

# Modelling and Optimization of Synthesis of Waste Sunflower Methyl Ester by Taguchi Approach

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**Abstract**— The application of used vegetable oil as feedstock for the synthesis of biodiesel has been found to be affordable and does not interfere with the food chain. This present study applied L16 Taguchi design to optimize the catalytic transesterification of waste sunflower oil to waste sunflower methyl ester (WSME). The predicted optimized conditions were catalyst: oil ratio of 2.5:1, reaction time of 75 min, reaction temperature of 90 °C, catalyst particle size of 55 µm and methanol:oil ratio of 8:1. The contribution factor of the significant process parameters is found to be 49.04 % for catalyst:oil ratio, 25.32 % for reaction temperature, 18.44 % for catalyst particle size, and 6.65 % for reaction time. The analysis of variance presented a p-value of 0.0047 and a correlation coefficient of 0.9945. The actual fatty acid (FA) conversion is in satisfactory agreement with the predicted value. Thus, the optimization of the percentage FA conversion using Taguchi design generated optimal parametric conditions for the cost-effective and time-saving transesterification of waste sunflower oil to WSME.

**Index Terms**—ANOVA, fatty acid, optimization, Taguchi design, transesterification.

## I. INTRODUCTION

The burning of fossil fuel to generate energy has come with lots of damaging consequences including air pollution which has led to continuous depletion of ozone layer, emission of greenhouse gas and particulate matter, the formation of smog and escalating global temperature. The application of derivatives of fossil fuel, particularly petroleum-based diesel (PBD) fuel in compression ignition (CI) engines are not only costly, requires highly technical refining process and architecture but also result in not-too-impressive engine performance and emission of regulated gases. When compared with spark ignition engines, CI engines have gained acceptance in on-road and off-road applications partly due to its strength, greater torque, better durability, better fuel economy, superior thermal efficiencies and higher power output [1]. However, the combustion of PBD fuel in CI engines heightens the emission of particulate matters (PM), carbon dioxide (CO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>), nitric oxide (NO<sub>x</sub>), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) as well as other unregulated but dangerous gases which are harmful to the environment [2] which are major precursor of global

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and utilization of PBD fuel will continue to emit higher carbon and other greenhouse gasses with its attendant effects warming. The exploitation, extraction, refining of fossil fuel on the environment and deterioration of air quality. The remedy to this situation is to invest in oxygenated fuels like biofuel (bioethanol and biodiesel) as viable alternatives [1, 3].

Biodiesel also branded as fatty acid methyl ester (FAME) is generated from straight vegetable oil through various techniques including pyrolysis, catalytic distillation transesterification, microwave technology, microemulsion, supercritical methanol [4-6]. Transesterification is the reaction of feedstock (oil) with alcohol (methanol or ethanol) in the presence of a catalyst (homogeneous, heterogeneous, enzyme) to synthesize biodiesel and glycerol. The advantages of the transesterification method include its low cost, high conversion efficiency, suitability for household and industrial adaptations, and the closeness of the properties of the product to PBD fuel [7, 8]. The choice of used vegetable oil as a biodiesel feedstock is reinforced by its affordable cost, availability, and non-interference with food security. Collection of used vegetable oil from consumers will prevent its unlawful disposal which usually results in blockage of drains and polluting terrestrial and aquatic habitats [9-11].

The application of conventional one-variable-at-a-time (OVAT) experimental technique is expensive, time-consuming, requires huge laboratory architecture and has not been able to unravel the mutual understanding among the parametric variables. OVAT is also deficient in identifying the significant parameters and the contributing factor of each parameter. In order to solve this problem, OVAT is often replaced by the use design of Experiment (DoE) software, which has the capacity to acquire most of the needed information from a minimum exposure of carefully scheduled experiments by concurrently altering all the process factors. DoE slashes the number of experimental runs, saves time, chemicals and feedstocks, and uncover the mutual interaction among the process independent parameters and the response [12, 13].

Taguchi orthogonal approach (OA) is easy to use, fast and suitable optimization tool that has effected desirable outcomes working within smaller interactions of parameters. In research, Buasri et al. [14] applied Taguchi L9 OA to optimize the process parameters in the transesterification of palm oil to FAME using calcined scallop waste shell. the researchers reported the effectiveness of Taguchi design to determine the optimal reaction conditions. Similarly, Singh and Verma [15] used Taguchi's L27 OA for the optimization of the process parameters in the generation of

methyl ester from waste cooking oil and reported that the approach predicted the optimum condition and the interactions between the parameters and the response. The application of Taguchi design to optimize process parameters in the transesterification of various feedstocks to biodiesel has been reported to have favourable outcomes with four to five variables investigated. These attempts have yielded optimum operating conditions, mutual interactions among the independent parameters as well as determining the contributing factors of each variable [16-18].

This study aims at optimizing independent parametric conditions for the transesterification of waste sunflower oil (WSFO) to waste sunflower methyl ester (WSME) using CaO catalyst produced from high-temperature calcination of waste chicken eggshell. The optimization of parametric conditions (reaction time, reaction temperature, catalyst amount, catalyst particle size and methanol to oil ratio) to predict free fatty acid (FFA) conversion using the Taguchi design will interrogate the relationship between the responses and the independent variables. The level of significance, the mutual interactions, and the contribution factor of the variables will be systematically established. The motivation is to unravel a model equation capable of predicting the responses within acceptable limits with the minimum number of experimental runs. To this end, the scope of this present study is limited to the adoption of the Taguchi method to model an equation to predict the responses within the set parametric factors and levels. The analysis of variance (ANOVA) of the resulting model will be carried out to estimate their implication and the parameters of the preferred model are uncovered using non-linear regression technique.

## II. MATERIAL AND METHOD

### A. Materials collection and preparation

Waste Sunflower (WSFO) sample was collected at the point of disposal from a takeaway outlet beside Howard College, University of KwaZulu-Natal (UKZN), Durban. The oil has been used repeatedly for fourteen (14) days to fry potato chips. The oil was heated to 110 °C and filtration to remove moisture and impurities. The acid value of the waste oil was determined in line with the American Oil Chemists' Society (AOCS) Ca 5a-40 standard [19].

Waste chicken eggshells were collected from restaurants at the Howard college campus' cafeteria, UKZN. The inner white membrane adhering to the shells were removed, washed and rinse severally with deionized water. The clean shells were oven-dried, pulverized and passed through a 75 µm sieve mesh. The resulting powder was subjected to high-temperature calcination of 900 °C for 3 hours as described in our earlier work [20]. The eggshell powder was subjected to x-ray diffraction (XRD) and scanning electron microscope (SEM) characterization. The calcined eggshell powder is later warehoused in an airtight glass vial in a desiccator to prevent contamination and oxidation. Methanol (analytical grade 99.5 %; Merck, South Africa, univAR) was used as alcohol.

### B. Transesterification process

Transesterification of WSFO was carried out in a 500 mL flat bottom flask. The acid value of WSFO allows for one

stage transesterification process. The filtered WSFO, methanol and calcined CaO derived from waste chicken eggshell powder were mixed in a flat bottom flask and heated to predetermined. A digital thermocouple was utilized to verify the temperature of the reacting mixture throughout the duration of the experiment. Different catalyst concentration, reaction temperature, reaction time, catalyst:oil and methanol:oil ratio were used during each batch of the transesterification process. A magnetic stirrer at 1200 rpm was used to ensure homogeneous mixing of the reacting solution throughout the process. The resulting mixture was thereafter filtered in a vacuum filtration set up to recover the catalyst. The filtered mixture was transferred to a separating funnel and permitted to settle for 12 hours and the glycerol coagulated at the bottom of the separating funnel. The glycerol is drained out and the remaining crude biodiesel is decanted without the glycerol layer and transferred into a glass container for further purification and analysis.

The FAME conversion (%) of WSFO to biodiesel were estimated by;

$$FFA\ conversion\ \% = \frac{Weight_{Triglycerol} - Weight_{Biodiesel}}{Weight_{Biodiesel}} \times 100\% \quad (1)$$

### C. GCMS analysis of WSME

The fatty acid composition of the WSME was determined using a Shimadzu gas chromatography-mass spectrometer (GCMS) using an ultra-alloy-5 capillary column and GCMS-QP2010 Plus software. A 2 µL sample was injected in splitless mode, helium served as the carrier gas and the total time was 39.81 min. The column temperature profile was as follows: 50 °C for 60 s; then increased at 15 °C/min until 180 °C held for 60 s; then increased at 7 °C/min until 230 °C held for 60 s; then increased at 5 °C/min until 350 °C and held at 350 °C for 5 min.

### D. Statistical analysis by Taguchi design

In order to effectively use the Taguchi design, pilot experimentation was conducted in triplicates to determine the independent and dependent parameters and their levels for FFA conversion. A suitable optimization technique was thereafter selected and assign parameters accordingly. The optimization tool was applied to generate a model equation and the predicted response. If the model is significant, the influence of the input parameters and the optimum factor of the significant process parameters are estimated appropriately to determine the best value of the response characteristic. The analysis of variance (ANOVA) was performed to unearth the significance of each parameter. The predicted response compared with the experimental data to determine the level of agreement.

## III. RESULT AND DISCUSSION

This section comprises the statistical analysis of the outcome of the Taguchi design, characterization of the catalyst and the GCMS analysis of the biodiesel.

TABLE I  
EXPERIMENTAL DESIGN MATRIX SHOWING THE ACTUAL, PREDICTED AND RESIDUAL VALUE

Run	Factors					FFA conversion (%)		Residual
	A	B	C	D	E	Actual Value	Predicted Value	
1	2.5	125	60	75	4	85.43	85.74	-0.31
2	1.5	90	45	75	8	86.76	86.37	0.39
3	1	90	60	55	6	78.32	77.78	0.54
4	1	75	45	45	4	69.45	69.76	-0.31
5	2.5	150	45	65	6	82.5	81.96	0.54
6	2.5	90	75	45	10	71.68	72.30	-0.62
7	2	150	60	45	8	73.78	73.39	0.39
8	1.5	150	75	55	4	85.51	85.82	-0.31
9	2	75	75	75	6	70.86	70.32	0.54
10	2	90	90	65	4	75.45	75.76	-0.31
11	1.5	125	90	45	6	87.54	87.00	0.54
12	1.5	75	60	65	10	81.66	82.28	-0.62
13	1	125	75	65	8	70.55	70.16	0.39
14	1	150	90	75	10	84.66	85.28	-0.62
15	2	125	45	55	10	76.58	77.20	-0.62
16	2.5	75	90	55	8	87.54	87.15	0.39

TABLE II  
ANALYSIS OF VARIANCE (ANOVA) OF MODEL AND PROCESS PARAMETERS

Source	Sum of Squares	Contribution factor (%)	Degree of freedom	Mean Square	F Value	p-value Prob > F	
Model	664.95	-	12	55.41	45.02	0.0047	Significant
A	327.91	49.04	3	109.30	88.81	0.0020	
B	44.48	6.65	3	14.83	12.05	0.0352	
C	169.28	25.32	3	56.43	45.85	0.0053	
D	123.27	18.44	3	41.09	33.39	0.0083	
Residual	3.69	0.55	3	1.23			
Cor Total	668.64	100	15				

A. Analysis of variance (ANOVA) of the transesterification process

The experimental design matrix of the actual, predicted and the residual values are shown in table I. The L16 Taguchi design brings up 16 runs. The actual FFA conversion data were generated from the actual experiments while the predicted data were generated by the model equation. The residual is the difference between the actual and the predicted values for each run. The actual FFA conversion ranges between 69.45 % and 87.54 % while the predicted FFA conversion ranges between 69.76 % and 87.15 %.

B. Analysis of variance (ANOVA) of the transesterification process

As shown in table II, the analysis of variance of the selected factorial model and the process parameters show that the model is significant. The p-value of 0.0047 indicates there is only a 0.47 % possibility that an F-value of 45.05 could happen due to noise. The value of probability > F less than 0.05 signposts that the model term is significant. From table II, catalyst:oil ratio, reaction time, reaction temperature, and catalyst particle size are the significant factors that influence the response. The effect of the individual process parameters is estimated by the contribution factor (%) using the following equation 2.

$$\% \text{ Contributing factor} = \frac{\text{Sum of squares of the particular variable}}{\text{Sum of squares of all the variables}} \times 100 \quad (2)$$

The catalyst:oil ratio has the highest contribution factor of 49.04 % making it the most significant parameter that influences FFA conversion followed by reaction temperature at 25.32 % and the catalyst particle size with contribution factor of 18.44 %. The calculated contribution factor for reaction time was found to be 6.65 %, making it the parameter with the least influence on the response.

The analysis of variance from the model, as shown in table III, of the correlation coefficient ( $R^2$ ), adjusted correlation coefficient ( $R_{adj}^2$ ), and the predicted correlation coefficient ( $R_{pred}^2$ ) are 0.9945, 0.9724 and 0.8429 respectively. The value of  $R_{pred}^2$  agrees reasonably with the  $R_{adj}^2$  since the difference between them is less than 0.2. The adequate precision measures the signal to noise ratio. The estimated value of 17.393 indicates adequate signal and greater than the 4 which is suitable. This confirms that the model can be utilized to traverse the design space. The standard deviation is 1.11 while the coefficient of variance is 1.4 % which are low enough and a sign that the model can accurately predict the optimum conditions with elevated accuracy [21-23].

TABLE III  
STATISTICAL PARAMETERS ESTIMATED FROM ANOVA STUDY

Parameter	Value	Parameter	Value
Standard Deviation	1.11	R-Squared	0.9945
Mean	79.27	Adj R-Squared	0.9724
C.V. %	1.40	Pred R-Squared	0.8429
PRESS	105.02	Adeq Precision	17.393
-2Log Likelihood	21.94	BIC	57.99
		AICc	229.94

C. Regression model equation

The analysis of the predicted regression model and the different process parameter were carried out using ANOVA.

The ANOVA has identified the significant parameters and their contribution factor to the achievement of the response. The analysis of the regression model was done with the significant process parameters while neglecting the insignificant process parameters using the model equation to estimate the coefficient of each significant process parameter. The regression model equation is shown in equation 3.

$$y = 79.27 - 3.52 * A[1] + 6.1 * A[2] - 5.1 * A[3] - 1.89 * B[1] - 1.21 * B[2] + 0.76 * B[3] - 0.44 * C[1] + 0.53 * C[2] - 4.62 * C[3] - 3.65 * D[1] + 2.72 * D[2] - 1.73 * D[3] \quad (3)$$

where  $y$  = FFA conversion (%),  $A[1]$ ,  $A[2]$ , and  $A[3]$  are the catalyst:oil ratio at the first, second and third levels respectively,  $B[1]$ ,  $B[2]$ , and  $B[3]$  are reaction time at the first, second, and third levels respectively,  $C[1]$ ,  $C[2]$ , and  $C[3]$  are reaction temperature at the first, second, and third levels respectively and  $D[1]$ ,  $D[2]$ , and  $D[3]$  are the catalyst particle size at the first, second, and third levels respectively in line with the factors and levels described in table I. The FFA conversion predicted by the model equation (Equation 3) is in agreement with the actual FFA conversion as shown in fig. 1, which confirms the effectiveness of the model to predict the response.

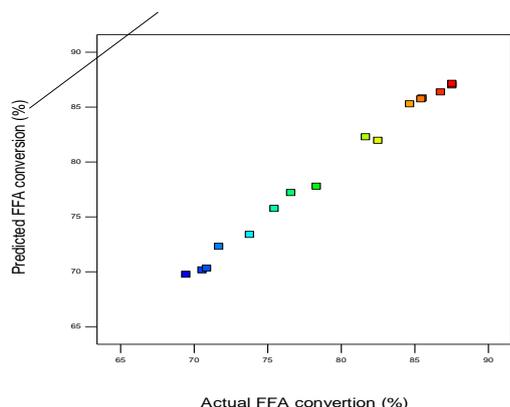


Fig. 1: The actual FFA conversion (%) against predicted FFA conversion (%)

#### D. Optimum condition

Results achieved from ANOVA indicated that methanol:oil ratio is an insignificant factor in the prediction of FFA conversion using the model established from Taguchi design. In order to achieve the best condition for FFA conversion, catalyst:oil ratio, reaction time, reaction temperature, and catalyst particle size are influential and are termed as significant process parameters. In this study, the optimum conditions are a catalyst:oil ratio of 2.5 %w/w, reaction time of 75 min, a reaction temperature of 90 °C, and catalyst particle size of 55 μm. These conditions, summarized in Table IV, are encapsulated in run 16 which also has the highest actual FFA conversion (table I).

Without a doubt, the model predicted the optimum response in agreement with the actual data.

TABLE IV  
OPTIMUM CONDITIONS FOR FFA CONVERSION (%)

Parameter (unit)	Optimum value
A: Catalyst:WSFO ratio (% w/w)	2.5:1
B: Reaction time (min)	75
C: Reaction temperature (°C)	90
D: Particle size of catalyst (μm)	55
E: Methanol:WSFO ratio	8:1

#### E. Influence of process parameters on FFA conversion

##### 1) Effect of catalyst:oil ratio

Fig. 4(a) shows the effect of catalyst:oil ratio on FFA conversion. Catalyst:oil ratio was varied between 1 %w/w and 2.5 %w/w at a reaction time of 125 min, reaction temperature of 60 °C catalyst particle size of 75 μm and methanol:oil ratio of 4:1. The maximum FFA conversion of 89 % was achieved at catalyst:oil ratio of 1.5:1 while the least FFA conversion rate of 78 % was gotten at the catalyst:oil ratio of 2:0. Though FFA conversion at 2.5:1 is also high, a catalyst:oil ratio of 1.5:1 is preferred for economic reasons [24].

##### 2) Effect of reaction temperature

Fig. 4(b) depicts the influence of reaction temperature (°C) on FFA conversion (%) when the catalyst:oil ratio was maintained at 2.5:1, reaction time at 125 min, catalyst particle size at 75 μm and methanol:oil ratio at 4:1. FFA conversion reduced after the temperature of 50 °C. The highest and least FFA conversion was achieved at 90 °C and 75 °C respectively. The reaction temperature of 90 °C, which is higher than the boiling point of methanol can only be achieved if the reacting container is covered to prevent the evaporation of methanol thereby decreasing the methanol concentration in the reacting mixture [25].

##### 3) Effect of reaction time

Fig. 4(c) shows the effects of reaction time on FFA conversion when catalyst:oil ratio was maintained at 2.5:1, reaction temperature at 60 °C, catalyst particle size at 75 μm and methanol:oil ratio at 4:1. The FFA conversion increases with the increase in reaction time. Bokhari et al. [26] advocated sufficient residence time to allow for the reactants to interrelate. However, with the use of a catalyst and the reversibility of the transesterification process, prolonging the reaction time might be costly and not advisable. A good balance between reaction time and the temperature is recommended for economical transesterification process [22].

##### 4) Effect of catalyst particle size

With a catalyst:oil ratio of 2.5:1, reaction time of 125 mins, a reaction temperature of 60 °C and methanol:oil ratio of 4:1, maximum FFA conversion of 80 % were recorded at 55 μm and 75 μm as shown in fig. 4(d). The four particle sizes of the catalyst resulted in high FFA conversion as a result of an increase in the surface contact area.

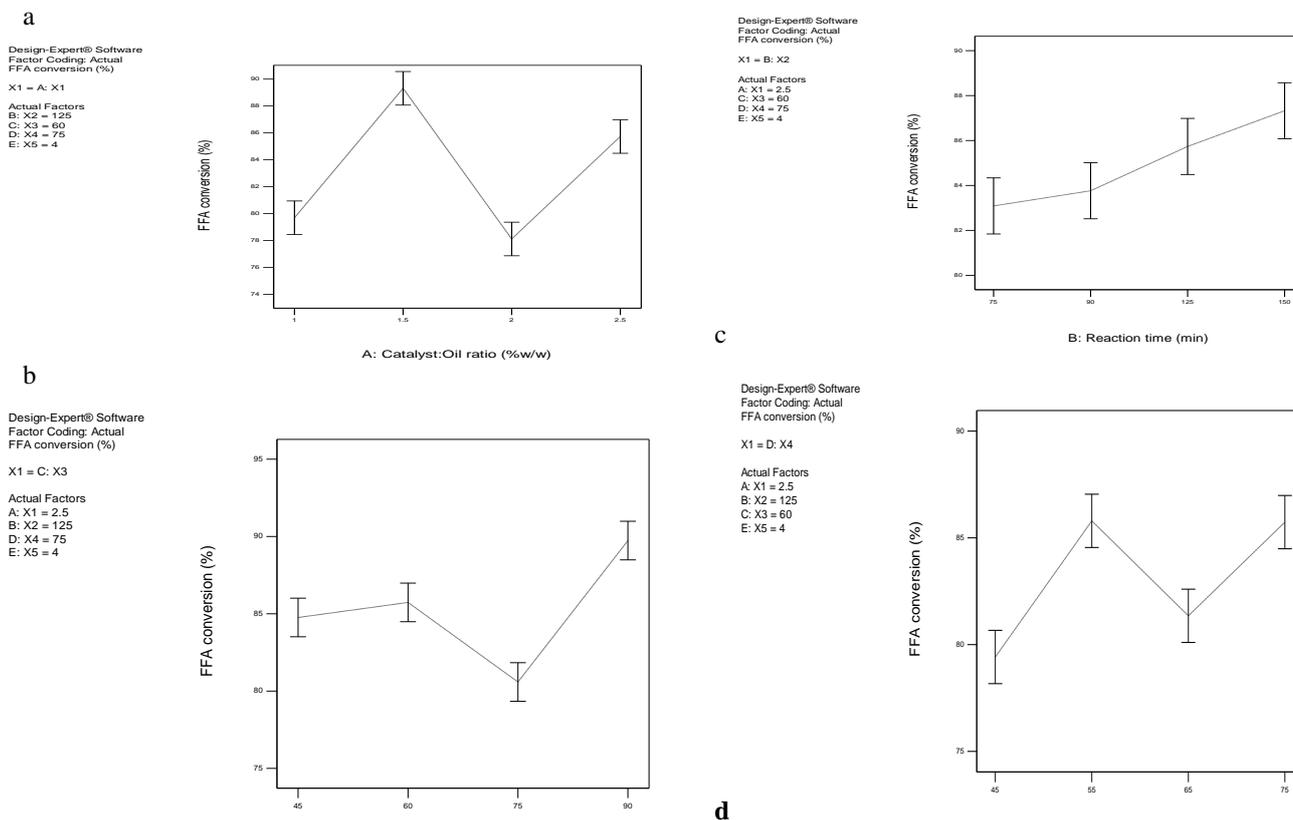


Fig. 4: Effect of (a) catalyst:oil ratio (b) reaction temperature (c) reaction time (d) catalyst particle size on FFA conversion (%)

#### F. Characterization of the eggshell catalyst

The waste chicken eggshell powder was calcined at 900 °C for 3 hours and the ensuing powder was characterized. Fig 5 shows the XRD pattern and SEM image of the calcined Eggshell powder. The XRD pattern of the calcined waste chicken eggshell powder reveals that it contained 63.8 % lime (CaO), 24.9 % portlandite (Ca(OH)<sub>2</sub>), 10.9 % calcium oxalate (C<sub>2</sub>H<sub>2</sub>CaO<sub>5</sub>) and 0.4 % calcite (CaCO<sub>3</sub>). The high CaO content is as a result of high-temperature calcination which has decomposed the CaCO<sub>3</sub> to CaO and CO<sub>2</sub>. The presence of Ca(OH)<sub>2</sub> might be due to atmospheric exposure during storage and analysis while the presence of 0.4 % CaCO<sub>3</sub> might be due to incomplete decomposition of CaCO<sub>3</sub> to CaO [27]. The SEM image shows that the calcined waste chicken eggshell powder showed irregular shape bonded together as aggregates with high specific surface area. The high surface area will enhance transesterification reaction and consequently improved FFA conversion than uncalcined eggshell powder [28].

#### G. FFA composition of FAME

The acid value of the waste sunflower oil was found to be 0.72 mg/g, making it suitable for the transesterification process. The outcome of transesterification of waste sunflower oil to waste sunflower methyl ester (WSME) using calcined waste chicken eggshell was subjected to GCMS analysis to determine its free fatty acid composition. Fig. 6 shows the chromatograph of the WSME to determine the FA composition. The peaks in the chromatograph indicate the individual FA. The WSME contains 73.72 % unsaturated FA and 26.28 % saturated FA as shown in Table V.

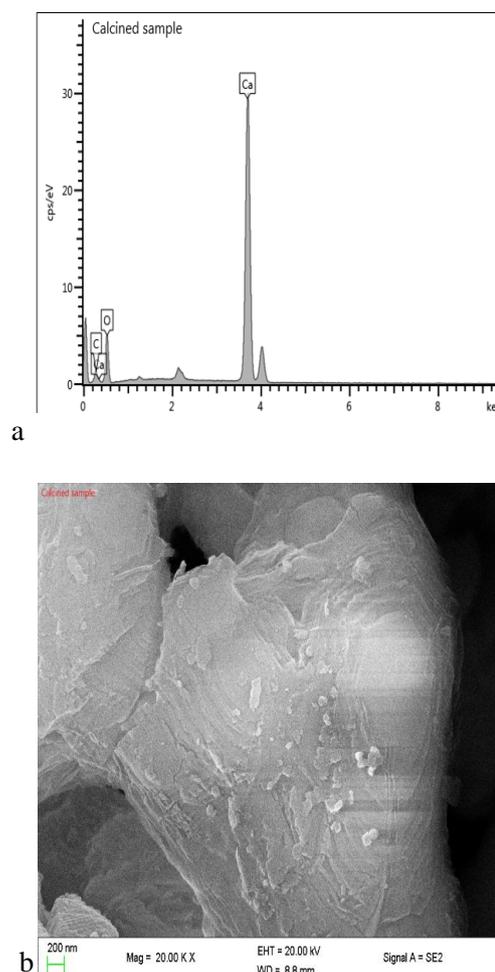


Fig. 5: (a) XRD pattern (b)SEM image of calcined waste chicken eggshell

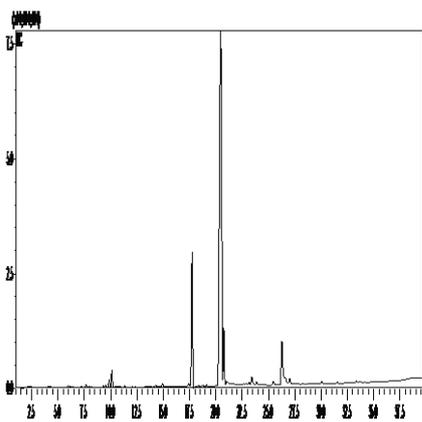


Fig. 6: Chromatograph of the FA composition of FAME from GCMS

TABLE V  
RESULT OF THE FA COMPOSITION OF WSME

Name	% Composition (WSME)
Palmitic acid	15.10
Linoleic acid	84.16
Behenic acid	0.73
Saturated fatty acid	26.28
Unsaturated fatty acid	73.72
Total	100

#### IV. CONCLUSION

The L16 Taguchi design has been applied to optimize the FFA conversion in the transesterification process of WSFO to WSME using calcined waste chicken eggshell. The model has been adjudged significant and regression model equation has predicted the response with 95 % assurance. The actual FFA conversion and the predicted FFA conversion has been found to be in agreement. The ANOVA results showed the coefficient of correlation and adjusted coefficient of correlation are 0.9945 and 0.9724 respectively. Also, the significant process parameters and their contribution factor have been found to be catalyst:WSFO ratio of 49.04 %, reaction temperature of 25.32 %, catalyst particle size of 18.44 % and reaction time of 6.65 %.

The optimum operating conditions for FFA conversion was found to be 2.5:1 catalyst:WSFO ratio, reaction time of 75 min, reaction temperature of 90 °C, catalyst particle size of 55 µm and methanol:WSFO ratio of 8:1. The XRD and SEM analyses of the eggshell catalyst showed the effectiveness of high-temperature calcination in decomposing CaCO<sub>3</sub> to CaO for effective transesterification reaction. The application of Taguchi OA has reduced the number of experimental runs to 16 and ensure a cost-effective transesterification of waste sunflower oil to FAME when compared with the conventional one-variable-at-a-time method.

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