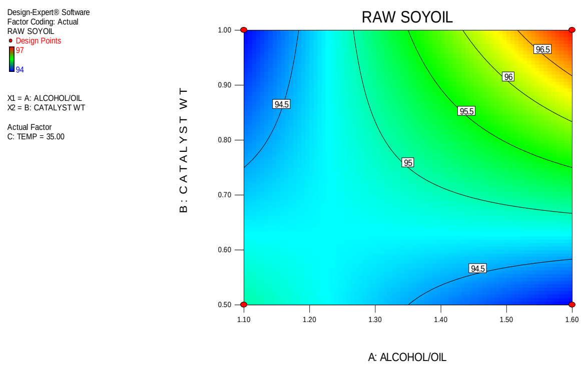

Figure 12: Contour Plot of Methanol-to-Oil Molar Ratio vs. Catalyst wt.

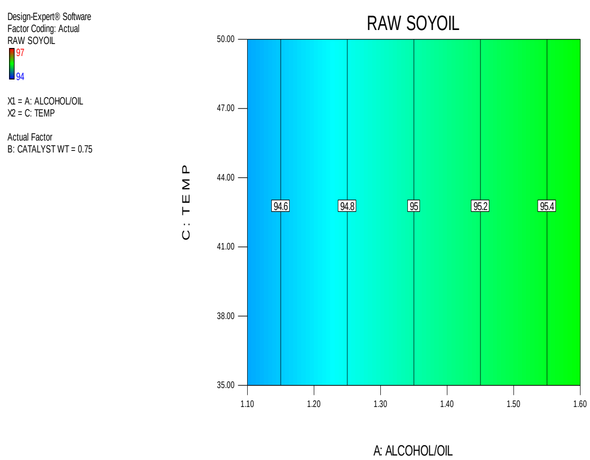

Figure 13. Contour Plot of Methanol-to-Oil Molar Ratio vs. Temperature.

A cubic plot is also drawn to show the interactions of the three process variables that were studied in this work as shown below. The plot show that the interaction effect on the refined soy oil is minimum at three locations of the cubic plot with a value of 94ml, and maximum settings at location (A+, B+, C-) with a value of 97ml.

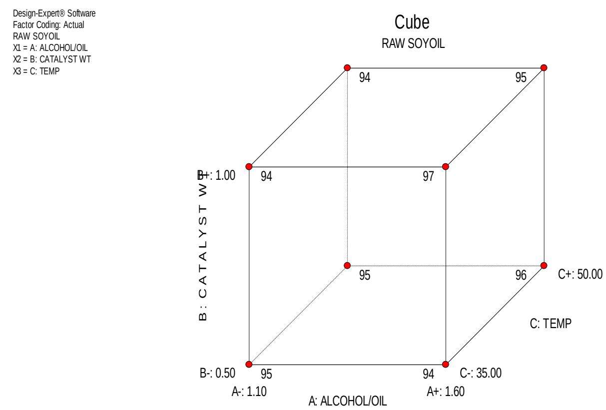

Figure 14: Cubic Interaction plot of the Three Process Variables.

CONCLUSION

In this work, the design of experiment was applied to optimize the synthesis process of ethylester from refined soy oil. A full two level factorial design has proved effective in the study of the influence of the process variables in the production of biodiesel. A response equation has been obtained for the yield of ester. From this equation, it is possible to predict adequately the operating conditions required to obtain a well-defined amount of ester. The study of the factors affecting the responses shows that, within the experimental range considered the highest triglyceride conversion rate of 97% was achieved after 2h of reaction at settings (A: 6:1, B: 1.0%, & C:35^{o}C). The optimal values of these parameters for achieving maximal conversion of oil to esters depended on the chemical and physical properties of the oil. The KOH having 1.0% concentration gave a complete conversion of triglycerides into esters based on higher yield.

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