

## Chemometrics Applied In Esterification Of Waste Cooking Oil For Biodiesel Synthesis

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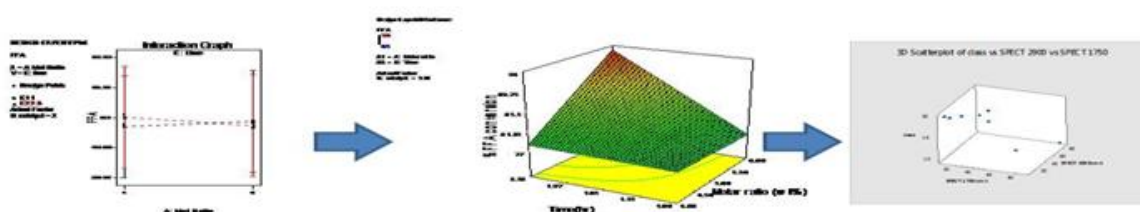
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### Abstrat:



Chemometric techniques are used as monitors in pretreatment of Waste Cooking Oil as a viable feedstock for biodiesel production at optimal reaction conditions using  $AlCl_3$  catalyst. The experimental design of three level-two factorial, response surface method (RSM) was able to effectively combine all the factors with factor interaction and response surface plot showing a good interaction of varying parameters and % free fatty acid (% FFA) conversion as response. Individual effect of factors indicated that Catalyst contributed 26.05 % to the responses while Alcohol-Oil molar ratio and Time combined, contributed 16.45%, all the three factors together had 20.97% effect on the responses. Linear discriminant analysis (LDA) successfully classified responses into two groups of moderate (1) to excellent (2), with corrected values after cross-validation having proportions of close to 1.000. Principal component analysis and fourier transformed infrared spectra (PCA-FTIR) analysis performed using log transformed spectra intensity of selected spectra regions from experiments showed component one (PC1) to be responsible for 85.64 % of variation in results while predictions were carried out by Principal component analysis and partial least square (PCA-PLS) methods. The high F-value (45.75) and coefficient of determination  $R_2$  close to one (0.8185) at 95% confidence level indicated the efficiency of the model.

**KeyWords :** RSM; PCA; FTIR; PLS; LDA; Chemometrics, waste cooking oil, biodiesel

### I. Introduction

In the last century, the consumption of energy has increased due to the change in human activities and significant growth of population. Petroleum fuels have been a key factor in the growth of industry, transportation, agricultural sector and many other areas serving basic human needs. The World's energy is mainly supplied by fossil fuels estimated at about 35.3% of the total in 2008. Present projections suggest an increased demand to 16 million tonnes per day (116 million barrels a day) by 2030. However, a global peak in oil production before 2035 has been predicted. The transport sector is a major consumer of petroleum fuels such as diesel, gasoline, liquefied petroleum gas (LPG) and compressed natural gas (CNG) [10]. Recently, many fuel developers have showed interests in alternative renewable fuels to substitute or compliment petroleum-based fuels. An alternative fuel shall be easily available, environment friendly and techno-economically competitive [1, 2]. Biodiesel or fatty acid methyl ester (FAME) is receiving increasing attention as an environmentally friendly and renewable alternative for the petroleum based diesel fuel [6]. The United State Standard Specification for Biodiesel (ASTM 6751) defines Biodiesel as a fuel comprising mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which can be used in diesel engines and heating systems [20].

Currently, the cost of biodiesel is high compared to conventional diesel oil because most of the biodiesel is produced from pure vegetable oil. Extensive use of edible oils may cause other significant problems such as starvation in developing countries. In Nigeria for instance, non-edible plant feedstock like jatropha has

been widely used in biodiesel production due to its low cultivation cost, and high oil yield. Current Estimated Oil Reserve in Nigeria is 35.9 billion barrels with natural daily production capacity of 2.7 million barrels of Crude Oil Gas is estimated at 185 trillion cubic feet of proven reserve as at (- OGJ). The 35.9 billion barrels of oil in reserve will be depleted by 30 – 36 years period, these gave rise to the Nigeria biofuel policy and incentives released in 2007 with the aim of spurring a vibrant bioenergy sector [22, 2]. By 2020, the projected peak of biofuel production would require about 500,000ha ~ 2% of the arable land (33million ha) in Nigeria [30]. However, the cost of biodiesel can be reduced by using low cost feedstock such as animal fat and waste cooking oil. The term “waste cooking oil” (WCO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. The use of waste cooking oil as feedstock reduces biodiesel production cost by about 60– 70% because the feedstock cost constitutes approximately 70–95% of the overall biodiesel production cost. It is reported that the prices of biodiesel will be reduced approximately to the half with the use of low cost feedstock [9, 13, 21, 34, 4]. However it would need to undergo a pre-treatment via esterification process before it could be used successfully in transesterification. This is due to their high free fatty acid (FFA) levels, which result in two major problems: (1) The catalyst is consumed resulting in either an increased catalyst concentration -and therefore higher chemical costs - or an incomplete or failed reaction (2) The reaction between the fatty acid molecule and catalyst creates soaps which manifest themselves as impurities in the biodiesel and must be washed out [19]. Free fatty acids are always present in oils, however mass concentrations above 4% will generate more soap than can be dealt with reasonably in a conventional catalyzed reaction and will prevent the reaction from going to completion in almost all cases [29]. Although transesterification is currently the best alternative for methyl ester production, the high free fatty acid present in waste cooking oil is still a problem and the esterification process still needs to be optimized, because some factors influence this reaction, such as catalyst type, alcohol type, molar alcohol/oil ratio, temperature, purity of the reagents, presence of water and amount of free fatty acids [25]. Several methods have been used to evaluate the quality of the process for biodiesel production, such as gas chromatography (GC) [20], high-performance liquid chromatography (HPLC) [28] and nuclear magnetic resonance (NMR) [14]. Furthermore, a Viscometer [11], Near Infrared Spectroscopy (NIR) and a multivariate approach [27], Fourier-Transformed Infrared (FTIR) Spectroscopy [32], Size Exclusion Chromatography (SEC) [5], Ultrasonic Measurement [8] and Fiber-Optic Near Infrared Spectroscopy with Correlation to <sup>1</sup>H Nuclear Magnetic Resonance Spectroscopy NMR [15] are some of the many analytical procedures developed to determine the composition of reaction mixtures during transesterification. There is therefore every need to properly evaluate, classify and quantify free fatty acids in esterified waste cooking oils using Chemometric tools before they are tranesterified to biodiesel. Chemometric techniques applied in this process would validate theoretically experimental findings.

Chemometric techniques in recent times has enabled modeling and optimization of single and multivariate reactions simultaneously, with cross-validated data presented in an easy to understand pictorial representations. Experimental design suggests a possible number of reactions among selected parameters therefore reducing total number of experiments to be carried out with expected outcomes while the Response Surface Methodology (RSM) modeling is used for determining optimal conditions for multivariate systems and individual and combined effect of factor interaction, it is considered an efficient technique for process evaluation. [17] experimental design analysis is useful in the solution for many types of industrial problems. A recent work Mbah G.O *et al* 2013 used it to check for factor interaction in biodiesel production from used soy oil. Multivariate methods using principal component regression (PCR), partial least square (PLS) and neural network (NN), have also been used to quantify biodiesel blends. [23] in addition to that, PCR and PLS regression were used to determine water and methanol in biodiesel samples with smaller validation and prediction errors. In association with chemometric tools such as principal component analysis (PCA) or hierarchical cluster analysis (HCA) methods, vibrational spectroscopy provides both qualitative and quantitative information [7] The advantage of using principal components scores from PCA is that such a method displays the clustering information of chemical species from multiple wavebands [16]. Spectroscopic analysis with pre-processing techniques for the application of principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used in this study to evaluate the infrared spectra of biodiesel and the reaction conditions for biodiesel production with high conversion using experimental factorial design. Samples analyzed by HATR/FTIR with PCA or HCA were compared with the conversion degree determined by gas chromatography analysis. Spectrofluorimetry is an analytical technique with attractive advantages because of its simplicity, rapidity, sensitivity, and selectivity. This technique, together with multivariate analysis (PCA) and Linear discriminant Analysis(LDA) was used to identify the addition of non transesterified residual vegetable oil, instead of biodiesel, to diesel oil. Also, spectrofluorimetry associated with Partial Least Square (PLS) has been used to determine the oxidation stability, concentration, viscosity and specific gravity of biodiesel-diesel blends. A method and a device sensor were developed to monitor the quality in process for the production of fuels using spectrofluorimetry total 3D and PCA. In this work, an analytical procedure was developed to monitor the esterification of waste cooking oil using spectroscopic techniques combined with Partial Least Squares (PLS)

regression, Linear discriminant analysis (LDA), Response surface methodology (RSM) and Principal component analysis (PCA) for the optimization of biodiesel production.

## **II. Experimental Section**

### **2.1 Materials and Methods**

Waste cooking oil (WCO) was obtained from different restaurants and pretreated by removing trace impurities while heating to remove residual moisture, physical and chemical properties of the oil was analysed by the following methods: Acid value (ASTM – D 974(00), Saponification value (ASTM - D 5558-95), Density ASTM method D – 1298 – (99), Moisture and Sediment (ASTM D2709 – 96) and Viscosity. Esterification of waste cooking oil was carried out by Aluminium Chloride catalyzed methanolysis with process parameters as shown in Table 3.

### **2.2 Spectroscopic Characterization of Waste Cooking Oil**

The FTIR analysis was carried out to investigate the position and presence of characteristic organic groups in the sample's structure, FTIR Analysis was carried out using KBr. The spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrometer (FTIR) within spectra range of 400-4000 $\text{cm}^{-1}$  with a resolution of 4 $\text{cm}^{-1}$ . All spectra were presented without baseline correction or normalization. Gas chromatography mass-spectrophotometer (GC-MS) a combination of two techniques used for separating the components in the mixtures was used to profile the esters in the waste cooking oil.

### **2.3 Chemometric Analysis**

#### **2.3.1 Response Surface Methodology (RSM)**

Experimental data generated using Design Expert statistical software (Stat-Ease Inc. USA) was analyzed via Response surface methodology (RSM) using a three factorial- two level design ( $3^2$ ). The response % free fatty acid conversion (% FFA) is initially fitted to the factors via multiple regressions. The quality of the fit is determined using the coefficient of determination ( $r^2$ ) and analysis of variance (ANOVA). The sum of squares and % contribution for main and interaction factor effects is calculated and significant factors (main and interaction) are identified by ANOVA technique [3]. The quadratic response surface model is fitted to the Equation. [33]. In this experiment the factor interactions was the focus to determine the influence of factors interaction on esterification of waste cooking oil with the aim of reducing the free fatty acid level.

#### **2.3.2 Multivariate Analysis**

Multivariate chemometric analyses; principal component analysis and partial least square regression analysis (PCA-PLS) were carried out to monitor the % free fatty acid conversion of the esterification process through predictive analyses by comparing spectroscopic technique of fourier transformed infrared (FTIR) spectra with Titrimetric analysis and the variance and coefficient of determination noted. Most influential spectral region among selected regions is extracted and it's intensities for each experiment used in prediction.

#### **2.3.3 Linear Discriminant Analysis**

A linear discriminant Analysis was carried out to classify and eliminate poorly converted fatty acid methyl esters (FAME) or poorly esterified samples, the % free fatty acid (% FFA) conversion of eight (8) esterification experiments was used as the training set of data, these is fitted into two groups of 1 (>80%) and 2 (<80%) from which the best free fatty acid conversion is deduced after cross-validation and correction of outliers. Correct classifications should give proportions of 1.000.

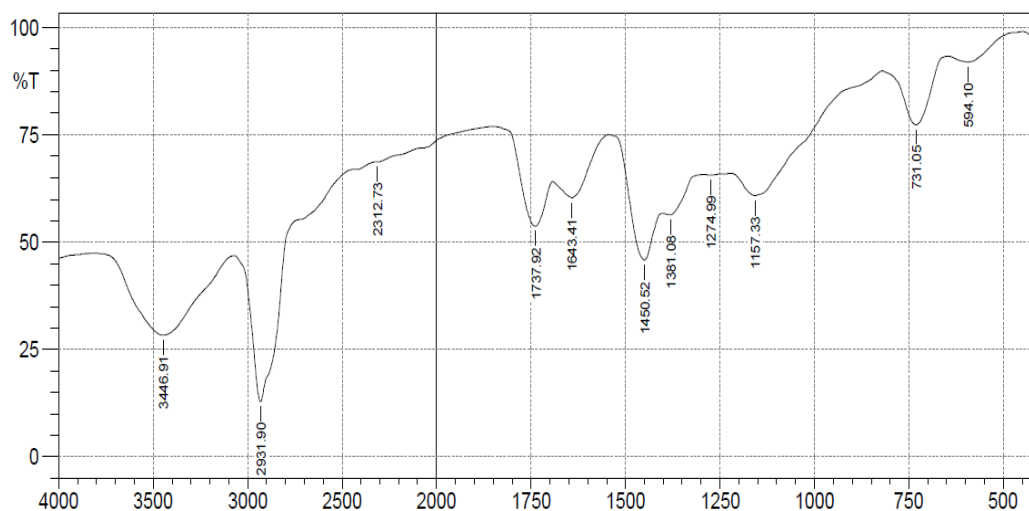
## **III. Results and Discussion**

### **3.1 Characterization of waste cooking oil**

Characterization was carried out to determine the physical and chemical properties of waste cooking oil And the results are shown in table 1. The FTIR Spectra of the waste cooking oil (WCO) indicated methylene group stretch and carboxylic acid group. Spectra is shown in figure 1. Table 2. Shows free fatty acids present in the waste cooking oil with the Gas Chromatography- Mass spectrometer shown in figure 2.

**Table 1 Physical and Chemical Properties of Waste Cooking Oil**

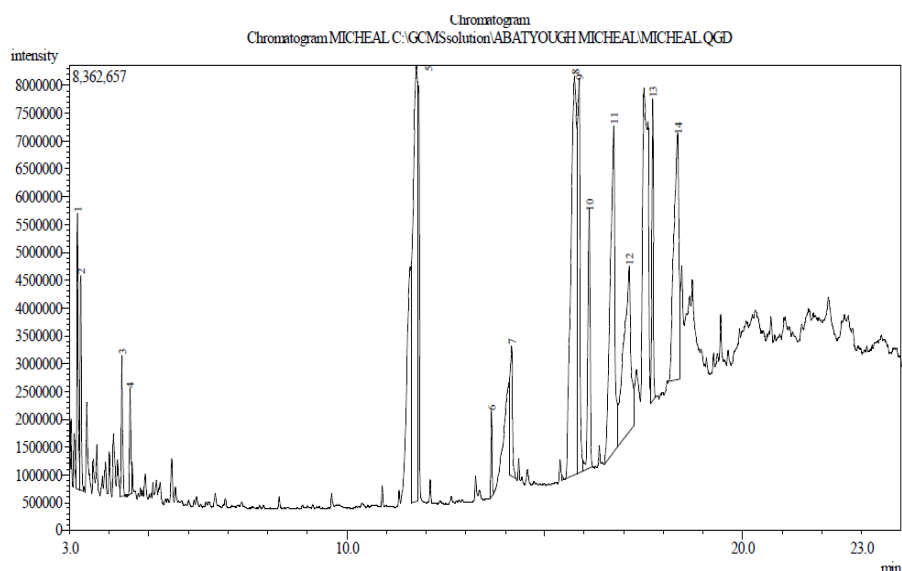
Parameter	Value	Method
Acid value	3.8 mgKOH/g	(ASTM – D 974(00))
Density	0.89 g/cm <sup>3</sup>	(ASTM- D1298 – 99)
Viscosity	18.6 mm <sup>2</sup>	(ASTM D 445-97)
Moisture and sediment	3.6 %	(ASTM D2709 – 96)
Saturated fatty acid	52.36 %	
Unsaturated fatty acid	41.95 %	



**Figure 1. Fourier Transformed Infrared (FTIR) Characterization of Waste Cooking Oil**

**Table 2. Free Fatty Acids present in Waste cooking oil**

Methyl Ester	Percentage Free Fatty Acid
Palmitic acid methyl ester (C16:0)	42.50
Myristic acid methyl ester(C14:0)	0.86
Stearic acid methyl ester(C18:0)	9.00
Oleic acid methyl ester(C18:1)	39.85
Linoleic acid methyl ester(18:2)	2.10



### 3.2 Physicochemical Properties of Waste Cooking Oil

The characterization of Waste cooking oil, both physical and chemical characteristics suggests it to be highly saturated. Hence the presence of high free fatty acids as observed in the Acid value of 3.8, free fatty acid profile indicates palmitic acid to be the highest saturated fatty acid while oleic acid having 39.85 is the highest mono-unsaturated fatty acid. with its high density and viscosity, the waste cooking oil will require to be pretreated via esterification before it can be transesterified into biodiesel.

### 3.3 Factor Interaction and Response Surface Plots for Esterification Reaction

The main effect interaction of factors is shown in table 4. and explains the contributions of individual factors and combined factors to the esterification process expressed as % conversion of free fatty acid. catalyst loading had the highest influence of 44.61% on %FFA conversion, interaction of methanol-oil molar ratio and reaction time and the interaction between catalyst load and reaction time had the same influence of 3.79% for the combined effect. The three factors interacting together had 30.98% while the lowest influence of 0.69% was for the interaction between catalyst loading and methanol-oil ratio. Generally the factors had a positive interaction and this accounts for the 94% high conversion on run seven (7) of the design of experiment.

**Table 3. Experimental Design with Responses**

Run	Molar ratio	Catalyst (wt%)	Time (hr)	%FFA Conveersion
1	6.00	2.00	2.30	67
2	6.00	5.00	1.00	71
3	4.00	5.00	1.00	87
4	4.00	5.00	2.30	83
5	6.00	2.00	1.00	71
6	4.00	2.00	2.30	79
7	6.00	5.00	2.30	94
8	4.00	2.00	1.00	70

**Table 4. Main effect of factors interaction**

Term	Effect	SumSqr	% Contribtn
A-Molar ratio	-4	32	4.9575
B-catalyst	12	288	44.6166
C-Time	6	72	11.1541
AB	1.5	4.5	0.6971
AC	3.5	24.5	3.7955
BC	3.5	24.5	3.7955
ABC	10	200	30.9837

$$\% \text{ FFA Conversion} = 77.75 + 6.00 (B) + 3.00 (C) + 0.75 (A * B) + 1.75 (A * C) + 1.75 (B * C) + 5.00 (A * B * C)$$

(1)

Response surface plots of percentage free fatty acid (%FFA) conversion in Figure. 4 shows the interaction between methanol–oil molar ratio and reaction time with respect to %FFA conversion. The conversion is seen to increase significantly at initial time, but insignificant change was observed for reaction time above 1.65hr. Increasing the time to higher hours decreased fatty acid conversion, this might be due to more methanol dissolving in the glycerol phase when the reaction time increased. Theoretically, increasing reaction time enhanced the esterification reaction since at higher time mass transfer rates among the reactants accelerated as the molecules gained more kinetic energy, and collided more eventually leading to higher conversion in a shorter period [24]. The same trend was also reported by Elsheikh *et al.* 2011 [12]. in esterification of crude palm oil using [BMIM][HSO<sub>4</sub>] 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 *et al.* 2006. [18] mentioned that it was related to the reaction time, where prolonged time favoured the backward reaction (i.e. hydrolysis of esters), which reduced the conversion.

Response surface plot for interaction between catalyst loading and methanol-oil molar ratio on %FFA conversion is illustrated in Figure 6. The conversion increased rapidly exceeding 86% for molar ratio of 6.0 regardless of any catalyst loading. Catalyst loading of 2 wt% had the highest impact on acid conversion. However, the effect of water produced during the esterification reaction significantly affects the process which could be improved by water removal in the mixture continuously.

Similarly interactions between reaction time and catalyst load against conversion is shown in Figure 8. The conversion for higher catalyst load remained almost constant as the conversion did not exceed 60%. Lower catalyst loadings gave better conversions, about 70% conversion was attained at 2wt% catalyst load and varying time. However %FFA conversion increased exponentially with increasing time and attained 89% conversion. The cross validation plot of actual % FFA conversions Vs Predicted % FFA conversions is shown in figure shows a straight line graph passing through the origin signifying a good prediction by analysis.

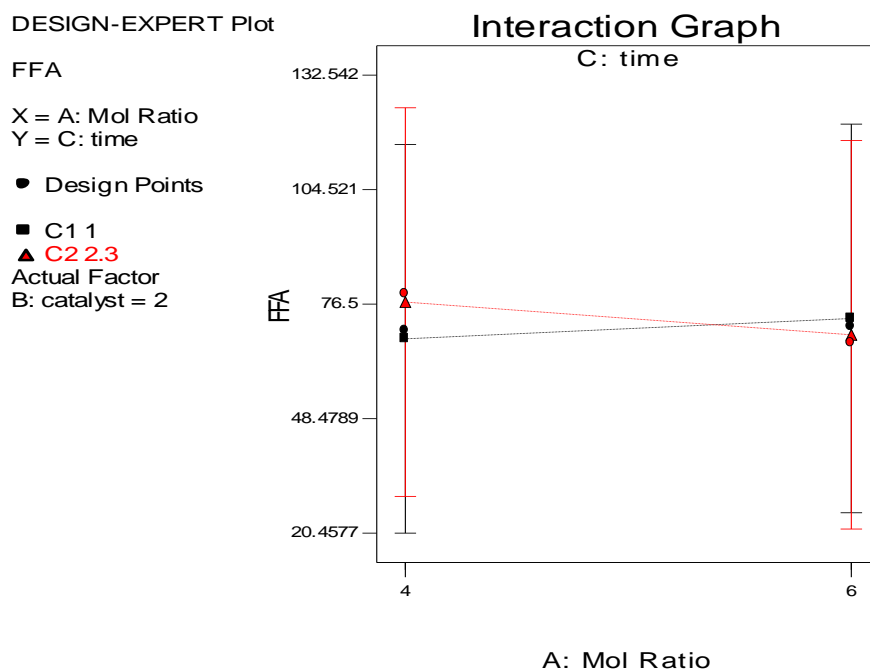


Figure 3. Factor interaction between time and methanol-oil molar ratio against %FFA conversion

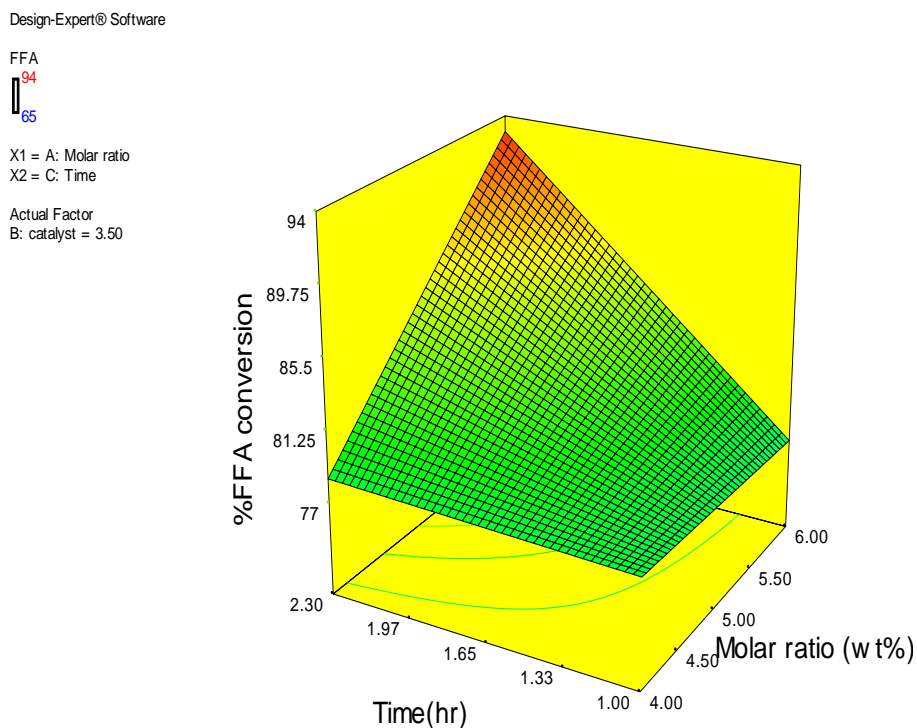


Figure 4. Response surface plot for factor interaction between time and molar ratio against %FFA conversion

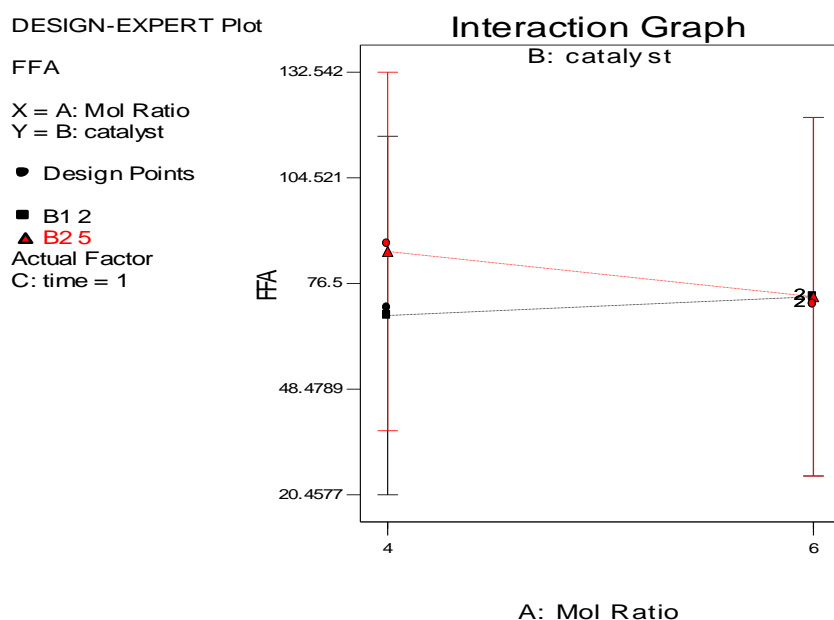


Figure 5. Factor interaction between catalyst and methanol-oil molar ratio against %FFA Conversion

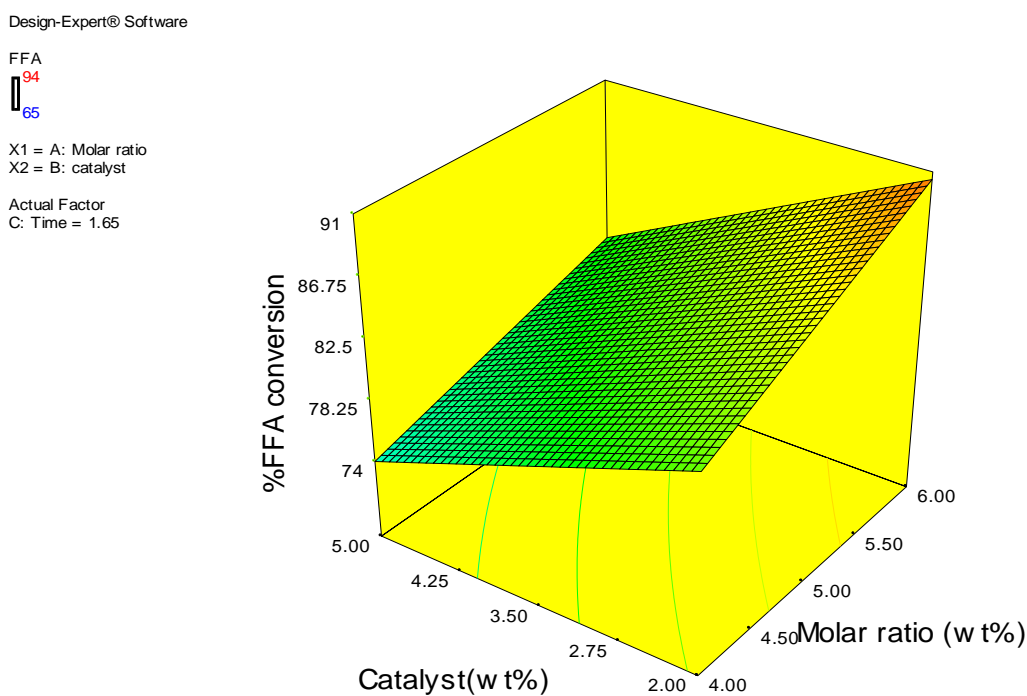


Figure 6. Response surface plot for factor interaction between catalyst and molar ratio against %FFA Conversion



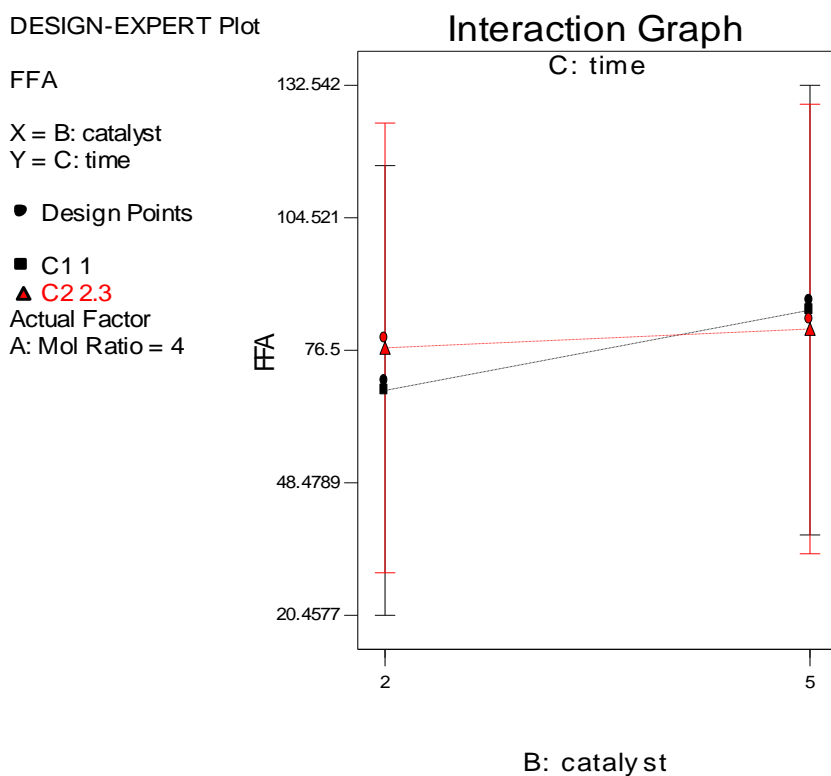


Figure 7. Factor interaction between time and catalyst against %FFA Conversion

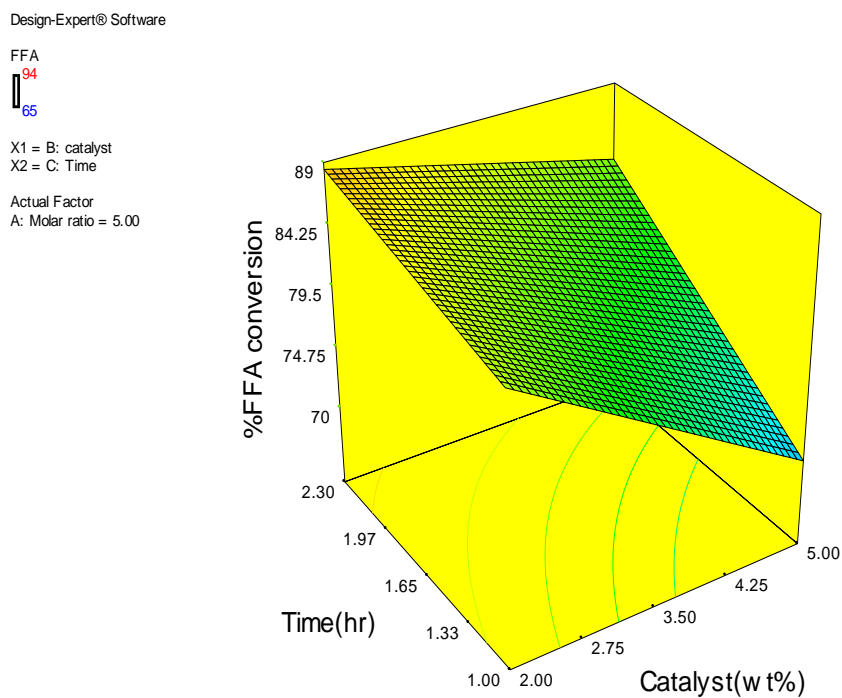


Figure 8. Response surface plot for factor interaction between time and catalyst against %FFA Conversion

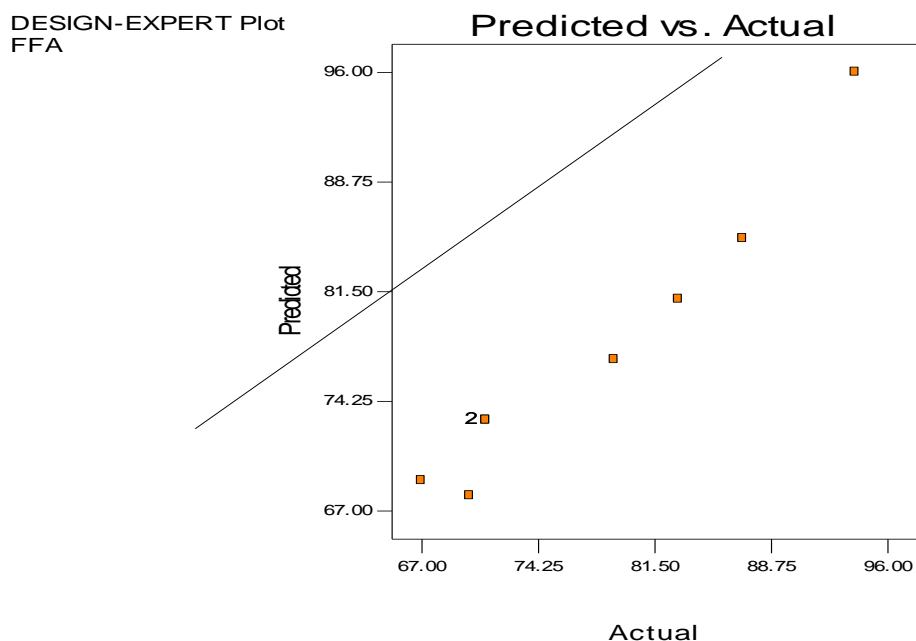


Figure 9. Plot of Actual % FFA conversions Vs Predicted % FFA conversions

### 3.4 Discriminant Analysis Classification of experimental Responses

Linear Discriminant Analysis (LDA) classification of experimental responses from the esterified waste cooking oil is shown in table 4. figure 9. shows 3D grouping of classes as scatter plots.

Table 5. Linear Discriminant Analysis Classification of esters %Free Fatty Acid methyl Conversion

		Original Values		Cross Validated values		Corrected Values	
		(1)	(2)	(1)	(2)	(1)	(2)
<b>Original</b>	Total N	3.0	5.0	3.0	5.0	2.0	6.0
	N Correct	3.0	5.0	2.0	5.0	2.0	6.0
	Misclassified	0.0	0.0	1.0	0.0	0.0	0.0
	Proportion	1.000	1.000	0.667	1.000	1.000	1.000
		<b>Squared distance</b> 11.2356			<b>Squared distance</b> 13.2410		
<b>MODEL</b>		(1)= -15.125 (-0.310) (0.705)			(1)= -14.438 (0.291) (0.119)		
		(2)= -2.313 (-0.115) (0.270)			(2)= -1.877 (0.039) (0.096)		

The LDA model was built by assigning y-values 0 and 1 to samples in the 2900cm<sup>-1</sup> and 1750cm<sup>-1</sup> classes as recommended by the principal component analysis of the spectra which showed these two spectra to have the highest factor loadings of 0.931 and 0.940 respectively. In the classification stage, a threshold value of 8.0 was adopted to discriminate the two classes. All samples in the training and cross-validation sets were correctly classified, meaning no false positives or false negatives were obtained. After Cross validation, previously predicted 100% correct classification in the Original set failed to pass as actually only 66.7% was predicted correctly. Removal of outliers gave the Corrected set a cross validated 100% correct classification. Only experiments three (3) and seven (7) were excellently converted, all others converted moderately. Figure 10. shows the classifications, moderate conversions are seen to be more drawn towards the 2.0 axis while excellent conversions held back to the 1.0 axis. The Linear Discriminant Analysis (LDA) models would be said to have provided accuracy, sensitivity and specificity rates of 100% for the validation and test sets.

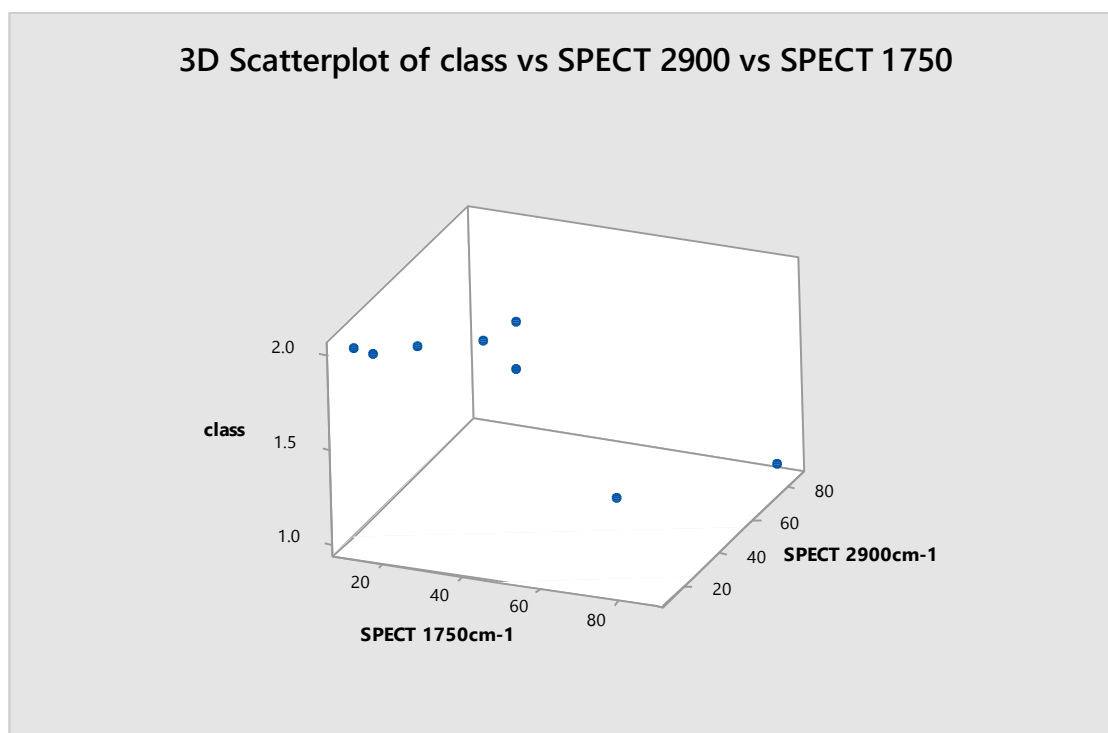


Figure 10. Scatter plot of classified % Fatty Acid Conversions

3.5 Multivariate analysis of %Free Fatty Acid Conversion

Table 6. FT-IR-PCA Extraction of components

Run	1750-1725 cm-1	1160-1050 cm-1	2,788- 3,037
1	16.80	49.19	11.59
2	11.63	11.45	12.39
3	58.86	59.44	54.09
4	51.51	44.72	15.41
5	24.86	61.64	18.33
6	40.81	99.46	39.92
7	86.46	93.07	85.22
8	38.02	39.32	27.47

The regions of the FTIR spectra with more important information were selected for multivariate analysis with principal component analysis (PCA). The selected regions were within the ranges of 649 – 1,816  $\text{cm}^{-1}$  and 2,788 – 3,037  $\text{cm}^{-1}$ , as shown in Table 6. In the spectral regions, there is chemical information from formed methyl esters and residual acylglycerols that did not transform during the methanolysis of the waste cooking oil [32]. The principal signals of the methyl esters were  $\nu\text{C}=\text{O}$  in 1700-1800  $\text{cm}^{-1}$   $\text{cm}^{-1}$ ,  $\text{CH}_2$  stretch in 2800-2900 $\text{cm}^{-1}$  and  $\nu\text{O}-\text{C}-\text{C}$  in 1160-1050  $\text{cm}^{-1}$ . The acylglycerols present similar signals but with small displacements that can be differentiated through the multivariate analysis technique.

PCA was performed on the reflectance spectra of the eight samples (24 spectrum) that were obtained in the reaction with experimental factorial design. After the preliminary analysis, the best conditions for data treatment were found and the principal components (PC) were calculated. outliers were detected and removed. With PCA it was possible to describe 85% of the data with component one alone as shown in table 7. And Scree plot in figure 11. Each calculated PC explains the individual contribution to the total variance. The factor loadings from Principal component one (PC1) at 0.940 showed the carbonyl region at 1720-1740 $\text{cm}^{-1}$  to have the highest chemical contribution to the response. These peak is known to have an ester group overlaped by a fatty acid which is stripped off by methanolysis of triglycerides, a change is observed around this peak after esterification as it becomes more intense and a reduction in the base area. The FT-IR/PCA developed for the chosen experimental factorial design proved that some experimental conditions are determining factors in reaching high conversion in biodiesel production by methanolysis of waste cooking oil.

Table 7. Total Variance of principal components Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	2.569	85.640	85.640	2.569	85.640	85.640
2	.267	8.887	94.527			
3	.164	5.473	100.000			

Extraction Method: Principal Component Analysis.

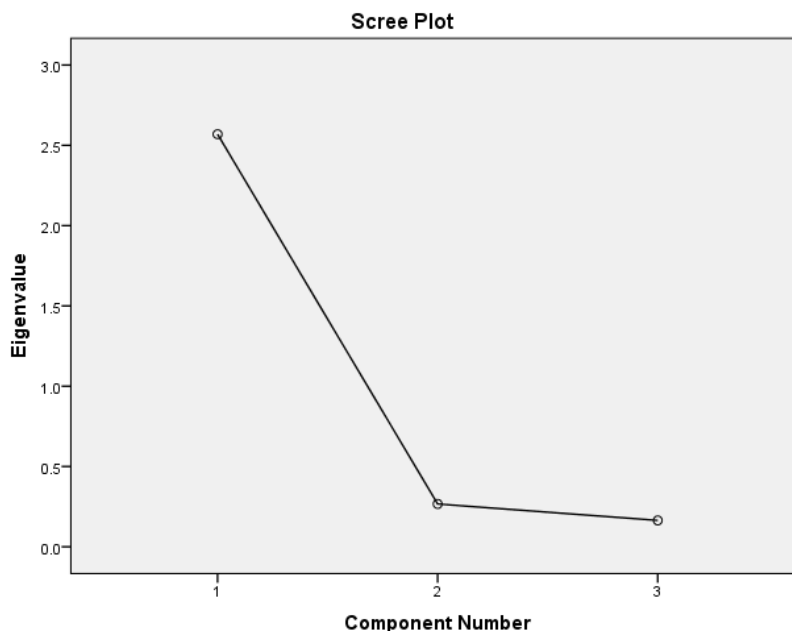


Figure 11. Scree plot of extracted components

### 3.6 FTIR-PLS prediction of %FFA Conversion

The FTIR spectra of the eight experimental design runs (experiments) were employed to derive a calibration equation relating FFA content to the integrated area of the (C=O) absorption of FFA (1700 - 1800  $\text{cm}^{-1}$ ) by a simple linear regression. This equation was subsequently used to predict the Free Fatty Acid (FFA) contents of eight (8) esterification experiments from FTIR spectra, and the predictions obtained were compared with the FFA contents determined by the standard titrimetric method (AOCS 1989). Taking the latter data as the true reference values, the accuracy of the FTIR predictions was assessed in terms of mean difference (MD) and standard deviation of the differences (SD) as suggested by [31].

The spectra of FTIR were reported for esterification of the waste cooking oil (WCO) at different reaction times, catalyst weight, and methanol-oil molar ratio. Knowing that during esterification reaction, the amounts of mono-, di- and triglycerides differ according to the reaction conditions, a PLS model was developed to monitor the reaction and evaluate the conversion of free fatty acids, Table 9. shows the FTIR predictions of % FFA Conversions obtained using the PLS model proposed. Figure 12. presents the graph of the predicted values relating to the reference titrimetric values for the PLS model, which was built using the FTIR spectra in the region of 1700 - 1800  $\text{cm}^{-1}$  as independent variables and the %FFA conversion values of titrimetric analysis as dependent variables. The region of 1700 - 1800  $\text{cm}^{-1}$  was chosen as independent variables to be a spectral region belonging to the group of ester carbonyls thus serving as a key parameter for the determination of conversion. As can be seen in the PLS model, the points are distributed around the line of bisection, showing that there is no systematic error in the predictions. In other words, there was a good correlation of this model determined by FTIR/PLS, showing a good P-value (0.001) < 0.05 and a coefficient of determination ( $R_2$ ) of 0.8185. This regression coefficient of the curve near to 1 indicates the efficiency of the model for making predictions above 80%. Thus, this PLS model served as reference model to determine the % FFA conversion of free fatty acids in the samples from esterification reaction at different reaction runs (experiments). The FTIR/PLS model has also been chosen in this work as a reference method, and has being used for predicting the yield of reaction of biodiesel production in Zagonel *et al.* 2004. In general, the proposed method (association between spectroscopic and PLS) was efficient for monitoring the esterification of waste cooking oil and is quite reliable for predicting the free fatty acid conversion to methyl esters in the esterification reactions.

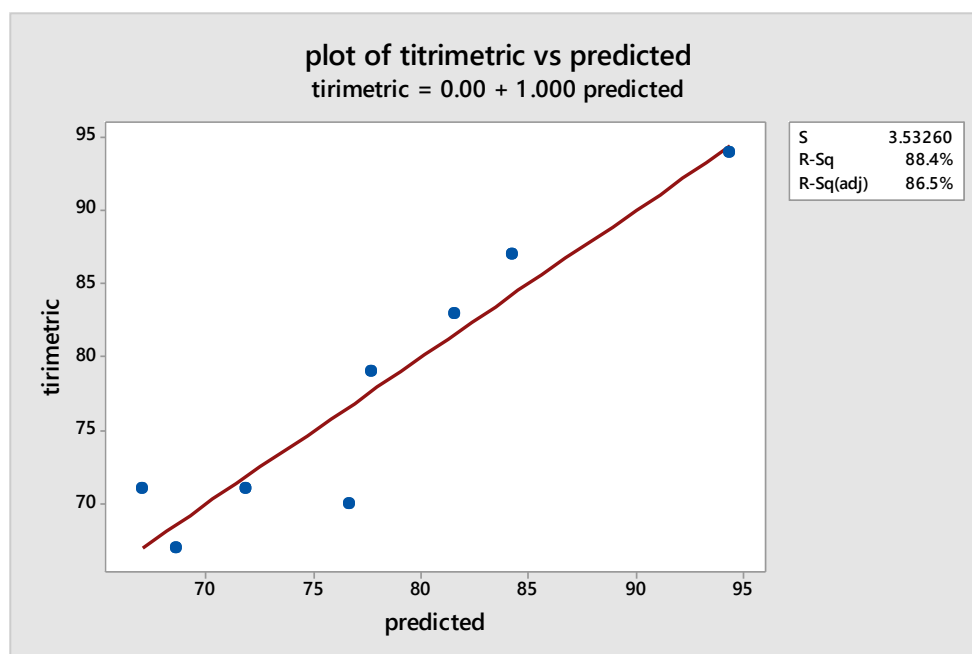
Table 8. ANOVA for FTIR –PLS Modelling

Source	Degree of Freedom	Sum of Squares	Mean Square	F-value	P-value
Regression	1	570.666	570.666	45.75	0.001
Residual Error	6	74.834	12.472		
Total	7	645.500			

Model equation:  
 $\%FFA \text{ Conversion} = (\text{FTIR}) 62.7247 + 0.3663 + 0.940249$  (2)

**Table 9. Predicted FT-IR Spectroscopic and Titrimetric Methods Compared**

Run	FT-IR (predicted)	Titrimetric Analysis
1	68.6	67
2	66.9	71
3	84.3	87
4	81.6	83
5	71.8	71
6	77.7	79
7	94.4	94
8	76.7	70



**Figure 12. % FFA Conversion plot of predicted FTIR Method against Titrimetric method**

#### IV. Conclusion

These research suggests that it is possible using Chemometric techniques; Response surface methodology (RSM), Linear discriminant analysis (LDA), Principal component Analysis (PCA) etc. and Spectroscopic methods to create a viable biodiesel feedstock from waste cooking oil by evaluating, classifying and also predicting percentage free fatty acid (% FFA) conversion in successive esterification processes in comparison to laboratory experimental methods. PLS-FTIR prediction gave 87% of the results to have been correctly predicted. Chemometric techniques would prove to be useful for researchers in developing countries with limited resources to enhance theoretical validation of results.

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