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Modelling and Optimization of Transesterification of Waste Sunflower Oil to Fatty Acid Methyl Ester: A case of Response Surface Methodology vs Taguchi Orthogonal Approach

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Abstract:
Determining the cost-effective process combinations that will achieve prime fatty acid methyl ester (FAME) is laborious, onerous and time-wasting using the experimental process; this has necessitated the need for modelling and optimization tools. This research study, utilizes and compares regression models developed by central composite design of randomized response surface methodology (RSM) and L16(4^15) Taguchi orthogonal approach for the optimization of five process parameters to predict FAME yield (%) for the transesterification of waste sunflower oil (WSFO). The process was catalyzed by calcium oxide developed from high temperature calcination of waste chicken eggshell powder. RSM predicted an optimum FAME yield of ~91 % at process parameters of 1.5 %w/w catalyst: WSFO ratio, catalyst particle size of 50 µm for a reaction time of 60 min, reaction temperature of 55 ºC; and, methanol: WSFO ratio of 6:1 in 32 runs. Taguchi, on the other hand, predicted a prime FAME yield of ~61 % under process operating parameters of catalyst: WSFO ratio = 1:1 %w/w, catalyst particle size = 75 µm, reaction time = 45 min, reaction temperature = 45 °C; and, methanol: WSFO ratio = 4:1 in 16 runs. The calculated coefficient of determination (R), adjusted R, and coefficient of variance were found to be 0.8167 %, 0.7743 % and 3.83 % respectively for the RSM method and 0.9085 %, 0.7711 % and 4.03 % respectively for the Taguchi method. RSM predicted marginally higher FAME yield but Taguchi was substantially more cost effective owing to 50 % fewer number of runs.

Keywords: ANOVA, FAME yield, optimization, response surface methodology, Taguchi

1. INTRODUCTION

Global warming, increased concern about emission of greenhouse gas, air pollution, explosive population growth, rapid industrial development, continuous depletion of petroleum fuel sources and the need for locally available energy sources has necessitated the quest for countries to survey alternative energy sources that are feasible, affordable, beneficial, and sustainable. The target energy sources are expected not only to minimize air pollution, slash global warming emissions, generate new jobs, create new industries in the value chain, expand power and energy supply, lessen reliance on coal and other fossil fuel sources but also to steer nations towards a cleaner, safer and healthier fuel and energy future. In order to meet this goal of switching from traditional pollution causing petroleum based fuels, researchers have paid a great deal of attention to development and testing of renewable energy sources. Biofuel, consisting mainly of bioethanol and biodiesel, produced 2.8 % of world energy consumption in 2015 and 3.1 % in 2017 [1] and is projected to increase to 3.8 % by 2023 [2]. Various countries, have through their renewable energy policy, set targets for renewable energy application. Usage and applicability of renewable energy in transport increased from 2.6 % in 2011 to 3.4 % in 2018 and is projected to increase to 3.8 % in 2023 as shown in Fig 1. In the same vein, biodiesel production is projected to continue to increase, particularly for the United States of America, Indonesia, Brazil, Malaysia between 2017 and 2023 as shown in Fig 2.

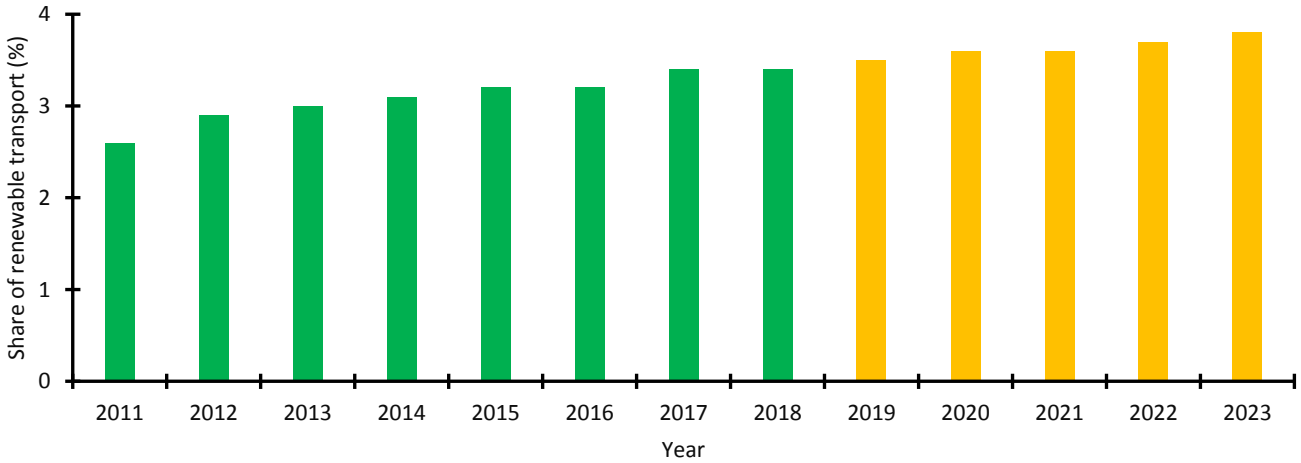


Figure 1. Global share of renewable transport (%) 2011 - 2023 [2].

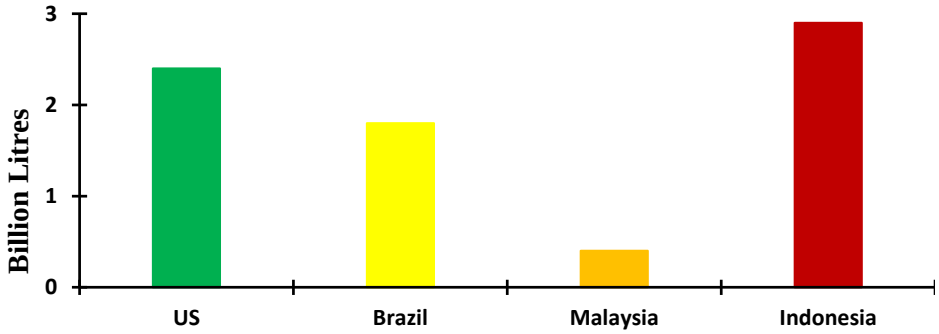


Figure 2. Projected change in biodiesel generation between 2017 and 2023 [2].

Biodiesel, which is usually referred to as fatty acid methyl esters (FAME), is not only a renewable, friendly, easy to produce, but also environmentally pleasant fuel for compression ignition (CI) engines. It is generally produced from a range of feedstock including animal fats, algae, vegetable oils, and other renewable biological sources. Among the proven methods of FAME production, namely, thermal cracking (pyrolysis) [3], microemulsion [4], hydrocarbon blending [5] etc., transesterification is the most common due to its simplicity, low equipment outlay and higher conversion efficiency [6]. The transesterification process is a reversible chemical reaction process where glyceride reacts with alcohol to generate biodiesel with or without catalysts. The alcohol can either be methanol or ethanol while the catalytic process is enhanced by acid, alkaline or enzymatic catalysts. After transesterification, the crude biodiesel must be purified to comply with international standards such as EN 14214 or ASTM D6751. Major benefits of biodiesel include its similar cetane number compared to petrol based diesel (PBD) fuel which allows high combustion efficiency, 90 % biodegradability within 21 days, reduced emission of hydrocarbon (UHC), carbon monoxide (CO), particulate matters (PM), sulphur oxide (SO_2), and aromatic compounds, and, compared to PBD fuel, low toxicity, high lubricity, more complete combustion and engine performance, safe handling, conversion of waste to fuel as well as other social, and economic benefits. In spite of these advantages, increased NOx emissions, high production cost, food security threat, etc. are among the shortcomings in the application of biodiesel [7, 8]. The application of used or waste cooking oil (WCO) to synthesize biodiesel will assuage the almost prohibitive cost of feedstock, prevent food crises arising from the utilization of edible vegetable oil as feedstock, as well as help in the proper disposal of WCO thereby preventing contamination of aquatic and terrestrial habitats.

Various techniques including response surface methodology (RSM), Taguchi orthogonal array [9], artificial neural networks (ANN) [10], matrix laboratory (MATLAB), Simulink, adaptive neuro-fuzzy inference systems (ANFIS) [11], Box-Behnken design [12], and genetic algorithm (GA) [13] have been engaged to optimize the transesterification of vegetable oil to FAME. These techniques can be used individually, in combination or comparison with other techniques using soft computing methods to optimize FAME production. The employment of RSM and Taguchi for the modelling and optimization of the transesterification process are documented in the literature. Karmakar et al. [14] explored the Taguchi orthogonal design to optimize biodiesel generation using castor oil as feedstock and reported that the tool yielded an affordable and sustainable optimization technique for synthesizing biodiesel from castor oil. Dhawane et al. [15] also employed the Taguchi orthogonal approach for the parametric optimization of generation of FAME using edible vegetable oil as feedstock and reported that the approach was easy and productive. Other research has supported the efficacy and effectiveness of Taguchi to successfully optimize the transesterification process and to achieve the lowest cost possible [16, 17]. RSM has been employed to design experiments, develop empirical models, and perform optimization of transesterification of oil to biodiesel as well as for property prediction [18-21].

Najafi et al. [22] applied a combination of ANN, ANFIS and RSM to estimate, predict and optimize the parametric factors that influence biodiesel yield during transesterification and reported that the models successfully predicted biodiesel yield and the outcomes were validated by the experimental data. The application of Taguchi method to predict and optimize the biodiesel production parameters has been reported to yield acceptable conditions for the economical generation of biodiesel from various feedstocks through the transesterification process [14, 15, 23]. Tan et al. [9] used the RSM and Taguchi methods for the optimization of transesterification of WCO to biodiesel and reported that the statistical tools provided favorable prediction outcomes and experimental validation of biodiesel yield. In general, the application of modelling, optimization tools and other soft computing techniques in the transesterification of WCO to biodiesel has been found to be cost effective and saves time, are less laborious, innovative, flexible, prevents multiple experimental processes, offers better understanding of the process and have the capability to forecast and predict "what-if" scenarios. Some of the parameters that influence biodiesel yield include reaction temperature, alcohol/feedstock molar ratio, catalyst concentration, reaction time, etc. [24-27].

The economics and cost analysis of FAME production has shown that cost of feedstock gulps over 70 % of the production expenses while raw materials and other consumables jointly take up 86 % of the production cost. Raw materials for transesterification process include the oil feedstock, catalyst, alcohol, and purification medium. The cost of input and other materials is a substantial part of the operating cost [28, 29]. The

use of the experimental processes, also known as the one-variable-at-a-time (OVAT) experimental technique, is not just expensive, onerous, burdensome, time-consuming, requires huge laboratory architecture but also consumes a high volume of materials. Materials are wasted in trying to determine the optimal parameters combinations for best yield. These identified drawbacks can be overcome by the use of optimization techniques with the capability of providing the required information from minimum runs by concurrently altering all the process factors. The use of design-of-experiment software reduces experimental runs, saves time, saves raw materials, and uncovers the mutual interactions going on among the various process independent parameters (inputs) and dependent variable (output) [30-32].

With the use of WCO as feedstock for transesterification gaining traction, the relevant questions that remain unanswered and which serve as the justification for this effort relate to the necessary conditions that facilitate the optimum biodiesel yield and catalyst recovery in the shortest time and lowest cost. The current study aims to use a combination of experimental and statistical techniques to interrogate the optimal operating parameters aimed at the transesterification of waste sunflower oil (WSFO) to biodiesel using calcium oxide (CaO) developed from calcined waste chicken eggshell (WCE) powder. The motivation is to investigate parameters that will ensure optimum FAME yield using both the RSM and Taguchi optimization methods.

The effects and influences of catalyst concentration, catalyst particle size, methanol to waste oil mole ratio, experimental reaction temperature and reaction time on FAME yield and FAME conversion were investigated and analyzed. The specific objectives were: (i) production of biodiesel from WSFO using CaO derived from calcined WCE powder; (ii) evaluation of the effects of the listed factors of biodiesel yield; (iii) comparison of the experimental FAME yield with the predicted FAME yield using RSM and Taguchi methods. The parameters studied were catalyst: WSFO ratio (%w/w), catalyst particle size (μm), reaction temperature (°C), reaction time (min) and methanol: WSFO ratio. Also, the interrelationship among these identified process parameters were studied using a three dimensional (3D) surface plots of RSM, ramps and other plots. The established models using the Taguchi orthogonal and RSM methods were appraised using statistical parameters including standard error, sum of squares, correlation coefficient (R), F- and p-values, standard deviation, coefficient of determination (R^2), and adjusted R^2 (R^2_{adj}).

II. MATERIALS AND METHODS

II.I. Materials collection

Waste Sunflower oil (WSFO) sample was sourced and collected from take away outlets close to Howard College campus, University of KwaZulu-Natal (UKZN), Durban, at the point of disposal. Available information showed that the waste oil had been used repeatedly for 14 days to fry potato chips. WCE was collected from restaurants within Howard College, UKZN. Methanol uniVAR (analytical grade) at 99.5 % purity was procured from Merck.

II.II. Materials treatment and preparation

The WSFO was heated in an electric heated to 120 °C for 90 min to eliminate water and sieved via vacuum filtration to remove food particles and other solids in the oil and later analyzed to determine the acid value, molecular weight and iodine number. The procedure for the preparation CaO catalyst via high temperature calcination of WCE powder has been described in our earlier work [33]. The eggshell powder was classified by using sieves of different pore sizes.

II.III. Transesterification process

The acid value of WSFO allows for a one stage transesterification process. The filtered WSFO, methanol and CaO derived from WCE shell powder were emptied into a round bottom flask and heated to a predetermined temperature and time and mixed at a predetermined speed (rpm) maintained by a magnetic stirrer. A digital thermocouple was utilized to verify the temperature of the reacting solution throughout the duration of the experiment. Different catalyst concentrations, catalyst particle size, reaction temperature and methanol:WSFO mole oil ratio were used during each batch of the transesterification process as shown in Table 1. A medium sized magnetic stirrer was employed to guarantee adequate and homogeneity of the reacting mixture maintained at a predetermined temperature, time and stirring speed throughout the process. The resulting solution was thereafter filtered in a vacuum filtration set up to recover the catalyst. The filtered mixture was transmitted into clean separating funnel and left to stay overnight. Glycerol was seen coagulated beneath the separating funnel. Thereafter, the coagulated glycerol was drained out while the remaining crude before the crude biodiesel was decanted and transferred into a glass container for further purification and analysis.

The FAME yield (%) of WSFO to biodiesel were estimated by Equation (1):

$$FAME\ yield\ \% = \frac{Weight_{Biodiesel}}{Weight_{Oil}} \times 100\% \quad (1)$$

II.IV. Modeling and optimization by RSM

The optimization of biodiesel yield and catalyst recovery arising from transesterification of WSFO into FAME was conducted by applying the central composite design (CCD) of the response surface methodology version of design of experiment (DoE) available on the Design-Expert software. The CCD of a randomized RSM is a very popular and effective optimization tool with full or fractional factorial point, axial point and centre point that can be duplicated for every combination of categorical factor level. In order to use DoE, several experiments are conducted to ascertain the prime factors for the best outcomes. RSM was later engaged to form a mathematical model to validate the outcomes of the experiments. The process parametric factors investigated for the optimization of the transesterification process of WSFO were catalyst weight: WSFO ratio, reaction time, reaction temperature, particle size of the catalyst and methanol-to-WSFO molar ratio as shown in Table 1. A total of 24 non-center

points and 6 center points and alpha of 2 gave rise to a total of 32 runs. The choice of this method was dictated by the number of variables and levels [34]. The data collected from 32 experimental runs were analyzed by RSM CCD by Design Expert Software10.0.8.0 version.

Table 1. Investigated parameters, notations and coded levels

Variable	Units	Notation	Coded factors level				
			-2	-1	0	1	2
Catalyst:WSFO	%w/w	X_1	0.5	1	1.5	2	2.5
Particle size of catalyst	µm	X_2	50	75	90	125	150
Reaction time	min	X_3	30	45	60	75	90
Reaction temperature	^oC	X_4	35	45	55	65	75
Methanol:WSFO ratio		X_5	2	4	6	8	10

II.V. Modeling and Optimization by Taguchi

Application of the Taguchi orthogonal array (OA), developed by Dr. Genichi Taguchi, allows for the investigation of every likely permutation of parameters, minimizes the number of tests and identifies and quantifies the interactive impacts of the parameters on a process by substantially reducing the cumbersome optimization procedure. Taguchi OA reduces the number of experiments without negatively affecting the operating parameters while retaining all the required details [35, 36]. Taguchi OA allows the implementation of various design designation from L4 (2^3), L8 (2^7) and up to L64(4^21). In this study, the L16(4^15) design was chosen which allows four levels and five parameters in the Taguchi technique. The number of runs, N, were estimated by means of Equation (2):

$$N = (L-1)P + 1 \quad (2)$$

Where P and L indicate number of parameters and levels, respectively. From Equation (2), the number of runs, using Taguchi OA, is 16 runs.

Table 2 shows the experimental design matrix developed by the Taguchi design. Experimental outcomes were analyzed via signal-to-noise (S/N) ratio for estimating the effect of the factors on FAME yield. The difference between the response and the anticipated result was calculated by S/N ratio as:

$$\frac{S}{N} = -10log_{10}\left(\frac{\Sigma\left(\frac{1}{y_i^2}\right)}{n}\right) \quad (3)$$

Where y_i = response value, and n = number of experimental runs.

Analysis of variance

The evaluation, prediction and measurement of the effects of parametric factors on the transesterification process by determining the effects of key factors i.e. the best factor levels from the tested factor levels for the optimal process parameters for the transesterification process are conducted by analysis of variance (ANOVA) or S/N ratio. However, S/N ratio is unable to identify the impact of these factors on the response, unlike ANOVA. The influence of each parameter in generating the response can be determined by calculating the contributing factor.

$$\%\ Contributing\ factor = \frac{Sum\ of\ squares\ of\ the\ particular\ variable\ (SS_f)}{Sum\ of\ squares\ of\ all\ the\ variable\ (SS_r)} \times 100 \quad (4)$$

ANOVA is targeted at increasing the percentage of FAME yield. The parameter with the highest percentage contribution factor is also reflected in the regression model equation employed to predict and validate the model from the RSM analysis of the actual data obtained from the actual experimental runs [37].

Table 2. Experimental design matrix generated by Taguchi

Run	X_1:Catalyst : WSFO (%w/w)	X_2:Particle size of catalyst (µm)	X_3: Reaction time (min)	X_4:Reaction temperature (^oC)	X_5: Methanol: WSFO ratio	FAME Yield %
1	1.5	75	60	65	10	85.43
2	2	125	45	55	10	86.76
3	2	150	60	45	8	78.32
4	1	150	90	75	10	69.45
5	1	90	60	55	6	82.5
6	2.5	125	60	75	4	71.68
7	2.5	90	75	45	10	73.78
8	2.5	150	45	65	6	85.51
9	2,5	75	90	55	8	70.86
10	1.5	150	75	55	4	75.45
11	2	75	75	75	6	87.54
12	1	75	45	45	4	81.66
13	1.5	90	45	75	8	70.55
14	1.5	125	90	45	6	84.66
15	1	125	75	65	8	76.58
16	2	90	90	65	4	87.54

III. RESULTS AND DISCUSSIONS

III.I. Response Surface Method statistical analysis

Table 3 presents the results of the transesterification of WSFO to FAME using RSM via CCD experimental design. The experimental (actual) FAME yield varied between 69.45 % and 90.55 %. The actual yields were evaluated to produce a suitable and workable regression model. An appropriate model was selected from mean, linear, quadratic, cubic, quartic etc. A

cubic regression model was generated and employed to predict optimal parameters for the transesterification of WSFO to biodiesel by the software. The best fit model for FAME yield is as shown in Equation (5).

$$y = 127.84 + 7.41X_1 - 1.86X_2 - 0.25X_3 + 0.22X_4 + 6.23X_5 - 0.11X_1X_4 + 0.028X_3X_5 - 0.019X_4X_5 - 1.38X_1^2 + 0.018X_2^2 - 0.51X_5^2 - 0.000051X_2^3 \quad (5)$$

Where y is the FAME yield (%), the catalyst WSFO ratio, particle size of catalyst, experimental reaction time, process reaction temperature, and methanol:WSFO ratio are denoted by X_1, X_2, X_3, X_4, and X_5, respectively. The interaction terms are X_3X_5 and X_4X_5, and X_1^2, X_2^2, X_5^2, and X_2^3 are quadratic (cubic) terms of the independent variables. Parameters with positive coefficients (linear, interaction or quadratic) have a desirable effect on FAME yield while those with a negative coefficient negatively affected FAME yield.

Table 3. Actual and predicted of FAME yield (%) by RSM

Run	X_1: Catalyst: WSFO (%w/w)	X_2: Particle size of catalyst (μm)	X_3: Reaction time (min)	X_4: Reaction temperature (°C)	X_5: Methanol: WSFO ratio	FAME yield (%)	
						Actual	Predicted
1	0.5	150	30	75	10	85.43	86.34
2	1.5	100	90	55	6	86.76	83.12
3	2.5	150	30	75	2	78.32	79.28
4	2.5	50	90	75	2	69.45	67.44
5	1.5	100	60	65	6	82.5	84.74
6	3.5	100	60	55	6	71.68	73.83
7	0.5	50	90	35	2	73.78	73.29
8	1.5	100	60	55	6	85.51	85.45
9	1.5	200	60	55	6	70.86	70.86
10	1.5	100	60	55	2	75.45	74.16
11	0.5	100	60	55	6	87.54	86
12	1.5	100	60	95	6	81.66	82.62
13	2.5	150	90	35	2	70.55	72.14
14	0.5	50	30	35	10	84.66	87.3
15	0.5	150	90	75	2	76.58	78.47
16	0.5	150	90	35	10	87.54	89.85
17	2.5	50	30	35	2	80.51	83.27
18	1.5	100	60	55	6	90.43	85.45
19	0.5	50	90	75	10	89.54	88.18
20	0.5	150	30	35	2	87.59	85.13
21	1.5	100	60	55	6	81.54	85.45
22	2.5	150	30	35	10	90.54	86.15
23	1.5	100	60	55	6	89.51	85.45
24	1.5	100	60	55	6	81.87	85.45
25	2.5	50	30	75	10	76.66	75.31
26	1.5	100	60	55	6	87.56	85.45
27	1.5	100	30	55	6	79.65	80.8
28	2.5	50	90	35	10	89.65	87.99
29	1.5	50	60	55	6	88.65	91.07
30	0.5	50	30	75	2	90.55	89.6
31	1.5	100	60	55	10	76.76	80.46
32	2.5	150	90	75	10	78.67	77.86

As shown in Table 3, the highest FAME yield, as predicted by RSM regression model, of 91.07 %, was obtained with catalyst:WSFO ratio = 1.5 %w/w, particle size of catalyst = 50 µm, reaction time = 60 min, process reaction temperature = 55 °C and methanol:WSFO ratio = 6:1, with reaction time being the most important parameter that influences FAME yield.

The model equation was appraised for statistical importance using the ANOVA test, R^2 and R^2_{adj}. The accuracy, and efficiency of the regression model in predicting the response were tested by ANOVA and the outcomes are shown in Table 4. The F-value and p-value of the model was estimated to be 9.86 and < 0.0001 respectively, indicating that the model was statistically significant at 95 % CI level ($p < 0.05$) [38]. In that scenario, X_1, X_2, X_3, X_4, X_4, X_1 X_4, X_3 X_5, X_1^2, X_2^2, X_5^2, and X_2^3 are statistically significant model terms while X_4X_5 is insignificant. The variable X_3 with the highest F-test value of 29.53, $p < 0.0001$ was the most statistically significant parameter indicating that reaction time was the most significant parameter for FAME yield. The F-value of 0.58 for the lack of fit denotes that it was not significant compared to the pure error. In addition, it was discovered that there is 80.58 % prospect that a Lack of Fit F-value of 0.58 could be instigated by noise. It is advantageous to have a non-significant Lack of Fit (Table 4).

Table 5 depicts the outcomes of test for significance of the model. Though the standard error of the intercept is high, the standard errors of most of the parameters are < 1 and the degree of freedom (df) associated with the parameters are 1. The measure of accuracy and precision of the model were ascertained by the R^2 and R^2_{adj} values. An R^2 value of 0.8617 reveals that 86.17 % of the entire data were consistent with the predicted data and variability [39]. R^2_{adj} of 0.7743 indicates an acceptable fitness for the model. An adequate precision (S/N ratio) above than 4 has been found to be desirable and advantageous. The S/N ratio of 11.789 is a pointer to the suitability of the model to traverse the design space and a further proof that the generated model is statistically significant [40] (Table 6). A standard deviation of 3.14 was recorded and the low value of coefficient of variation (CV) of 3.83 % is a sign of good accuracy and dependability of this model [41].

The highest FAME production yield of 91.07 % forecasted by the RSM model was accomplished at a catalyst: WSFO ratio of 1.5 %w/w, particle size of catalyst of 50 µm, a reaction time of 60 min, a reaction temperature of 55 °C and a methanol: WSFO ratio of 6:1, with reaction time being the most important parameter that influenced FAME yield, as clearly displayed in Table 3.

Table 4. ANOVA for FAME yield

Source	Sum of Squares	df	Mean Square	F Value	p-value Probability > F	
Model	1170.13	12	97.51	9.86	< 0.0001	significant
Linear						
Catalyst:WSFO ratio (X_1)	65.77	1	65.77	6.65	0.0184	
Particle size of catalyst (X_2)	159.62	1	159.62	16.15	0.0007	
Reaction time (X_3)	291.98	1	291.98	29.53	< 0.0001	
Reaction temperature (X_4)	56.33	1	56.33	5.70	0.0275	
Methanol: WSFO ratio (X_4)	145.88	1	145.88	14.76	0.0011	
Interaction						
X_1 X_4	84.09	1	84.09	8.51	0.0089	
X_3 X_5	187.14	1	187.14	18.93	0.0003	
X_4 X_5	37.70	1	37.70	3.81	0.0657	
Quadratic						
X_1^2	53.67	1	53.67	5.43	0.0310	
X_2^2	172.06	1	172.06	17.40	0.0005	
X_5^2	170.97	1	170.97	17.29	0.0005	
X_2^3	188.72	1	188.72	19.09	0.0003	
Residual	187.84	19	9.89			
Lack of Fit	116.30	14	8.31	0.58	0.8058	not significant
Pure Error	71.54	5	14.31			
Total	1357.97	31				

Table 5. Test of significance

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	127.84	1	13.52	99.55	156.13	
Linear						
Catalyst:WSFO ratio (X_1)	7.41	1	2.87	1.40	13.43	20.05
Particle size of catalyst (X_2)	-1.86	1	0.46	-2.83	-0.89	1133.89
Reaction time (X_3)	-0.25	1	0.046	-0.34	-0.15	3.94
Reaction temperature (X_4)	0.22	1	0.091	0.027	0.41	6.66
Methanol: WSFO ratio (X_5)	6.23	1	1.62	2.84	9.63	76.71
Interaction						
$X_1 X_4$	-0.11	1	0.039	-0.20	-0.032	15.16
$X_3 X_5$	0.028	1	0.0066	0.015	0.042	8.41
$X_4 X_5$	-0.019	1	0.0098	-0.040	0.0014	12.33
Quadratic						
X_1^2	-1.38	1	0.59	-2.63	-0.14	8.78
X_2^2	0.018	1	0.0042	0.0088	0.026	4546.17
X_5^2	-0.51	1	0.12	-0.76	-0.25	65.75
X_2^3	-0.000051	1	0.000012	-0.000075	-0.000026	1242.64

Table 6. ANOVA of regression equation

Parameter	Value	Parameter	Value
Standard Deviation	3.14	R^2	0.8617
Mean	82.12	Adj R^2	0.7743
C.V. %	3.83	Predicted R^2	N/A
PRESS	N/A	Adequate Precision	11.789
-2 Log Likelihood	147.45	BIC	192.50
		AICc	193.67

Process parameters interactions

Design expert version 10 was applied to produce 3D response surface plots in order to comprehend the connections, interrelationship, and interactions among the process variables affecting the selected process response (FAME yield) as generated by Equation 4. The response surface plots show the interactions, relationships and correlations of two different variables in the study while maintaining the other variables at a fixed value. Figure 2 shows the 3D plots with the y axis offset from the x axis at a value of 20.

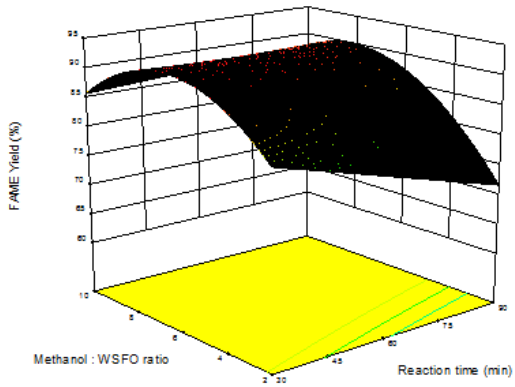
a. Influence of methanol:WSFO ratio and reaction time on FAME yield

Figure 2a shows the relationship between reaction time and methanol:WSFO ratio against FAME yield (%) while keeping catalyst:WSFO ratio, particle size of catalyst, reaction temperature constant as 2.5:1 %w/w, 50 µm and 35 ºC in that order. As the methanol to WSFO ratio increases from 2:1 to 8:1, the proportion of FAME yield increases from 70 % to 90 % but decreases to 82 % when the methanol to WSFO ratio increases beyond 8:1. This confirms earlier reports that sufficient methanol to oil ratio positively impact on FAME yield in the production of biodiesel through transesterification

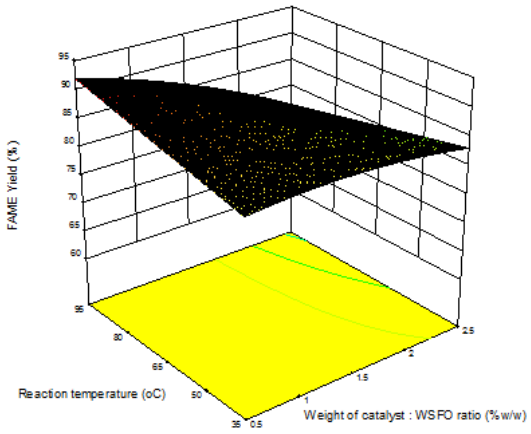
reaction. A higher methanol to oil ratio will also precipitate more FAME formation [42]. Similarly, as the process reaction time increases from 30 mins to 90 mins, FAME yield increases. This may be attributable to sufficient contact time between the reactants which results in higher yield [43]. The interaction of methanol: WSFO ratio and process reaction time have negative impacts on FAME yield (Table 5).

b. Influence of catalyst to WSFO ratio and reaction temperature on FAME yield

The interactions between reaction temperature and catalyst: WSFO ratio against FAME yield at constant catalyst particle size, reaction time, and methanol to WSFO ratio of 150 µm, 30 min and 2:1 respectively is displayed in Figure 2b. From the plot, the highest proportion of FAME generation of about 92 % was achieved at 95 °C and 0.5 %w/w catalyst to WSFO ratio while the least FAME yield of 78 % was recorded at 95 °C and 2.5:1 catalyst: WSFO ratio. FAME yield decreases from 92 % to 77 % when the catalyst: WSFO improved from 0.5 %w/w to 2.5 %w/w. When the transesterification process reaction temperature was escalated from 35 °C to 95 °C the FAME production yield reduced from 84 % to 78 %. The catalyst to WSFO ratio had more of an effect on FAME yield than reaction temperature. The combination of these two variables had negative effects on FAME yield (Table 5).



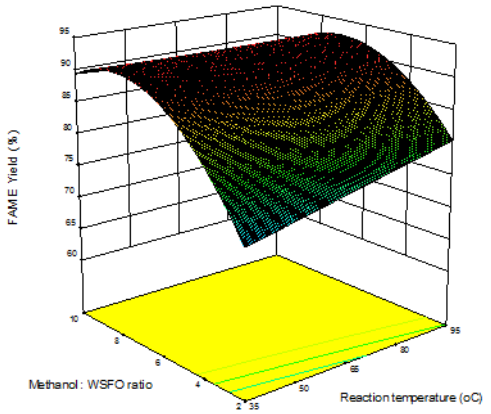
(a)



(b)

c. Influence of methanol to WSFO ratio and reaction temperature on FAME yield

The mutual interaction between the methanol to WSFO ratio and process reaction temperature on FAME yield is depicted in Figure 2c. Catalyst: WSFO ratio, particle size of catalyst and reaction time were kept constant at 0.5 %w/w, 50 µm and 90 min respectively to adequately show the interaction between these two variables. As shown in Tables 4 and 5, the combination of methanol to WSFO ratio and reaction temperature had a negative but insignificant impact on FAME yield. As shown in the plot, the highest FAME yield was attained at a methanol: WSFO oil ratio of 6:1 and reaction temperature of 95 °C, while the least FAME yield was achieved at 2:1 methanol: WSFO ratio and 35 °C reaction temperature. An increase in reaction temperature from 35 °C to 88 °C resulted in a slight reduction in FAME yield from 92 % to 86 %, while an increase in methanol: WSFO ratio from 2:1 to 8:1 led to an increament in FAME yield from 73 % to 90 %. A further increment in methanol:WSFO ratio, to 10:1, however, caused a reduction in FAME yield to 88 %. The effect of methanol:WSFO ratio was more pronounced than that of reaction temperature.



(c)

Figure 2. 3D response surface plots for (a) methanol: WSFO ratio and reaction time (b) catalyst:WSFO ratio and reaction temperature (c) methanol:WSFO and reaction temperature.

III.II. Taguchi method

a. Analysis of variance (ANOVA)

The outcomes and consequences of the prediction of FAME yield from the transesterification process using the L16 Taguchi orthogonal approach is depicted in Table 7. The F-value and the sum of squares are estimated and applied to determine the influence of the parameters on the response.

In this study, with the sum of squares of 607.44 and mean square of 67.49, the model is considered significant. The

F-value and p-value of 6.62 and 0.0161 respectively corroborates that the model generated by Taguchi method is significant. Also, the p-value shows that there is only 1.61 % likelihood that the value of the F-value achieved occurred due to the preponderance of noise. Consequently, the model is considered fit and significant enough for the optimization of FAME yield of the transesterification process of WSFO within the selected process parameters. From the ANOVA study, it has been shown that only three out of the five process parameters, namely, catalyst:WSFO (%w/w), reaction temperature (°C), and methanol:WSFO ratio, have a substantial influence on the dependent variable (response). The effects of reaction time and particle size of the catalyst was negligible. Among the three parameters having significant influence, the methanol: WSFO ratio with F-value and the sum of squares value of 7.92 and 242.43 respectively showed the highest influence on FAME yield. The significance of each process parameters was further authenticated by calculating the contribution factor (CF) of each significant parametric factor in the process. Equation (4) was employed to calculate the contribution factors. The methanol: WSFO ratio, catalyst: WSFO ratio and reaction temperature contribute 36.26 %, 30.42 % and 24.16 % respectively to FAME yield through transesterification process as shown in Table 8. The contribution factor result agrees with the ANOVA result showing that the methanol: WSFO ratio has the highest influence on FAME yield.

Table 7. Analysis of variance (ANOVA of model and process parameters

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value Prob > F	
Model	607.44	9	67.49	6.62	0.0161	significant
X_1: Catalyst: WSFO (%w/w)	203.43	3	67.81	6.65	0.0246	
X_4: Reaction temperature (^oC)	161.58	3	53.86	5.28	0.0404	
X_5: Methanol: WSFO ratio	242.43	3	80.81	7.92	0.0165	
Residual	61.21	6	10.20			
Total	668.64	15				

Table 8. Contribution factor the significant parameter on FAME yield

Parameter (unit)	Contribution factor (%)
Catalyst:WSFO (%w/w)	30.42
Reaction temperature (^oC)	24.16
Methanol:WSFO ratio	36.26
Residual	9.15

From the parameters estimated from the analysis of variance, as shown in Table 9, R^2 was found to be 0.9085. The R^2 value, being close to unity, shows its linearity and fitness for the selected model. The value obtained for R^2_{adj} was found to be 0.7711 while the predicted R^2 was 0.349 for the preferred model. Adequate precision is a degree of the S/N ratio and as shown in Table 9, the adequate precision value obtained was 7.914 which is almost double the required tolerable accuracy of 4 for any model. The adequate precision of 7.914 shows that the model has the capability to forecast the dependent variable and adequately optimize FAME yield. Furthermore, the standard deviation was estimated to be 3.19 while the coefficient of variance was 4.03 % which confirmed the capability of the model to predict the optimum parameters with satisfactory precision [15, 44].

Table 9. Statistical parameters estimated from ANOVA

Parameter	Value	Parameter	Value
Standard Deviation	3.19	R^2	0.9085
Mean	79.27	Adjusted R^2	0.7711
C.V. %	4.03	Predicted R^2	0.3490
PRESS	435.26	Adequate Precision	7.914
-2 Log Likelihood	66.87	BIC	94.60
		AICc	130.87

b. Regression model equation from Taguchi method

ANOVA was used to develop a model and identify the individual parameters that were significant to the generation of the desired response. Significant parameters were considered and escalated while the insignificant parameters were relegated. The CI of the model parameters are 95 % which indicated a very high assurance level of the mathematical model to forecast the FAME yield. The Taguchi method mathematical model equation (Equation (6)) relate the three parameters that are significant in predicting the response.

$$y = 79.27 - 1.72X_1[1] - 0.24X_1[2] + 5.77X_1[3] + 0.34X_4[1] - 0.34X_4[2] + 5.5X_4[3] - 0.18X_5[1] + 5.79X_5[2] - 5.19X_5[3] \quad (6)$$

Where y = FAME yield (%), $X_1[1]$, $X_1[2]$ and $X_1[3]$ are the weight of catalyst:WSFO ratio, $X_4[1], X_2[2]$and $X_4[3]$ are reaction temperature, and $X_5[1], X_5[2]$and $X_5[3]$ are the methanol:WSFO ratio as shown in Table 10.

The degree of freedom for the model is unity while the CI is 95 % and the standard error of the parameters is 1.38 (Table 10). The linear regression model equation has the capacity to predict FAME yield using the parameters and data given in Table 2. The influence of the three significant parameters on the

biodiesel yield is displayed in Fig 3 (a, b, c).

Table 10. Coefficients in terms of coded for categoric factors and actual for other factors

Term	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	79.27	1	0.80	77.31	81.22
$X_1[1]$	-1.72	1	1.38	-5.10	1.66
$X_1[2]$	-0.24	1	1.38	-3.63	3.14
$X_1[3]$	5.77	1	1.38	2.39	9.16
$X_4[1]$	0.34	1	1.38	-3.05	3.72
$X_4[2]$	-0.37	1	1.38	-3.76	3.01
$X_4[3]$	4.50	1	1.38	1.11	7.88
$X_5[1]$	-0.18	1	1.38	-3.57	3.20
$X_5[2]$	5.79	1	1.38	2.40	9.17
$X_5[3]$	-5.19	1	1.38	-8.57	-1.81

[1], [2] and [3] represent first, second and third level respectively

III.III. Effect of individual significant parameters on FAME yield predicted by Taguchi method

Three process parameters have significant influence on FAME yield as predicted by Taguchi method. The three parameters are represented in Equation (6) while their individual contribution factors are shown in Table 8.

a. Effect of catalyst:WSFO ratio

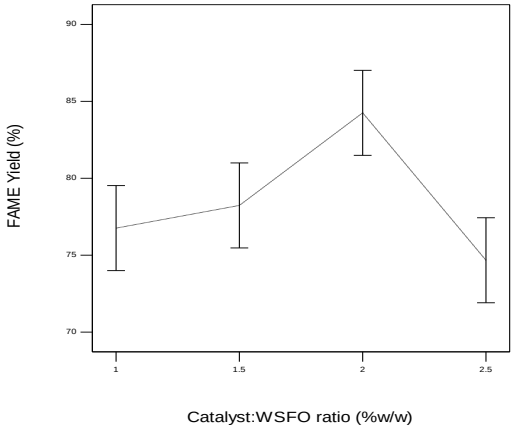
At reaction time of 45 min, catalyst particle size of 125 µm and reaction temperature of 55 °C, the effect of catalyst:WSFO ratio was measured. As shown in Fig 3a, maximum FAME yield of 84 % was attained with a catalyst:WSFO ration of 2:1. A higher concentration of the resulted in a drastic reduction in FAME yield. This may be a direct consequence of excessive catalyst loading which could accelerate the reverse reaction during transesterification. Comparable outcomes have earlier been reported by Sirisomboonchai et al. [45] and Gupta and Ratho [46].

b. Effect of reaction temperature

The proportion of FAME yield was studied at four different temperature levels, namely 45 °C, 55 °C, 65 °C and 75 °C. As shown in Fig 3b the maximum FAME yield of 89 % was accomplished at a reaction temperature of 65 °C when the catalyst: WSFO ratio, catalyst particle size, reaction time and methanol: WSFO ratio were maintained at 2:1 %w/w, 125 µm, 45 min and 10:1 respectively. A further improvement of the reaction temperature to 75 °C reduced the FAME yield to 80 %. This is due to the fact that at high temperatures methanol is lost due to evaporation and this impedes the transesterification reaction which alters the methanol to oil ratio resulting in saponification. Reaction temperature above methanol boiling point (65 °C) is counterproductive [47, 48]. Outcomes of previous research by Maneerung et al. [49], Dhawane et al. [15], Karmakar et al. [14] supported the results of this study in this regard.

c. Effect of methanol:WSFO ratio

Methanol: WSFO ratio is the most important factor in FAME yield (Table 8). Under the reaction conditions of catalyst: WSFO ration of 2 %w/w, catalyst particle size of 125 µm, reaction time of 45 min, and reaction temperature of 55 °C, the highest FAME yield of 90 % was obtained at a methanol: WSFO ratio of 6:1. Theoretically, a methanol: oil ratio of 3:1 is a prerequisite to producing biodiesel and water. However, careful adjustment of molar ratio can result in optimum use of alcohol and formation of more product. Excessive methanol to oil ratio impedes FAME yield, especially when the catalyst concentration is kept constant [50, 51].



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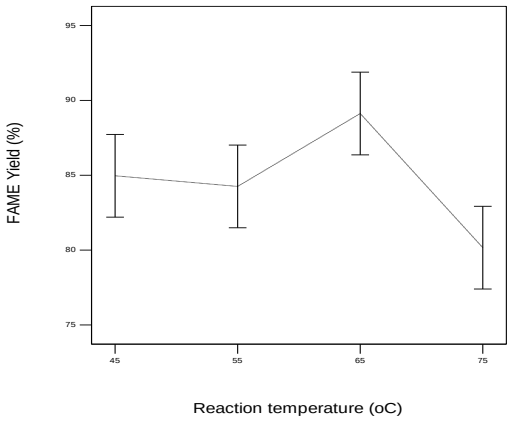

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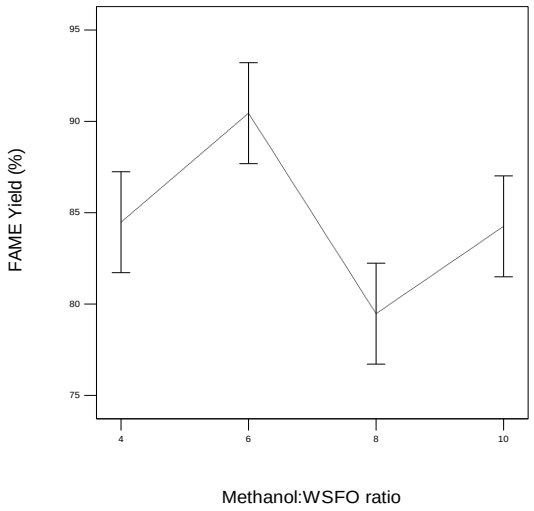


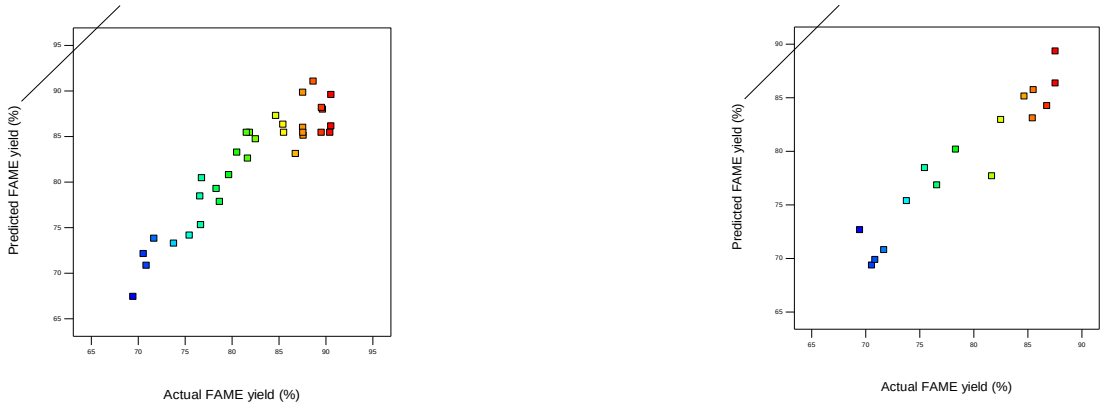
c.

Figure 3. (a) Effect of catalyst: WSFO ratio (%w/w), (b) reaction temperature (°C), and (c) methanol: WSFO ratio of FAME yield (%).

III.III. Comparison of RSM and Taguchi method

In this present study, the outcome of prediction of FAME yield using RSM optimization technique was compared with that of Taguchi OA method. The results of the two optimization techniques are similar and in agreement. Both techniques threw up the significant parameters for the prediction of FAME yield with the set factors and levels. The two techniques formulated model equations based on the significant factors they predicted. There are agreements in the parameters that RSM and Taguchi method found to be significant to the models. In this regard, catalyst: WSFO ratio, reaction temperature, and methanol: WSFO ratio were found to be dominant. In terms of number of data, the Taguchi method required lesser experimental data and always utilized linear regression, while RSM could also use quadratic or cubic regression [9, 52].

As shown in Fig 4a and Fig 4b, the pattern of the predicted and actual FAME yield was similar, indicating agreement between the two optimization techniques [14, 53]. As shown in Fig 5, the actual and RSM predicted data agreed to a large extent, indicating the accuracy of RSM in predicting the response. However, more pronounced deviations between the actual and predicted yield were noticed between runs 17 and 24. This can be attributed to the outcome of the different interactions among the process parameters. The lower and upper constraints of the range for all the investigated process parameters were contained in the optimization process. With the FAME yield maximized, the optimal value of the parametric factors which engender a desirability function of unity are shown in Fig 6a and Fig 6b. Maximized FAME yields of 93.42 % and 89.13 % were obtained from the RSM and Taguchi orthogonal methods respectively. The desirability function of the RSM and Taguchi method were within the span of the optimum operating process conditions for the response within the range of level of factors. The import of the desirability function was to obtain an optimal response from the model. Table 11 presents a comparison between the outcomes of the utilization of the response surface methodology and Taguchi methods to optimize FAME yield. While the RSM models obtained five significant parameters that can influence FAME yield, Taguchi presented only three. The Optimum FAME yield predicted by RSM was higher than that predicted by Taguchi. The parameter which had the highest influence on FAME yield according to RSM and Taguchi were reaction time and methanol: WSFO ratio respectively.



(a) (b)

Figure 4. Predicted vs actual FAME yield (a) RSM (b) Taguchi method.

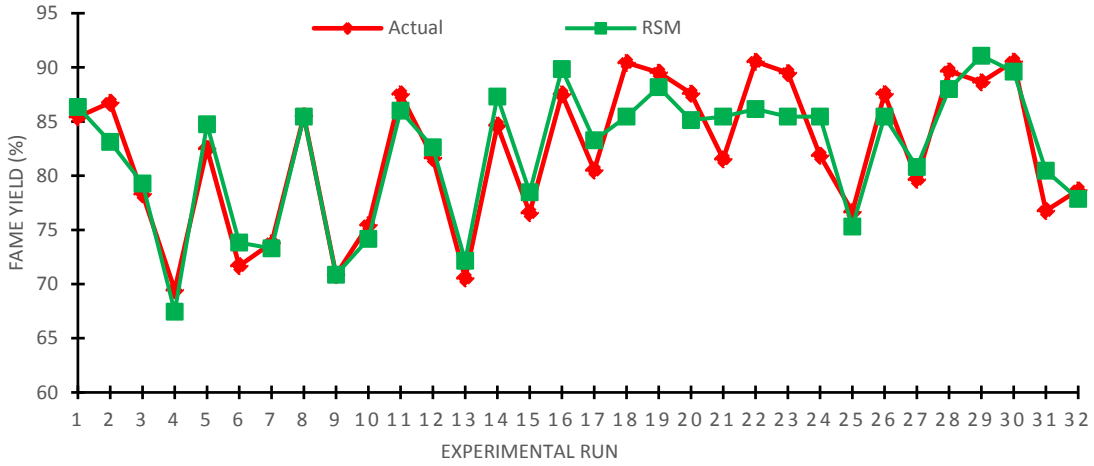
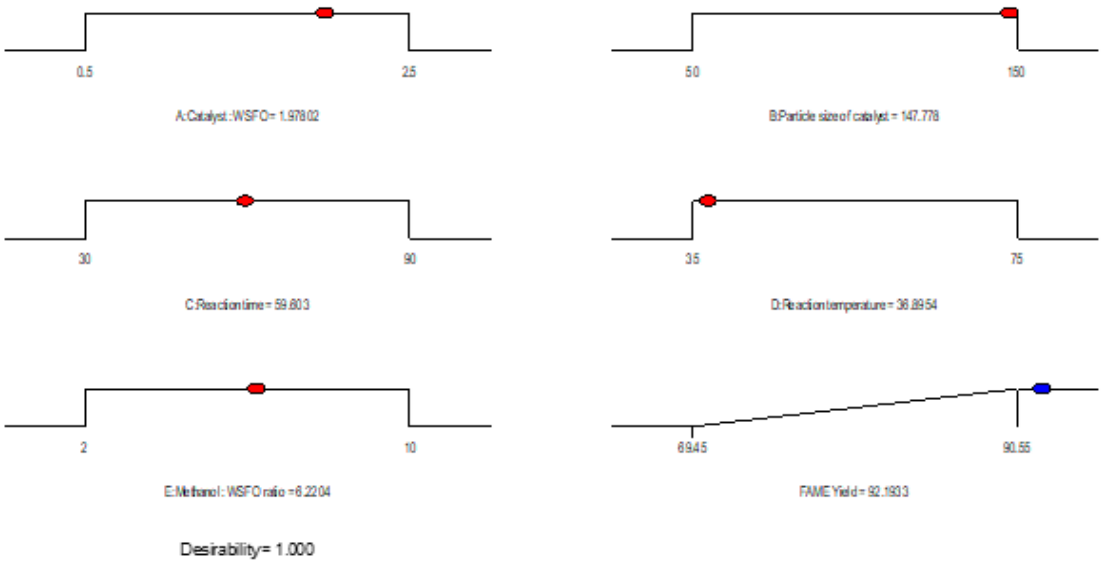
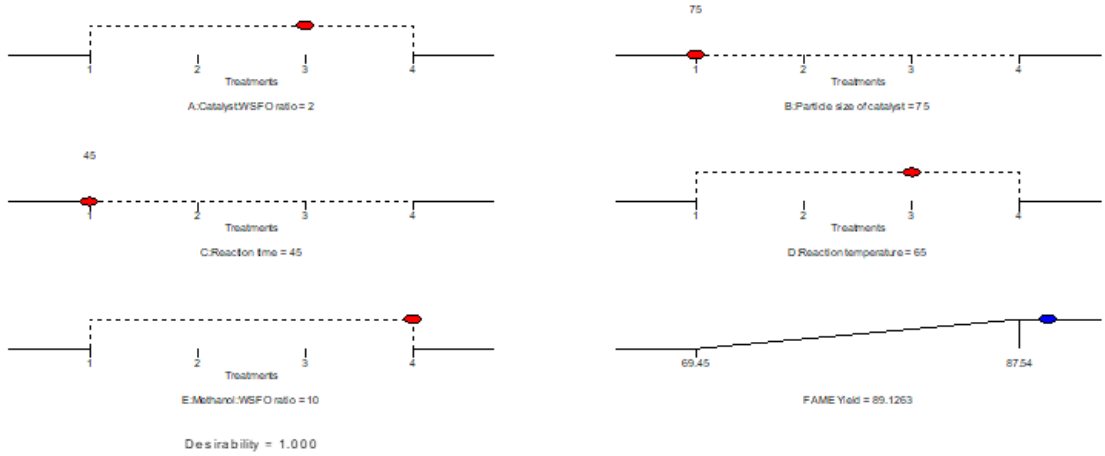


Figure 5. A plot of FAME yield (%) against actual and RSM predicted data



(a)



(b)

Figure 6. The optimal reaction condition through (a) RSM, (b) Taguchi method

Table 11. Comparison of Optimum conditions for RSM and Taguchi

Criteria	RSM	Taguchi
Catalyst:WSFO ratio (%w/w)	1.5:1	1:1
Reaction temperature (°C)	55	75
Reaction time (min)	60	45
Particle size of catalyst (µm)	50	45
Methanol: WSFO ratio	6:1	4:1
Predicted highest FAME yield (%)	91.07	61.16
Significant parameters	• Catalyst:WSFO ratio (%w/w) • Methanol: WSFO ratio • Reaction time (min) • Reaction temperature (°C) • Particle size of catalyst (µm)	• Reaction temperature (°C) • Catalyst:WSFO ratio (%w/w) • Methanol: WSFO ratio
Most significant parameter	Reaction time	Methanol: WSFO ratio
No of runs	32	16
R^2	0.8617	0.9085
R^2_{adj}	0.7743	0.7711
C V (%)	3.83	4.03

IV. CONCLUSION

In this study, the RSM and Taguchi orthogonal methods, both from Design Expert version 10, were adapted to model and optimize the transesterification of WSFO using WCE powder prepared through high temperature calcination. Using the statistical parameters of R^2, $R^2_{adj}, CF,$ and $CV,$ the outcome of RSM and Taguchi predictions were compared to establish which was the more accurate and cost effective method between the two. The following outcomes are worth highlighting:

i. The models generated by the RSM and Taguchi methods were significant and the model equations derived therefrom predicted FAME yield within acceptable error.

ii. The optimum FAME yield predicted by RSM was higher than that predicted by Taguchi, showing RSM to be a better optimization technique.

iii. RSM predicted FAME yield of 91.07 % with optimum operation condition of 1.5 %w/w catalyst:WSFO ratio, process time of 60 min, catalyst particle size of 50 µm, reaction temperature of 55 °C and methanol:WSFO ratio of 6:1. Taguchi, on the other hand, predicted a FAME yield of 61.16 % under optimum operating parameters of 1.1 %w/w catalyst to WSFO ratio, reaction time of 45 min, reaction temperature of 45 °C, 75 µm catalyst particle size and methanol:WSFO ratio of 4:1.

iv. The five tested parameters were discovered to be significant by the RSM model with reaction time (min) predicted as the most statistically significant parameter. Of the three parameters predicted to be significant by Taguchi method, methanol: WSFO ratio was the most significant since it had the highest F-value.

v. From the analysis of variance for FAME yield, both the R^2 and R^2_{adj} showed that the models were validated and consistent with the predicted value confirming the acceptability and adequacy of the models.

vi. Though RSM was found to be more accurate, the Taguchi method with 16 runs was observed to be more cost effective and less time consuming than RSM with 32 runs.

From the foregoing, it is safe to conclude that both the RSM and Taguchi methods are useful, efficient, and effective for the optimization of FAME yield in a transesterification process of waste sunflower oil. RSM is more reliable especially in

handling more parameters with nonlinear relationship among the process parameters and response because it predicted higher yield and more value for money. However, Taguchi is more cost effective in the handling processes with a linear relationship between the parameters and the response.

REFERENCES

[1] REN21. Renewables 2018 Global Status Report. Available online: http://www.ren21.net/wp-content/uploads/2018/06/17-8652_GSR2018_FullReport_web_final_.pdf (accessed on 14 Feb. 2019).

[2] International, Energy, and Agency. Renewables 2018. Market Analysis and Forecast from 2018 to 2023. Available online: https://www.iea.org/renewables2018/ (accessed on14 Feb. 2019).

[3] Zhao, C.; Yang, L.; Xing, S.; Luo, W.; Wang, Z.; Lv, P. Biodiesel Production by a Highly Effective Renewable Catalyst from Pyrolytic Rice Husk. *J. Cleaner Prod.* **2018**, *199*, 772–780,. https://doi.org/10.1016/j.jclepro.2018.07.242

[4] Leng, L.; Han, P.; Yuan, X.; Li, J.; Zhou, W. Biodiesel Microemulsion Upgrading and Thermogravimetric Study of Bio-oil produced by Liquefaction of Different Sludges. *Energy* **2018**, *153*, 1061-1072, https://doi.org/10.1016/j.energy.2018.04.087.

[5] Abbaszaadeh, A.; Ghobadian, B.; Omidkhah, M.R.; Najafi, G. Current Biodiesel Production Technologies: A Comparative Review. *Energy Convers. Manage.* **2012**, *63*, 138-148, 2012/11/01/, https://doi.org/10.1016/j.enconman.2012.02.027

[6] Baskar, G.; Aiswarya, R.; Trends in Catalytic Production of Biodiesel from Various Feedstocks. *Renewable and Sustainable Energy Rev*. **2016**, *57*, 496-504. DOI: 10.1016/j.rser.2015.12.101

[7] Santana, H. S.; Tortola, D. S.; Reis, É. M.; Silva, J. L.; Taranto, O. P. Transesterification Reaction of Sunflower Oil and Ethanol for Biodiesel Synthesis in Microchannel Reactor: Experimental and Simulation Studies. *Chem. Eng. J*. **2016**, *302*, 752-762. https://doi.org/10.1016/j.cej.2016.05.122

[8] Tan, Y. H.; Abdullah, M. O.; Nolasco-Hipolito, C. The Potential of Waste Cooking Oil-Based Biodiesel using Heterogeneous Catalyst Derived from Various Calcined Eggshells Coupled with an Emulsification Technique: A Review on the Emission Reduction and Engine Performance. *Renewable and Sustainable Energy Rev.* **2015**, *47*, 589-603. https://doi.org/10.1016/j.rser.2015.03.048

[9] Tan, Y. H.; Abdullah, M. O.; Nolasco-Hipolito, C.; Zauzi, N. S. A. Application of RSM and Taguchi Methods for Optimizing the of Waste Cooking Oil Catalyzed by Solid Ostrich and Chicken-Eggshell Derived CaO. *Renewable Energy* **2017**, *114*, 437-447. https://doi.org/10.1016/j.renene.2017.07.024

[10] Sarve, A.; Sonawane, S. S.; Varma, M. N. Ultrasound Assisted Biodiesel Production from Sesame (Sesamum indicum L.) Oil using Barium Hydroxide as a Heterogeneous Catalyst: Comparative Assessment of Prediction Abilities between Response Surface Methodology (RSM) and Artificial Neural Network (ANN). *Ultrason. Sonochem.* **2015**, *26*, 218-228. https://doi.org/10.1016/j.ultsonch.2015.01.013

[11] Mostafaei, M.; Javadikia, H.; Naderloo, L. Modeling the Effects of Ultrasound Power and Reactor Dimension on the Biodiesel Production Yield: Comparison of Prediction Abilities Between Response Surface Methodology (RSM) and Adaptive Neuro-Fuzzy Inference System (ANFIS). *Energy* **2016**, *115*, 626-636. https://doi.org/10.1016/j.energy.2016.09.028

[12] Veljković, V. B.; Veličković, A. V.; Avramović, J. M. Stamenković, O. S. Modeling of Biodiesel Production: Performance Comparison of Box–Behnken, Face Central Composite and Full Factorial Design. *Chinese J. Chem. Eng*. **2018**. https://doi.org/10.1016/j.cjche.2018.08.002

[13] Corral Bobadilla, M.; Fernández Martínez, R.; Lostado Lorza, R.; Somovilla Gómez, F.; Vergara González, E. Optimizing Biodiesel Production from Waste Cooking Oil Using Genetic Algorithm-Based Support Vector Machines. *Energies* **2018**, *11*, 2995. https://doi.org/10.3390/en11112995

[14] Karmakar, B.; Dhawane, S. H.; Halder, G. Optimization of Biodiesel Production from Castor Oil by Taguchi Design. *J. Environ. Chem. Eng*. **2018**, *6*, 2684-2695.

[15] Dhawane, S. H.; Karmakar, B.; Ghosh, S., Halder, G. Parametric Optimisation of Biodiesel Synthesis from Waste Cooking Oil via Taguchi Approach. *J. Environ. Chem. Eng*. **2018**, *6*, 3971-3980. https://doi.org/10.1016/j.jece.2018.05.053

[16] Hassan S. Z.; Vinjamur, M. Parametric Effects on Kinetics of Esterification for Biodiesel Production: A Taguchi Approach. *Chem. Eng. Sci.* **2014**, *110*, 94-104.

[17] Sharma, S. K. Use of Taguchi Method for Optimization of Biodiesel Production from Waste Cooking Oil. *Invertis J. Renewable Energy* **2018**, *8*, 59-63.

[18] Patrick, M. J. A.; Whitcomb, J. *RSM Simplified: Optimizing Processes Using Response Surface Methods for Design of Experiments*. CRC Press: Boca Raton, FL, USA, 2004.

[19] Sulaiman, N. F.; Bakar, W. A.; Toemen, S.; Kamal, N. M.; Nadarajan, R. In depth Investigation of Bi-Functional, Cu/Zn/γ-Al2O3 Catalyst in Biodiesel Production from Low-Grade Cooking Oil: Optimization using Response Surface Methodology. *Renewable Energy*, **2019**, *135*, 408-416. https://doi.org/10.1016/j.renene.2018.11.111

[20] Nguyen, H.; Huong, D.; Juan, H.-Y.; Su, C.-H.; Chien, C.-C. Liquid Lipase-Catalyzed Esterification of Oleic

Acid with Methanol for Biodiesel Production in the Presence of Superabsorbent Polymer: Optimization by using Response Surface Methodology. *Energies*, **2018**, *11*, 1085. https://doi.org/10.3390/en11051085

[21] Anwar, M.; Rasul, M. G.; Ashwath, N. Production Optimization and Quality Assessment of Papaya (Carica papaya) Biodiesel with Response Surface Methodology. *Energy Convers. Manage.* **2018**, *156*, 103-112. DOI: 10.1016/j.enconman.2017.11.004

[22] Najafi, B.; Faizollahzadeh Ardabili, S.; Shamshirband, S.; Chau, K.-w.; Rabczuk, T. Application of ANNs, ANFIS and RSM to Estimating and Optimizing the Parameters that affect the Yield and Cost of Biodiesel Production. *Eng. Appl. Comput. Fluid Mech*. **2018**, *12*, 611-624.

[23] Adewale, P.; Vithanage, L. N.; Christopher, L. Optimization of Enzyme-Catalyzed Biodiesel Production from Crude Tall Oil using Taguchi Method. *Energy Convers. Manage.* **2017**, *154*, 81-91. DOI: 10.1016/j.enconman.2017.10.045

[24] Na, J. W.; Lee, J.-C.; Kim, H.-W. Biodiesel Production from Waste Cooking Grease: Optimization and Comparative Productivity Assessment. *KSCE J. Civ. Eng*. **2019**, *23*, 1000. https://doi.org/10.1007/s12205-019-0827-2

[25] Aghbashlo, M.; Hosseinpour, S.; Tabatabaei, M.; Soufiyan, M. M. Multi-Objective Exergetic and Technical Optimization of a Piezoelectric Ultrasonic Reactor Applied to Synthesize Biodiesel from Waste Cooking Oil (WCO) using Soft Computing Techniques. *Fuel*, **2019**, 235, 100-112. https://doi.org/10.1016/j.fuel.2018.07.095

[26] Esonye, C.; Onukwuli, O. D.; Ofoefule, A. U. Optimization of Methyl Ester Production from Prunus Amygdalus Seed Oil Using Response Surface Methodology and Artificial Neural Networks. *Renewable Energy*, **2019**, *130*, 61-72. https://doi.org/10.1016/j.renene.2018.06.036

[27] Kurniasih E.; Pardi, P. Analysis of Process Variables on Biodiesel Transesterification Reaction using Taguchi Method. *IOP Conf. Ser.: Mater. Sci. Eng*. **2018**, 420, 012034. doi:10.1088/1757-899X/420/1/012034

[28] Skarlis, S.; Kondili, E.; Kaldellis, J. K. Small-Scale Biodiesel Production Economics: A Case Study Focus on Crete Island. J. Cleaner Prod. **2012**, *20*, 20-26. https://doi.org/10.1016/j.jclepro.2011.08.011

[29] Sun J. et al. Microalgae Biodiesel Production in China: A Preliminary Economic Analysis. *Renewable and Sustainable Energy Rev*. **2019**, *104*, 296-306. https://doi.org/10.1016/j.rser.2019.01.021

[30] Akalın, M. K.; Karagöz, S.; Akyüz, M. Supercritical Ethanol Extraction of Bio-Oils from German Beech Wood: Design of Experiments. *Ind. Crops Prod.* **2013**, *49*, 720-729. https://doi.org/10.1016/j.indcrop.2013.06.036

[31] Gebremariam S. N.; Marchetti, J. M. Economics of Biodiesel Production: Review. *Energy Convers. Manage*, **2018**, *168*, 74-84. https://doi.org/10.1016/j.enconman.2018.05.002

[32] Joshi, S.; Hadiya, P.; Shah, M.; Sircar, A. Techno-Economical and Experimental Analysis of Biodiesel Production from Used Cooking Oil. *BioPhysical Economics Resource Quality*, **2019**, *4*, 2. DOI: 10.1007/s41247-018-0050-7

[33] Awogbemi, O.; Inambao, F. L.; Onuh, E. I. Development and Characterization of Chicken Eggshell waste as Potential Catalyst for Biodiesel Production. International Journal of Mechanical Engineering and Technology, **2018**, *9*, 1329-1346.

[34] Bu, X.; Xie, G.; Peng, Y.; Chen, Y. Kinetic Modeling and Optimization of Flotation Process in a Cyclonic Microbubble Flotation Column using Composite Central Design Methodology. *Int. J. Miner. Process*. **2016**, *157*, 175-183. https://doi.org/10.1016/j.minpro.2016.11.006

[35] Kumar, R. S.; Sureshkumar, K.; Velraj, R. Optimization of Biodiesel Production from Manilkara zapota (L.) Seed Oil using Taguchi Method. *Fuel*, **2015**, *140*, 90-96. https://doi.org/10.1016/j.fuel.2014.09.103

[36] Singh T. S.; Verma, T. N. Taguchi Design Approach for Extraction of Methyl Ester from Waste Cooking Oil using Synthesized CaO as Heterogeneous Catalyst: Response Surface Methodology Optimization. *Energy Convers. Manage*, **2019**, *182*, 383-397. https://doi.org/10.1016/j.enconman.2018.12.077

[37] Dhawane, S. H.; Kumar, T.; Halder, G. Biodiesel Synthesis from Hevea brasiliensis Oil Employing Carbon Supported Heterogeneous Catalyst: Optimization by Taguchi Method. *Renewable Energy* **2016**, *89*, 506-514, https://doi.org/10.1016/j.renene.2015.12.027

[38] Veličković, A. V.; Stamenković, O. S.; Todorović, Z. B.; Veljković, V. B. Application of the Full Factorial Design to Optimization of Base-Catalyzed Sunflower Oil Ethanolysis. *Fuel* **2013**, *104*, 433-442. https://doi.org/10.1016/j.fuel.2012.08.015

[39] Betiku E.; Ajala, S. O. Modeling and Optimization of Thevetia peruviana (yellow oleander) Oil Biodiesel Synthesis via Musa paradisiacal (plantain) Peels as Heterogeneous Base Catalyst: A Case of Artificial Neural Network vs. Response Surface Methodology. *Ind. Crops Prod.* **2014**, *53*, 314-322.

https://doi.org/10.1016/j.indcrop.2013.12.046

[40] Pandit P. R.; Fulekar, M. H. Egg Shell Waste as Heterogeneous Nanocatalyst for Biodiesel Production: Optimized by Response Surface Methodology. *J. Environ. Manage*. **2017**, *198*, 319-329. https://doi.org/10.1016/j.jenvman.2017.04.100

[41] Namwong, S.; Punsuvon, V.; Arirop, W. Process Optimization of Ethyl Ester Biodiesel Production from Used Vegetable Oil under Sodium Methoxide Catalyst

and its Purification by Ion Exchange Resin. *Applied Mech Materials*, **2017**, *873*, 89-94. https://doi.org/10.4028/www.scientific.net/AMM.873.89

[42] Betiku, E.; Akintunde, A. M.; Ojumu, T. V. Banana Peels as A Biobase Catalyst for Fatty Acid Methyl Esters Production Using Napoleon's plume (Bauhinia monandra) Seed Oil: A Process Parameters Optimization Study. *Energy*, **2016**, 103, 797-806. https://doi.org/10.1016/j.energy.2016.02.138

[43] Olutoye, M. A.; Lee, S. C.; Hameed, B. H. Synthesis of Fatty Acid Methyl Ester from Palm Oil (Elaeis Guineensis) with Ky(MgCa)2xO3 as Heterogeneous Catalyst. *Bioresour. Technol*. **2011**, *102*, 10777-10783. DOI: 10.1016/j.biortech.2011.09.033

[44] Kılıç, M.; Uzun, B. B.; Pütün, E.; Pütün, A. E. Optimization of Biodiesel Production from Castor Oil Using Factorial Design. *Fuel Process. Technol,* **2013**, *111*, 105-110.

https://doi.org/10.1016/j.fuproc.2012.05.032

[45] Sirisomboonchai S. et al. Biodiesel Production from Waste Cooking Oil Using Calcined Scallop Shell as Catalyst. *Energy Convers. Manage* **2015**, *95*, 242-247, https://doi.org/10.1016/j.enconman.2015.02.044

[46] Gupta A. R.; Rathod, V. K. Waste Cooking Oil and Waste Chicken Eggshells Derived Solid Base Catalyst for The Biodiesel Production: Optimization and Kinetics. *Waste Manage.* **2018**, *79*, 169-178, 2018/09/01/ 2018. https://doi.org/10.1016/j.wasman.2018.07.022

[47] Pradhan, S.; Madankar, C.; Mohanty, P.; Naik, S. Optimization of Reactive Extraction of Castor Seed to Produce Biodiesel Using Response Surface Methodology. *Fuel*, **2010**, *97*, 848-855. https://doi.org/10.1016/j.fuel.2012.02.052

[48] Tshizanga, N.; Aransiola, E. F.; Oyekola, O. Optimisation of Biodiesel Production from Waste Vegetable Oil and Eggshell Ash. *S. Afr. J. Chem. Eng*, **2017**, *23*, 145-156. https://doi.org/10.1016/j.sajce.2017.05.003

[49] Maneerung, T.; Kawi, S.; Dai, Y.; Wang, C.-H. Sustainable Biodiesel Production via Transesterification of Waste Cooking Oil by using Cao Catalysts Prepared from Chicken Manure. *Energy Convers. Manage* **2016**, *123*, 487-497.

https://doi.org/10.1016/j.enconman.2016.06.071

[50] Bokhari, A.; Chuah, L. F.; Yusup, S.; Klemeš, J. J.; Kamil, R. N. M. Optimisation on Pretreatment of Rubber Seed (Hevea brasiliensis) Oil via Esterification Reaction in a Hydrodynamic Cavitation Reactor. *Bioresour. Technol*. **2016**, *199*, 414-422.

https://doi.org/10.1016/j.biortech.2015.08.013

[51] Jazie, A.; Pramanik, H.; Sinha, A.; Jazie, A. Egg Shell as Eco-Friendly Catalyst for Transesterification of Rapeseed Oil: Optimization for Biodiesel Production. *Int. J. Sustainable Dev. Green Econ.* **2013**, *2*, 27-32.

[52] Varatharajulu, M.; Jayaprakash, G.; Baskar, N.; Kumar, B. S. Comparison of Response Surface Methodology and Taguchi Analysis for Determining Appropriate Drilling Parameters of Duplex 2205. *Asian J. Res. Soc. Sci. and Human.* **2017**, *7*, 1237-1251.

[53] Dhawane, S. H.; Kumar, T.; Halder, G. Central Composite Design Approach Towards Optimization of Flamboyant Pods Derived Steam Activated Carbon for its use as Heterogeneous Catalyst in Transesterification of Hevea brasiliensis oil. *Energy Convers. Manage.* **2015**, *100*, 277-287.

https://doi.org/10.1016/j.enconman.2015.04.083