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Optimization of *Gossypium arboreum* seed oil biodiesel production by central composite rotatable model of response surface methodology and evaluation of its fuel properties

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The need for green based technologies to provide both affordable and environmentally sustainable energy and the ever increasing energy demand of the nations across the globe has led the way for economy based energy research. In this research work, *Gossypium arboreum* seed oil biodiesel production was optimized using a five-level-three-factor central composite rotatable design model of response surface methodology to study the synergistic and antagonistic effects of the catalyst concentration, reaction temperature and time, using base catalyzed transesterification process. The results indicated suitable vegetable oil properties for a single step transesterification reaction. In addition, the least square reduced cubic model used produced the optimal percentage yield for the optimization, yielding a predicted yield of 94.93±6.92% for catalyst concentration of 0.53% by weight of the oil, 60°C for 105 m. The fuel properties of the samples showed linear regression values of 0.980 and 0.933 for viscosity and specific gravity respectively. The model reliability tests conducted were found to be impressive and conclusively can be for the optimization of the oil under stated conditions.

Key words: Biodiesel, *Gossypium arboreum,* interaction, response, yield.

INTRODUCTION

Energy production and consumption are playing critical roles in regional and continental politics across different parts of the world considering the availability, affordability and sustainability of energy in the development of economies and to attain the Millennium Development Goals. In order to address these issues alongside with the increasing energy demand, petroleum crisis and environmental degradation call for renewable energy like biodiesel. Biodiesel derived from vegetable oils or animal fats has emerged as one of the promising alternatives. Biodiesel according to many researchers, is defined as the mono-alkyl esters of long chain fatty acids derived from oils and fats of bio-origin, produced by transesterification of vegetable oils using alcohol in presence of catalyst that conforms to ASTM D-6159 specifications (Cherng-Yuan and Jung-Chi, 2010;

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Kapilan et al., 2009). The use of Straight Vegetable Oils (SVO) in energy production processes has been studied but in the last three decades, renewed interest in biodiesel and bioethanol has re-instigated the research into vegetable oils science and engineering which established that biodiesel is a possible substitute or supplement to mineral diesel for engine and other applications.

A number of vegetable oils have been identified as potential feedstock for production of Biodiesel. However, the availability and sustainability of feedstock is widely accepted as a major challenge in biodiesel production and commercialization. In developing countries like India and many Asian countries where the research and innovations in renewable energy is largely explored, various vegetable oils such as Jatropha, Karanja, Javoba, Mahua etc. from different geo-climatic conditions have been transesterified into biodiesel.

There are different technologies available for the production of biodiesel and many more are expected to emerge in the near future. The most widely used method worldwide however, remains transesterification process to form an alkyl-ester of the fatty acid along with glycerol as a byproduct of the reaction. If the alcohol used in transesterification is methanol or ethanol the resulting alkyl-ester is called Fatty Acid Methyl Ester (FAME) or Fatty Acid Ethyl Ester (FAEE). The application of statistical and mathematical models in designing scientific experiment is a long standing tradition, but in recent times the development of sophisticated analytical and mathematical model based softwares has been appreciated by researchers in different fields.

In recent times, Response Surface Methodology (RSM) in experimental design has increasingly attracted the attention of many researchers. This is due to its advantages primarily in reducing the number of experiments and understanding the pattern in which the measured response is affected by the corresponding changes in variables (Nuran, 2007). The main advantage of RSM is that it enables the improvement of the product from predicted property values and its ability to predict the interactions of more than two or more factors (interactive effects) and effects due to collective contributions of the measured response. The most widely used RSM model is the Central Composite Rotatable Design (CCRD).

A number of researches have been carried out using this model in different areas of scientific experiments. A brief review of literature is provided below. For example Aslan 2008, applied the RSM based on CCRD for modeling and optimization of a multi-gravity separator for Chromite concentration. The author concluded that the predicted values were consistent with the observed values suggesting that the model was suitable for simulation of the experiment under the stated conditions with reasonable precision. The use of the model was also employed by Muhammad et al. (2013) in conducting a microwave-assisted pyrolysis of palm kernel shell optimization, using RSM based on CCRD and concluded that RSM was capable of studying the pyrolysis of the samples under the stated conditions of 30 g mass of oil, 31.5 m reaction time and 100 ml/m nitrogen flow rate. The fact that the method was suitable for other areas of applications was supported by the work of Muazu et al. (2012), who studied and developed a mathematical model for the transesterification of *Jatropha curcas* seed oil using factorial analysis to predict the optimal yield and concluded that the model was found suitable in predicting simulations under the conditions of the study.

In addition, Goyal et al. (2013) studied the adulteration of *Jatropha curcas* seed oil biodiesel optimized by RSM with kerosene. The authors adopted a five-level-four factorial CCRD and obtained about 98.3% optimal yield at the conditions stated in the article. As a final review on the accuracy and wide application of this model, Vicente et al. 1998 applied CCRD in conducting factorial design of experiments for optimization of biodiesel production using refined sunflower oil under homogeneous and heterogeneous catalysis, and concluded that temperature and catalyst concentration have the most significant effects on the yield. An exhaustive review of existing literatures concluded that CCRD based on RSM is one of the most widely accepted techniques for multi-variable optimization with potential application in production of biodiesel and process control. The mutual interaction between various factors affecting the biodiesel production has significant effect on the fuel quality of final product which has to be brought within the ambit of corresponding international standards. It was clear that the design model was capable of predicting and simulating the design with agreeable precision.

The chemical composition of vegetable oil determines to a large extent, the quality of FAMEs that can be produced from such oil. For example, some fuel properties of biodiesel are greatly affected by the structural composition of the oil especially the fatty acid composition. These properties include the ignition quality, heat of combustion, cold flow, oxidation stability viscosity and lubricity while the fatty acid composition affects the engine performance of biodiesel because highly saturated methyl esters have higher cetane values and oxidation stability, but poorer low-temperature flow properties than that are unsaturated (Nakpong and Wootthikanokkhan, 2010; Okoro and Roland, 2011). This clearly explained why most work on biodiesel is focused on using unsaturated oils such as *Jatropha curcas, Karanja* and *Gossypium* arboretum to mention but a few. Another oil property that affects the quality of biodiesel is the acid value of the parent oil. Acid value determines the degree of the completion in the transesterification process; hence, oils with high acid values require a post treatment stage before transesterification becomes feasible, while oils with low acid values such as *Gossypium arboreum* can be transesterified to biodiesel

directly. Jumat et al. (2010) studied the changes in acid values of the same feedstock and attributed the changes to the quality of the oil as well as other factors such as immature seeds and poor storage conditions. It is therefore imperative to study the properties of vegetable oils in production of biodiesel.

Studying the fuel properties of biodiesel is the most important aspect of biodiesel production simply because the properties of any substance that has to be used in diesel engine must conform to the internationally accepted standard such as the ASTM or EN. This is because the fuel properties of one vegetable oil's fatty acid methyl ester can vary significantly with another due to its fatty acid composition (Karnwal et al., 2010).

In this study, the production of biodiesel from *Gossypium arboreum* seed oil FAME (Biodiesel) was optimized by the application of CCRD model based on RSM with the response in terms of percentage yield. With a view to understanding the main and interactive effects of the selected factors such as catalyst concentration, reaction temperature and time of the design set up on percentage yield, predicting a model equation that can best fit into actual model and finally studying the fuel properties of all samples to understand the effects of the design matrix combination on the viscosity, density and specific gravity of the FAMEs.

MATERIALS AND METHODS

The materials and the reagents used in this study were analytical grade (AnalaR) chemicals except otherwise stated, and all the glassware, containers and tools were washed with liquid detergent first, rinsed with 20% (v/v) nitric acid and finally rinsed with distilled water. The oil was purchased from a local vendor in Delhi.

Analysis of *Gossypium arboreum* seed oil

The fuel properties of the neat *Gossypium arboreum* seed oil were determined by standard methods of analysis. The densities (g/cm^3) and specific gravities were measured using density-meter while the kinematic viscosity (at 40°C) was measured. The calorific values were evaluated using and oxygen bomb calorimeter. The physico-chemical properties of both pure oil and the FAME such as acid value and the % Free Fatty Acids (FFA) were also measured using 0.1N NaOH titration, while the oxidation stability index measurement was conducted using Rancimat apparatus. The analysis of the cold filter plugging point was conducted using ASTM D6371 standard on the CFPP measuring equipment. Table 1 highlights some fuel properties of *Gossypium arboreum* seed oil and FAME tested and compared to biodiesel ASTM D6751-07 standards; while Table 2 presents the equipment specifications and the standard methods of analysis for fuel properties.

Experimental design

A response surface methodology was employed using a central composite rotatable design model which is a second order model that includes factorial points, axial points and augmented central points. In this study, the design was performed using a Design of Experiment software "Design of Expert 8.0.7.1 academic version". The independent variables in the design were the catalyst concentration (% wt of oil), reaction temperature (°C) and time (m) to achieve high value of biodiesel yield (%) set as the measurable response factor. The factors were varied over 5 levels set out after the successful completion of the preliminary studies conducted earlier. The coded values and design matrix were presented in the Table 3. The total number of treatments combinations was 20 experimental runs from the formula below:

$$N = 2^k + 2k + N_o$$

Where k is the number of independent variables and N_o is the number of repetition of experiments at the central point for the design to be rotatable. Table 3 shows the variables and their respective levels calculated. The values of each factor levels were computed by setting the lowest and highest levels of each factor as $X_{max.}$ and $X_{min.}$

Transesterification of *Gossypium arboreum* seed oil

A calculated amount of *Gossypium arboreum* seed oil was weighed into a 250 ml conical flask. The oil was initially heated to 120°C and was maintained at that temperature for about 10 m on a heating mantle. The temperature was then allowed to drop to the reaction temperature required. Calculated amount of potassium hydroxide (KOH) flakes was added into a fixed volume of methanol to form the sodium methoxide solution. The mole ratio of oil to Methanol (1:6) was used all through the experiments based on literature and preliminary results of this experiment obtained earlier. In addition, the reaction was maintained at a constant stirring speed of 550 rpm on a heating mantle at the required temperature and reaction time according to the experimental design matrix in Table 3. After the reaction was completed, the mixture was transferred into a 500 ml capacity separating funnel and allowed to stand overnight for gravity separation. The lower layer of glycerin was carefully removed and weighed while the top layer of FAME was washed several times with warm water to almost neutrality. The final biodiesel was heated to 120°C to remove excess water and methanol. The percentage yields were calculated using the formula proposed by Goyal et al. (2013):

% Yield =Initial weight (g) of Oil used/Final weight (g) of Biodiesel *100

The samples were immediately analyzed for fuel and physico-chemical properties according to standard methods then stored in air-tight containers in a cupboard.

RESULTS

The physico-chemical and fuel properties of both the pure oil and the FAME of *Gossypium arboreum* were presented in Table 1 showing the mean of triplicate analysis of each parameter. Table 2 highlighted the standard methods employed and the instrumentation specifications used for the analysis. The coded values and the factor levels of the design matrix for the optimization of *Gossypium arboreum* seed oil biodiesel production was presented in Table 3, while Table 4 presents the factors combinations and their corresponding predicted and actual percentage yields

Table 1. Comparative physico-chemical and fuel properties of *Gossypium arboreum* seed oil, its FAME and biodiesel standards

Parameter	Unit	Pure vegetable Oil	Gossypium arboreum biodiesel	Biodiesel standard ASTM D6751
Acid Value (mg/KOH/g)	mg/KOH/g	0.47	0.16	0.50
FFA	**%**	0.23	0.08	0.25
Density 15°C	g/cm^3	0.92042	0.88238	0.86
Kin. viscosity 40°C	mm^2/s	33.7827	4.3113	4 – 6
Specific Gravity	-	0.9213	0.8836	0.86 – 0.90
Calorific Value	MJ/Kg		39.4585	36
CFPP Value	°C	ND	5	NA
OSI	Hours	ND	> 6hrs except No. 5	EN 14112 (minimum of 3 h)

* ND means analysis not determined.

Table 2. Equipment specifications and standard methods for fuel properties measurement.

S/N	Property	Equipment	Standard
1	Density/Specific gravity	Antor paar DMA 4500	ASTM D1298
2	Viscosity	Viscometer	ASTM D445
3	OSI	873 Biodiesel Rancimat	ASTM D227
4	Acid Number	Titrametric method	ASTM D974-07
5	CFPP	Linetronic Technologies	ASTM D6371
6	FFA	Titrametric method	ASTM D974-07

Table 3. Independent variables and levels to be used for CCRD for biodiesel optimization process.

Independent variable	Code	Levels				
		-1	-0.5	0	+0.5	+1
Catalyst Concentration (% wt)	X_1	0.25	0.5	0.75	1.0	1.25
Temperature (°C)	X_2	40	45	50	55	60
Reaction Time (Mins)	X_3	45	60	75	90	105

expressed as the weight of the final FAMEs produced. Table 5, presents the computed ANOVA for the data showing the significance of the main and interactive effects of the factors combination as it affects the response (yield).

The results were also presented by various figures enumerated in the text. Figure 1 presents the normal probability plot of residuals showing the normality of residuals. Figure 2 presents the correlation between the actual and the predicted values of the yields showing the linear agreement between the two values indicating the measure of accuracy among the results. The contour plots for the interaction between the catalyst concentration and the temperature was presented in Figure 3

Table 4. Central Composite Design Experimental Design showing predicted and observed yield

Expt. No.	Coded Levels			Actual Yield (%)	Predicted Yield (%)
	X_1	X_2	X_3		
1	-1	-1	-1	73.43	74.05
2	-1	-1	+1	86.84	86.5
3	-1	+1	-1	96.32	97.43
4	-1	+1	+1	97.6	97.76
5	+1	-1	-1	93.01	94.06
6	+1	-1	+1	96.81	96.91
7	+1	+1	-1	85.65	87.2
8	+1	+1	+1	92.86	93.45
9	0	0	-0.5	90.42	88.97
10	0	0	+0.5	97.35	98.17
11	0	-0.5	0	83.57	83.3
12	0	+0.5	0	94.96	93.53
13	-0.5	0	0	88.24	87.9
14	+0.5	0	0	95.95	94.58
15	0	0	0	92.53	93.57
16	0	0	0	95.35	93.57
17	0	0	0	93.52	93.57
18	0	0	0	94.79	93.57
19	0	0	0	92.41	93.57
20	0	0	0	93.58	93.57

Table 5. Table of Analysis of Variance (ANOVA)

ANOVA for response surface reduced cubic model analysis of variance table [Partial sum of squares - Type III]						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	**Remarks**
Model	630.87	9	70.1	35.7	< 0.0001	Significant
A-Catalyst Conc.	53.8	1	53.8	27.4	<0.0004	Significant
B-Temperature	126.08	1	126.08	64.21	< 0.0001	Significant
C-Time	102.17	1	102.17	52.04	< 0.0001	Significant
AB	252.68	1	252.68	128.68	< 0.0001	Significant
AC	1.69	1	1.69	0.86	0.375	Not significant
BC	9.5	1	9.5	4.84	0.0524	Not significant
A^2	9.85	1	9.85	5.02	0.049	Significant
B^2	48.39	1	48.39	24.65	0.0006	Significant
ABC	30.19	1	30.19	15.37	0.0029	Significant
Residual	19.64	10	1.96			
Lack of Fit	12.64	5	2.53	1.81	0.2656	Not significant
Pure Error	6.99	5	1.4			
Cor Total	650.5	19				
Std. Dev.	1.40					
R-Squared	0.9698					

and the response surface plot showing the optimal yield position on the surface of catalyst concentration against the temperature was presented in Figure 4.

In the results, some fuel properties of the different batches of biodiesel produced in the optimization stage of *Gossypium arboreum* seed oil were tested. The density (g/cm^3), specific gravity, viscosities (mm^2/s) and calorific value (MJ/Kg) of samples were presented in Figure 5.

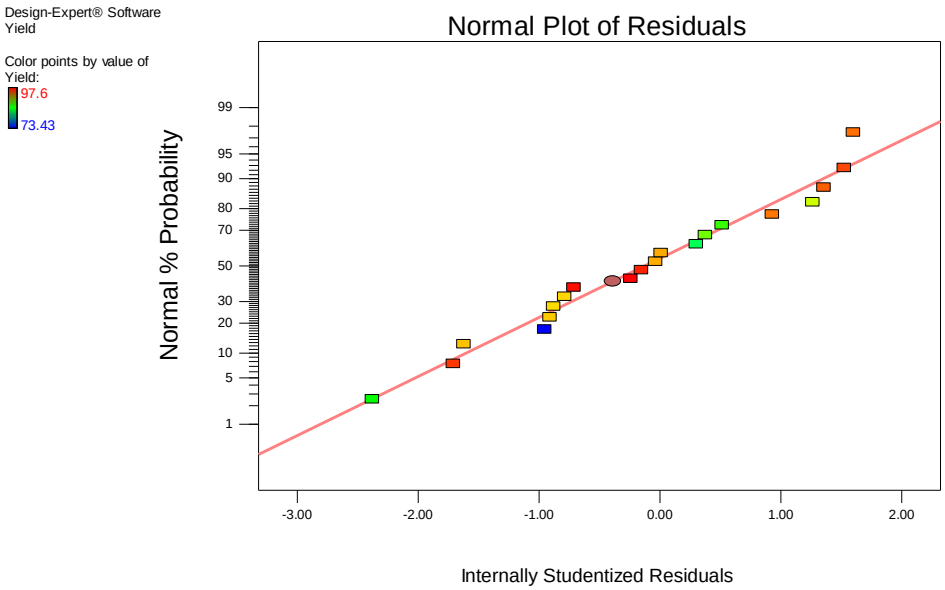

Figure 1. Normal and Probability Plot of Residuals.

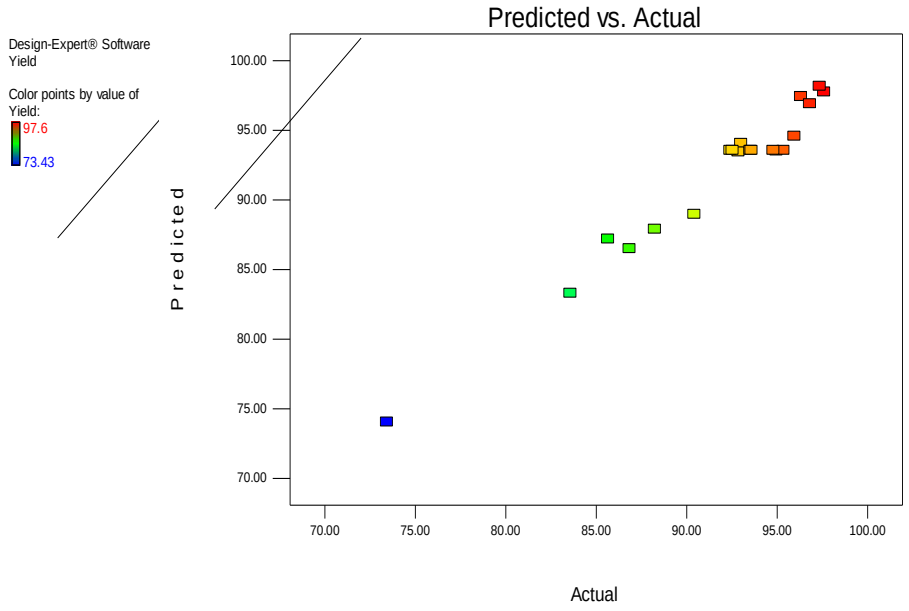

Figure 2. Plot of Predicted versus the Actual.

DISCUSSION

Physic-chemical properties of Gossypium arboreum oil and FAMEs

The results of the physico-chemical properties of the oil and the FAME of *Gossypium arboreum* seed oil revealed that the pure oil has a very low A.V of 0.47% (mg/KOH/g) just like the A.V of Soybean oil was found to be 0.75% as reported by Sima et al. 2009. Other feedstock such as *Jatropha curcas* having A.V in the range of 6.171 to 29.60% (mg/KOH/g) are considered to be very high A.V. as reported by different authors respectively (Jinlin et al., 2011; Mohammed-Dabo et al., 2012). The A.V value of the corresponding FAMEs of the oil in this study was further reduced to 0.16% due to transesterification. The maximum acid value of biodiesel according to ASTM D6751-08 is 0.5 (mg/KOH/g) which means that the pure

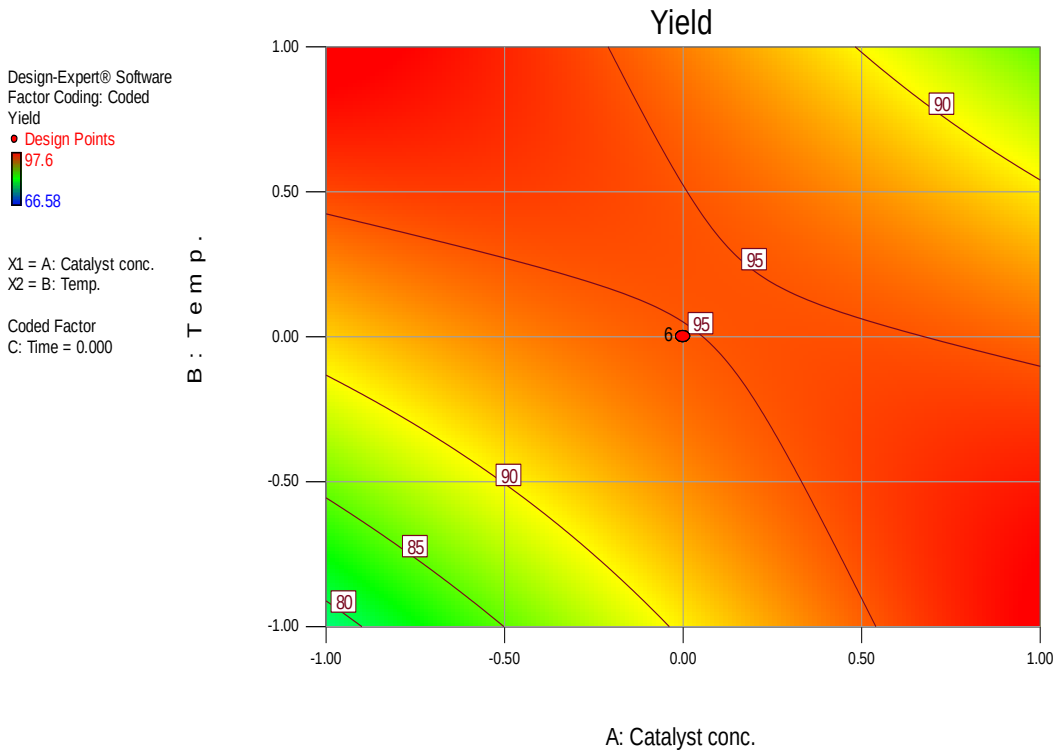

Figure 3. Contour Plot graph of interaction of Mole ratio and Temperature.

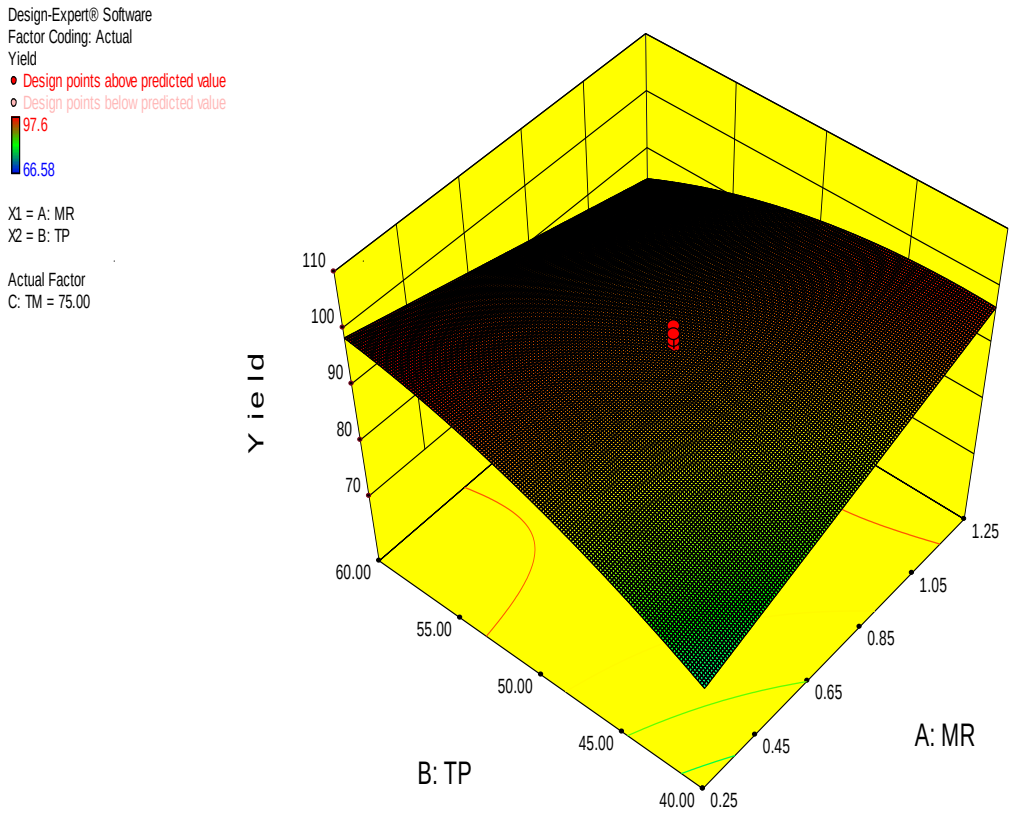

Figure 4. Graph of Response Surface of yield ploted for Mole ratio of catalyst and temperature.

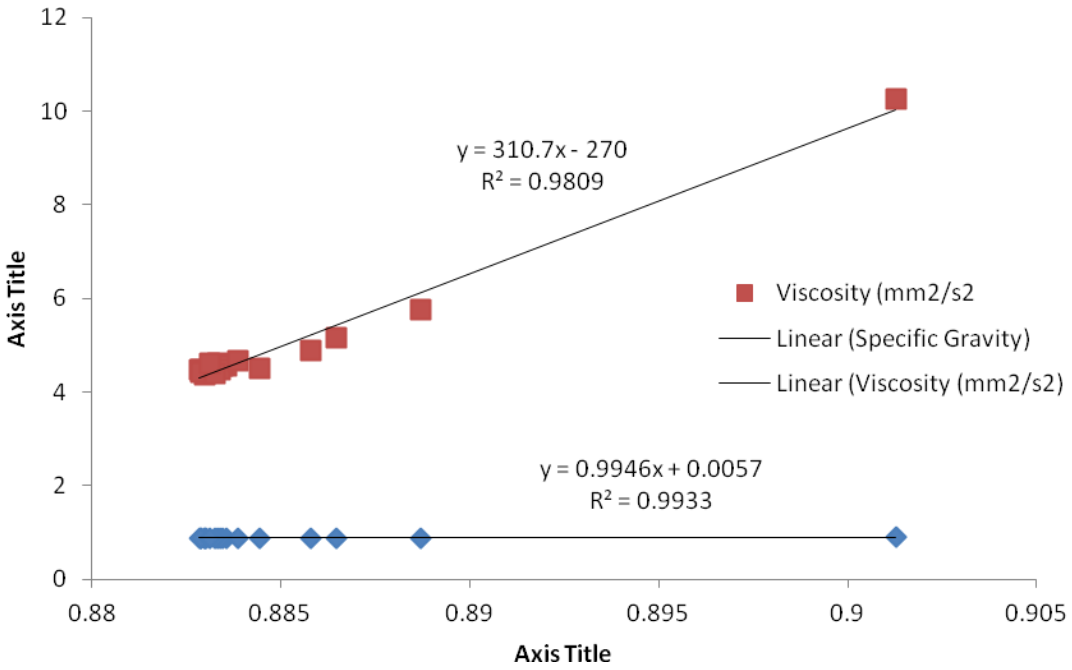

Figure 5. Graph of viscosity and specific gravity.

oil has not exceeded this limit even before the transesterification reaction. The mean value of % FFA of *Gossypium arboreum* seed oil was 0.24%. The % FFA indicates the amount of free fatty acids that can be reacted freely on addition of suitable reagent during esterification. Low FFA value of less than 2% requires no esterification step, since the transesterification reaction can proceed conveniently (Ezeanyanaso et al., 2012). The measure of the Oxidation Stability Index (OSI) of biodiesel is determined by the induction time of the volatile acids formed when biodiesel samples are subjected to oxidation reaction supported by atmospheric oxygen. Oxidation products of FAMEs are various forms of acids or polymers, which can cause fuel system deposits and lead to filter plugging when present in high concentrations. The result of the OSI for the FAME was greater than 6 h which exceeded the minimum three hours limit according to the EN 14112 standard. A lower induction time less than the acceptable limit makes the biodiesel susceptible to oxidation while a higher value indicates better stability (Sharma et al., 2010).

Fuel properties of FAME

The density of biodiesel is an important parameter in determining the quality of any substance that is claimed to be biodiesel or diesel. The density is the mass of a substance per unit volume of that substance. From Figure 5, samples optimized by central composite showed some variations in the density (g/cm^3). The highest density (0.92 g/cm^3) value was recorded in sample 1. This was the only value that was outrageous and far above the acceptable limit for density of biodiesel (0.850-0.890 g/cm^3). This could be attributed to the effect of low temperature (40°C) according to the design. The order of decreasing density is affected by the increase in temperature as well as the reaction time. This finding was consistent with that reported by (Ezeanyanaso et al., 2012). It was observed that the densities of biodiesels produced at lower temperature were found to be high even though it were still within the range of acceptable limits internationally. Reaction time may not have significant effect on density but the catalyst concentration could have positive effects if the parameters were to be studied separately. Specific gravity in most studies conducted on fuel properties of FAMEs has been found to exhibit similar trends as the density because it is a function of density. This fact was further established by the results of this study. The graph of the specific gravity of the *Gossypium arboreum* seed oil FAMEs was found to be in similar trend with a regression value of R^2 0.933 for specific gravity.

The viscosity of a biodiesel is defined as the shear stress to the shear rate for a fluid often measured using viscometer in measuring the viscosities of SVO and their corresponding MEs (Ezeanyanaso et al., 2011). In this study, kinematic viscosities of samples were all within the acceptable limits for biodiesel; the range viscosity values was 4.3601 – 10.26949 (mm^2/s) while the value of the linear graph R^2 was found to be 0.980 for viscosity. The viscosity was lower than the kinematic viscosity value of

Jatropha curcas of 4.756 (mm^2/s) for B100 biodiesel reported by (Amish et al., 2011). High viscosity is reported to decrease complete atomization of the biodiesel in engines and result into power loss; while on the other hand it improves the spray pattern of injected biodiesel during combustion (Aydin et al., 2011). All authors generally, accepted that higher viscosity was not desirable for better engine performance and combustion. The calorific value of a biodiesel is the measure of the energy released during combustion of biodiesel in an engine, making it one of the most important fuel properties of biodiesel that determines the power output on application on engines. Higher calorific value entails good combustion and much energy is released (Jinlin et al., 2011). The biodiesel produced from *Gossypium arboreum* seed oil has an average calorific value of 39.3902 (MJ/Kg) which was found to be in agreement with other biodiesels produced from different feedstock. *Jatropha curcas* was reported to have the calorific value of 40.59 and 37.05 (MJ/Kg) for the same feedstock as reported by different authors (Goyal et al., 2013; Muazu et al., 2012).

Optimization of FAME production

A total of 20 experiments were performed to obtain the actual values for the optimization. The results of the predicted and actual values of the percentage yields of the optimization of biodiesel production of the seed oil by RSM based on CCRD was presented in Table 4. The values of experimental yields obtained showed close range with the predicted values, when the predicted values are quite close to the experimental values. This is an indication of the validity and reliability of the developed model for establishing a correlation between the process variables and the production yield (Leung et al., 2011). From the results, it could be deduced that actual percentage yields of the factorial points were in good agreement with the predicted yields except for run number 7 (+1,+1,-1), where the actual yield was 85.65% and the corresponding predicted yield was 87.2%. The low reaction temperature (40°C) and highest catalyst concentration of 1.25% could be responsible for the low yield since the temperature retards the completion of the mass transfer required to take the reaction into completion. Yield decreases significantly with increasing catalyst concentration due to the excessive addition of catalyst which cause more triglyceride to react with alkali catalyst to form soap which in turn deceases the yield; increase the pH of the biodiesel; which requires thorough washing with water to remove the left over catalyst, resulting in further loss of methyl esters (Sharma et al., 2010; Leung et al., 2011).

The range of actual percentage yields of the eight factorial points was from 73.43 to 97.60% with the highest value of 97.6% while the predicted values range from 74.05 to 97.76% having the highest value of 97.76% at the factorial combination point (-1, +1, +1). This point has the lowest catalyst concentration (0.25%) reacting under highest reaction temperature and time. Both the reaction time and temperature have positive effects on the percentage response (yield). The initial stage of the transesterification proceeds very slowly due to mass transfer resistance between the alcohol and the oil, the reaction then proceeds faster as soon as the resistance is overcome. Longer reaction time increases the conversion rate of the fatty acids to form biodiesel while the increase in biodiesel yield at higher temperature is due to the fact that viscosity of oils decreases at high temperatures and results in an increased reaction rate and shortened reaction time, thereby, increasing the biodiesel yield. It also increases with increase in reaction time at low catalyst concentration (Goyal et al., 2013; Leung et al., 2011).

The lower and upper limits of the range for all the 20 experimental sets (73.43 and 97.35%) were found within the factorial points suggesting the accuracy of the model design. Overall, the percentage mean of the experimental yield was 91.76±5.85% indicating that the percentage yield of the *Gossypium arboreum* seed oil biodiesel production was still low compared to other vegetable oils.

Sharma et al. 2010 reported an optimal yield of 97.43% conversion of FAME of *Pongamia pinnata* oil using heterogeneous catalyst developed which was attributed to the efficiency of heterogeneous catalyzed transesterification reaction over homogeneous catalyzed transesterification process. Xiaohun et al. 2011 reported a value of 97% as the optimal actual yield at methanol/oil ratio of 7.9, temperature of 53°C at a reaction time of 45 m and stirring speed of 268 rpm and 1% catalysts concentration for cotton seed oil which was further improved via optimization of the biodiesel using ultrasonic set up and reported a high yield of 95% within 10 m of the reaction at 25°C, 1:6 mole ratio, 1% by weight of NaOH and 40 kHz power of ultrasonic irradiation.

In this research, the overall average of the actual percentage yield was 91.25% which was higher than the average predicted yield of 82.18%. *Gossypium arboreum* seed oil could have such magnificent yield of FAME especially when considering the low A.V of the pure oil that enable the transesterification process to take place with no need of esterification.

Analysis of variance (ANOVA)

Analysis of variance was applied on the data to estimate the effects of main and interactive effects of the factor combinations on the yield. From Table 5, Response Surface Reduced cubic model based on Partial Sum of Squares Type III (aka Partial) is the sum of squares (SS) corresponding to each effect adjusted for every other effect in the model as chosen after testing the

reproducibility of the model suggested by the software and compared with the obtained results; while the insignificant terms of the model were corrected by automatic backward and stepwise correction model (Noordin et al., 2004). It was clear that all three factors under examination as well as the model were statistically significant p<.01 while the intercept yield from the coefficient table indicated a high yield of 93.56% with the main effects (temperature, time and catalysts concentration) showing significance of p <.01, for the factor A, factor B was significant with p <.01 and factor C was p <.10 respectively. Generally, p-values lower than 0.05 indicate that the overall model is significant due to large number of individual significant terms which is desirable in indicating that they have effect on the response and was sufficient to represent the actual relationship between the response and the independent variables (Goyal et al., 2013; Simas et al., 2009; Razali et al., 2010).

This relationship can be represented by the second order polynomial equation used in predicting the response surface linear regression as a function of the independent variables and their interactions (Basri et al., 2010).

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{3} \beta_{ij} x_i x_j \quad (1)$$

Where X_i and X_j are the uncoded independent variables β_o is the intercept, β_i, β_{ii} and β_{ij} represent the linear, quadratic and interaction constant coefficients respectively, while Y is the response (Yield).

Interaction effects

The effects of independent variables on the yields were also accompanied by the effects of their interactions. These are the effects due to multiples of one factor and another or the same factor. These interaction factors must be considered as the individual effect plot does not give information regarding the significant interaction involved (Basri et al., 2007). These effects resulting from the multiples of either the same factors or two factors are known as compounding or interaction effects. From the ANOVA (Table 5), it was visible that only the interaction of the catalyst concentration and reaction of the temperature (AB p-0.01) was significant for the first order polynomials of the independent factor combinations while the rest of the first order terms were not significant implying that the term has effect on the response (yield); while the interactions between the catalyst concentrations and the reaction time (A * C) was insignificant. The interactions effect between the reaction temperature and the time (B * C) had no significant effect on the yields.

In addition, the second polynomial terms were all statistically significant at different levels of significance. This signified that, the so called insignifant interactions (A * C and B * C) in the first order are actually significant as the sample population increases. However, been significant does not defines positive or negative effect on the yield, rather it means that when such a term is increased or decreased a corresponding change in the response is expected. From the results, it could be suggested that factors A and B as well as their corresponding interactions have much impact on the yield than C. In order to determine the positive and negative contributions of independent and interactive terms in the model, the response equation is employed to calculate both the coded and un-coded values of the response.

Response equation

The final empirical model of the response for the un-coded values of the factors was generated as shown below:

$$Y= -72.79+115.96A+3.97B+0.78C-2.09AB-0.67AC-0.13BC–3.29A^2 -0.01B^2-0.01ABC \quad (2)$$

The response equation shows the coefficients of the full regression equation and their statistical significance as well as the actual impact of each model term on the yield. In the above equation, the sign (+ or -) in front of each term indicates a synergistic or antagonistic effect on the yield respectively (Razali et al., 2010).

Reliability of the model

In determining the model reliability, the R^2 value also known as determination or regression coefficient is important in indicating the model fitness. A high value of the predicted R^2 value is an indication of precision. In Table 5, R^2 (0.9698) shows that only 3.02% of the total variation on the yield could not be explained by the model, the more the value approaches unity, the better the model fits the experimental data (Basri et al., 2007). Other additional information on the data reliability are the values CV and the R^2_{adj}. All the information obtained was used in the point prediction of the optimal yield and the results indicated the yield value of 94.93±6.92% at 95% confidence level.

The probability of finding the optimal point of the actual and the predicted yield is represented by the normal probability plots of residuals (Nuran, 2007). The contour plots are important tools in interpreting the interaction of only two factors while keeping the other factor at a constant value of arbitrary zero. This is presented on the plane of the plot showing the contour lines coming closer

to the centre point as the temperature increases and the mole ratio of the catalyst as well. Therefore the overall effects of all these unresolved interactions results in decrease in yield on a general note, contour lines give an insight into the interaction effects that could be further explained by the plot of interactions. It is very difficult to completely separate and identify the effects of complex aliasing in a large design and the interpretation of their significance is mainly resolved by screening design (Nuran, 2007).

The response surface plot of the optimization was plotted for the effect of temperature of the reaction against the catalyst concentration at a constant reaction time. The plot highlighted the effects of these factors on the response with an increasing yield on the increase of the factors while the effect of time was considered constant.

Conclusion

The following conclusions are drawn on the study conducted on the optimization of *Gossypium arboreum* seed oil biodiesel using conventional homogenous transesterification:

(1) The physico-chemical properties of the pure vegetable oil (such as low FFA value, relative oxidation stability) used.
(2) RSM based on CCRD was found to be suitable for the optimization yielding a predicted yield of the yield value of 94.93±6.92% for catalyst concentration of 0.53% by weight of the oil, 60°C against 105 m reaction time at 95% confidence level.
(3) The independent factors evaluated in this study (Catalyst concentration, reaction temperature and time) were found to be significant in the first order except for the reaction time, while all their second order interactions were significant on the percentage yields.
(4) The fuel properties of all the samples indicated linear regression in the order of R^2, were found to be 0.980 and 0.933 viscosity and specific gravity respectively. It was also observed that the fuel quality of some biodiesels produced especially at lower factor levels were relative.
(5) The study concluded that the model was suitable of the optimization.

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