Optimal Process Conditions for Enhanced Co-Solvent Based Transesterification of Tigernut Oil

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Abstract: A two-step transesterification of tigernut oil with methanol in di-ethyl ether (co-solvent) was carried out, and a four-factors-four-levels central composite design optimization study was also carried out to maximize the yield of the biodiesel. A maximum yield of 89.3% was obtained under the optimal transestrification conditions of methanol-to-oil volume ratio of 7:1, catalyst loading of 1.0 w/w %, temperature of 36 ^{o}C and reaction time of 30 minutes. Furthermore, analysis of the biodiesel produced showed that its kinematic viscosity (5.58 mm^2/s) and pour point (6 ℃) fell within the ASTM range, while its cloud point (14 ℃) was very close to the ASTM range. Its flash point of 185 ℃ was however, on the high side. Additionally, characterization of the tiger nut oil biodiesel using GC-MS confirmed the presence of methyl ester on the biodiesel sample.

Keywords: Biodiesel; Co-solvent; Design; Optimization; Tiger nut oil; Transesterification.

Introduction

Among all the alternative sources of energy that has been investigated by researchers, biodiesel has carved an important niche for itself for several reasons. Biodiesel is one of the renewable, nontoxic and environmental friendly alternative fuels that can be used in a diesel engine with little or no modification to the engine. In comparison to petrodiesel, biodiesel is highly biodegradable, has minimal toxicity, zero emissions of aromatic compounds, no sulphur emissions, ultra-low carbon monoxide emissions and much less particulate matter emissions (Datta *et al*., 2014).

The word 'biodiesel' has been used for trans-esterified vegetable oil, or animal fat to describe its use as a diesel fuel. Transesterification can be defined as the reaction between vegetable oils or animal fats and a low-molecular weight alcohol such as methanol or ethanol in the presence of a base or acid catalyst (Dabo *et al*., 2012). The invention of the diesel engine has been credited to Rudolph Diesel, a German mechanical engineer. In 1893, he published a paper entitled '*the theory and construction of a rational heat engine*'. What the paper described was a revolutionary engine in which air would be compressed by a piston to a very high pressure thereby generating a high temperature. Rudolph Diesel designed his prototype engines to run on vegetable oil and he used peanut oil to fuel one of his engines at the Paris Exposition of 1900. However, some operational problems were reported due to the high viscosity of vegetable oils compared to petroleum diesel fuel, which results in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves. Attempts to overcome these problems included heating of the vegetable oil, blending it with petroleum-derived diesel fuel or ethanol, cracking and pyrolysis of the oils, and transesterification of the oils. Transesterification was found to be the best method because it was suitable to a broad range of feedstock, and the quality of biodiesel produced through this method is

close to the quality of conventional diesel (Abbaszaadeh *et al*., 2012).

Various types of vegetable oils such as castor seed oil, rapeseed oil, sunflower oil, jatropha seed oil and palm kernel oil have been used in the production of biodiesel. For example Olutoye *et al*. (2016) carried out the synthesis of biodiesel from palm kernel oil using mixed clay-eggshell heterogeneous catalysts. Jatropha seed oil has also been widely studied and used for the production of biodiesel with good results (Saleh *et al*., 2015; Reddy *et al*., 2016). Soybean oil is also another widely studied source of biodiesel. Özener *et al*. (2014) carried out detailed study of the effects of soybean biodiesel on the diesel engine performance, emissions and combustion characteristics. Akaagerger *et al*. (2016) successfully used desert date seed oil to produce biodiesel. In the present work, biodiesel was synthesized from tigernut oil. Tiger nut (*Cyperus esculentus*) is a crop that is widespread across much of the world. It is found in most of the Eastern Hemisphere, including Southern Europe, Africa and Madagascar, as well as the Middle East and the Indian subcontinent. It is particularly abundant locally, in the northern and middle belt states of Nigeria. In the present work, homogenous catalysis was used to transesterify the tiger nut oil in a mixture of methanol and di-ethyl ether (used as co-solvent), with potassium hydroxide as catalyst. The use of co-solvent has been reported by several researchers where they established the efficacy of a co-solvent in lowering the reaction temperature (Dabo *et al*., 2012; Luu *et al*., 2014; Athlulya *et al*., 2017). Furthermore, It has been proven by many researchers that the yield of biodiesel is highly dependent on the transesterification process parameters such as the reaction temperature, amount of catalyst relative to feed, reaction time, alcohol to oil molar ratio and the speed of agitation (Ayetor *et al*., 2015; Murugesan *et al*., 2015; Reddy *et al*., 2016; Mahmudul *et al*., 2017). In order to avoid the problem of saponification, a two-step conversion process was used for the synthesis of biodiesel from the tiger nut oil. These are: first, the acid-catalyzed esterification of the tiger nut oil and then secondly, the base-catalyzed transesterification of the tiger nut oil. Acid-catalyzed esterification pretreatment is used to lower the FFA content by converting them to esters. The acid-catalyzed esterification requires additional acid and methanol usage. But if it is not carried out, then the FFAs will react with the base catalyst to form soap thus using up valuable catalyst in the process (Gebremariam & Marchetti, 2017).

Computer-aided statistical design of experiments is a powerful tool that is used to acquire and analyze data from the influence of process parameters on the yield of fatty acid methyl ester from oils, rapidly and efficiently, using a minimum number of experiments. This method has been employed in this work to optimize the process parameters that gives the maximum biodiesel yield. The aim of experimental design is therefore to optimize the yield of the biodiesel that is to be produced by first carrying out a mathematical model using Surface Response Methodology (RSM). The Central Composite Design method was selected for the design of the experiment and the experiment for the modeling and optimization was designed using a five-levels-four-factors central composite design (CCD) with the help of Design Expert Software 6.06. The objective of this research is therefore: to contribute to the vast body of literature on biodiesel by investigating a novel source of this valuable

fuel namely tiger nuts. And secondly, but equally important is to provide an economic opportunity to our local farmers who specialize in the production of tiger nuts by making it a cash crop of international repute.

Methodology

Extraction and Transesterification of the Tiger Nut Oil

The tiger nut was obtained from a market in Minna, Niger state Nigeria. The seeds were first cleaned and sorted to remove dirt and other impurities and thereafter, fifty kg of the seeds was then poured into the oil expelling machine and 5 liters (5000 cm^3) of the oil was extracted from the seeds after the operation. This translated to an oil yield of about 9 wt % given that the density of tiger nut oil is about 0.8956 kg/cm^3. The oil obtained was then sieved to remove any solid particles. The raw oil was then characterized to determine its moisture content (ASTM D2709), peroxide value (ASTM D1832), acid value (ASTM D664), density (ASTM D4052) and free fatty acid content, (ASTM D5555). For the base-catalyzed transesterification of the raw tiger nut oil, 100 grams of the oil was measured and poured into a 150 cm^3 conical flask and heated to a temperature of 36 ℃ using a water bath. A solution of sodium methoxide was prepared in a 250 cm^3 flask. 0.9 grams of sodium hydroxide was dissolved in 68.06 grams of analytical grade methanol (approximately 99.5 % purity), and to this solution, 85.93 cm^3 of diethyl ether (the co-solvent) was added. The resulting solution was added to the oil being stirred in the conical flask at 32 ℃ and the reaction was allowed to proceed for 60 minutes. The mixture was left to settle for 24 hours in a separating funnel. After settling the upper layer, i.e. the biodiesel layer, was decanted into a separate beaker. The lower layer which comprises of glycerol and soap were collected from the bottom of the funnel. The biodiesel was then washed to remove any remaining methanol, glycerin, catalyst, soaps and other impurities. The quantity of biodiesel collected was then measured and recorded.

Characterization of the Biodiesel Produced

The physiochemical/fuel properties of the biodiesel produced from the tiger nut oil was determined and compared with ASTM specifications. The following properties were investigated: flash point (ASTM D93), pour point (ASTM D97), cloud point (ASTM D2500), acid value (ASTM D664), iodine value (ASTM D1959), saponification value and kinematic viscosity (ASTM D2983), amongst others. Furthermore, a gas-chromatography mass-spectrometer (GCMS) analysis was carried out on the biodiesel produced in order to identify the chemical constituents and functional groups present. The Tiger nut biodiesel sample was injected into the chromatography column through a long capillary tubing. As the sample entered the column, it vaporized and moved through the column by a stream of carrier gas. The components of tiger nut biodiesel sample have different molecular weight and solubility and so travelled at different speeds. The components of the tiger nut biodiesel were separated as they travel through the column. As the separated components exited the gas chromatography column, they enter the source chamber of the mass spectrometer which detects, quantifies, analyses and identified the various components of the tiger nut biodiesel sample. The result of the quantitative analyses was displayed as

chromatogram on a computer screen connected to the machine.

Design of the Experiment

The design generated 30 runs and the effect of the transesterification process variables (i.e., the oil-to-methanol mole ratio with coded value (X1), the catalyst weight with coded value (X2), the reaction temperature with coded value (X3) and reaction time with coded value symbol (X4)) were investigated. Table I presents the five-levels-four factors central composite design for the tiger nut oil conversion via transesterification. The relationship between the yield of biodiesel and the interaction between the four independent variables is given by the equation

$$Y = \alpha_0 + \sum_{j=1}^{4} \alpha_j X_j + \sum_{i,j=1}^{4} \alpha_{ij} X_i X_j + \sum_{j=1}^{4} \alpha_{jj} X_j^2 \quad (1)$$

where Y is the biodiesel yield, X_i and X_j represent the process parameters, α_0 is the offset term, α_j is the regression coefficient for the linear term, α_{ij} is the regression coefficient for the first order term and α_{jj} is the regression coefficient for quadratic effect. A comprehensive design matrix including the values of the responses obtained from the experimental work was then generated from which the ANOVA for the model was then obtained.

A multiple regression analysis was done using Design Expert software 6.06 to fit the model to the experimental data in order to obtain the fitted quadratic response model. A model equation in terms of actual factors including the non – significant terms for biodiesel yield is given by the truncated second order polynomial equation

$$Y = 77.50 - 2.31 X_1 + 0.68X_2 - 6.41X_3 + 0.16X_4 - 0.57X_1X_2 - 0.66 X_1X_3 - 0.82X_1X_4 - 1.34X_2X_3 + 3.44X_2X_4 - 0.92X_3X_4 \quad (2)$$

The adequacy of the selected quadratic model was confirmed from the ANOVA table generated using the Design Expert Software. The results of the analysis of variance (ANOVA) for the response surface model is presented in Table II.

Results and Discussion

Table III present the result of the characterization of the raw tiger nut oil while Table IV presents the result of characterization of the biodiesel produced. The moisture content of the feed was measured and found to be about 1.13%wt while the free acid content of the feed stood at about 1.927 $mgKOH/100g$. Water and free fatty acid (FFA) contents in the feed are critical factors in the transesterification reaction because research has shown that the transesterification reaction will not occur if the free fatty acid value of the oil is above 3 wt % (Olutoye, 2015). Also, the presence of water in the feed causes the triglycerides to break down into FFAs and diglycerides (Gebremariam & Marchetti, 2017). Bouaid *et al*. (2016) have shown that the yield of methyl ester (ME) decreased from 97.2% to 95% when the FFA content of the oil increased from 0% to 4%. The FFA content of the biodiesel produced was also determined and found to be about 0.4908 $\%wt$, which was just under the 0.5 $\%wt$ maximum recommended by the ASTM specifications. Furthermore, a detailed study of the effect of FFA and its effects on diesel engine performance has shown that high FFA contents in biodiesels can prove deleterious to internal combustion engines (Canakci, 2001). Other important ASTM specifications on biodiesel are the specifications on the biodiesel viscosity, flash point and pour point. The high viscosity of vegetable oils is

one of the major reasons why they must be trans-esterified before they can be used in internal combustion engines. Problems such as piston ring sticking and thickening of the lubricating oil has arisen where engines have been fuelled with vegetable oils (Canakci, 2001). In the present study, the kinematic viscosity of the tiger nut biodiesel oil produced was found to be

Table V: Experimental range and levels of the independent variables

Variables	Symbols	Coded Factor Levels				
		low (-1)		0	High (+1)	
Methanol-to-oil mole ratio	X_1	5:1	6:1	7:1	8:1	9:1
Catalyst weight (grams)	X_2	0.8	0.9	1.0	1.1	1.2
Temperature (^oC)	X_3	30	32	36	38	40
Time (min)	X_4	30	40	50	60	70

Table VI: Analysis of Variance for the Response Surface Model

Source	Sum of Squares	Df	Mean Square	F Value	p-value	
Model	1161.90	14	82.99	1221.87	<0.0001	Significant
X_1	56.31	1	56.31	828.96	<0.0001	
X_2	6.07	1	6.07	89.31	<0.0001	
X_3	256.24	1	256.24	3772.57	<0.0001	
X_4	0.27	1	0.27	4.00	0.0640	
X_1X_2	5.04	1	5.04	74.13	<0.0001	
X_1X_3	12.11	1	12.11	178.22	<0.0001	
X_1X_4	9.53	1	9.53	140.33	<0.0001	
X_2X_3	50.22	1	50.22	739.34	<0.0001	
X_2X_4	167.30	1	167.30	2463.03	<0.0001	
X_3X_4	21.08	1	21.08	310.30	<0.0001	
X_1^2	149.50	1	149.50	2200.99	<0.0001	
X_2^2	128.58	1	128.58	1893.04	<0.0001	
X_3^2	267.99	1	267.99	3945.50	<0.0001	
X_4^2	176.97	1	176.97	2605.46	<0.0001	
Residual	1.02	15	0.068			
Lack of Fit	0.98	2.9	0.098	12.24	0.0064	insignificant
Pure of Error	0.040	5	8.00E-03			
Cor Total	1162.92	29				
$SD = 0.26,$	$R^2 = 0.9991,$	$Adj\ R^2 = 0.9983$				

Table VII: Results from the Analysis of the Raw Tiger nut Oil

Properties	Unit	ASTM Test	Tigernut Oil
Free fatty acid	$mgKOH/100g$	D5555	1.927
Acid value	$mgKOH/100g$	D664	3.854
Peroxide value	mmol/kg	D1832	1.490
Moisture content	%wt	D2709	1.13
Density	g/cm^3	D4052	0.8956

about 5.58 *mm^2/sec*, which fell within the recommended ASTM range. The flash point of the biodiesel produced fell outside the ASTM range (about 30 % higher). The high flash point was probably due to the residual methanol in the biodiesel after washing since excess methanol was used during the transesterification reaction based on the recommendation from literature (Wong *et al*., 2015; Talha & Sulaiman, 2016). The pour point fell within the ASTM range while the cloud point was a little higher (about 14 %). Pour point and cloud point are low temperature properties of diesel fuels and they can significantly affect the performance of the engine under low temperature conditions. At harsh, cold conditions and low temperatures, the heavy

Table VIII: Results from the Analysis of the Tiger nut Oil Biodiesel produced

PROPERTIES	UNIT	ASTM TEST	TIGERNUT BIODIESEL	ASTM SPECIFICATION
Color	-		Yellow	-
Moisture Content	$\%wt$	D2709	0.02	0.05 max
Acid value	$mgKOH/g$	D664	0.98175	1 max
% FFA	$\%wt$	D5555	0.4908	0.5 max
Specific gravity @ 25	-	D4052	0.8772	0.87-0.90
Iodine value	$Mgiodine/g$	D1959	53.38	-
Saponification value	$mgKOH/g$	AOAC 25	158.905	-
Kinematic viscosity	mm^2/sec	D2983	5.58	1.9-6.0
Flash point	℃	D93	185	130
Cloud point	℃	D2500	14	-3 to 12
Pour point	℃	D97	6	-5 to 10

aliphatic groups in the oil start to form solid crystals called wax. As the temperature drops further, these newly formed crystals start to aggregate and finally plug the engine filter. In harsh cases the diesel fuel may even stop flowing. The temperature at which fuel stops to flow is called the pour point. In the oil industry, cloud point refers to the temperature below which wax in diesel or biowax in biodiesels forms a cloudy appearance. Fig. 1 presents the result of the analysis of the biodiesel produced using Gas-chromatography-mass spectrometer (GC-MS) in order to determine its molecular composition. The result of the GC-MS analysis confirms the

presence of methyl ester on the biodiesel sample. The highest peak (peak 28) was identified to be 11- Octadecenoic acid, methyl ester and other lower peaks were also identified as methyl esters present in the biodiesel sample.

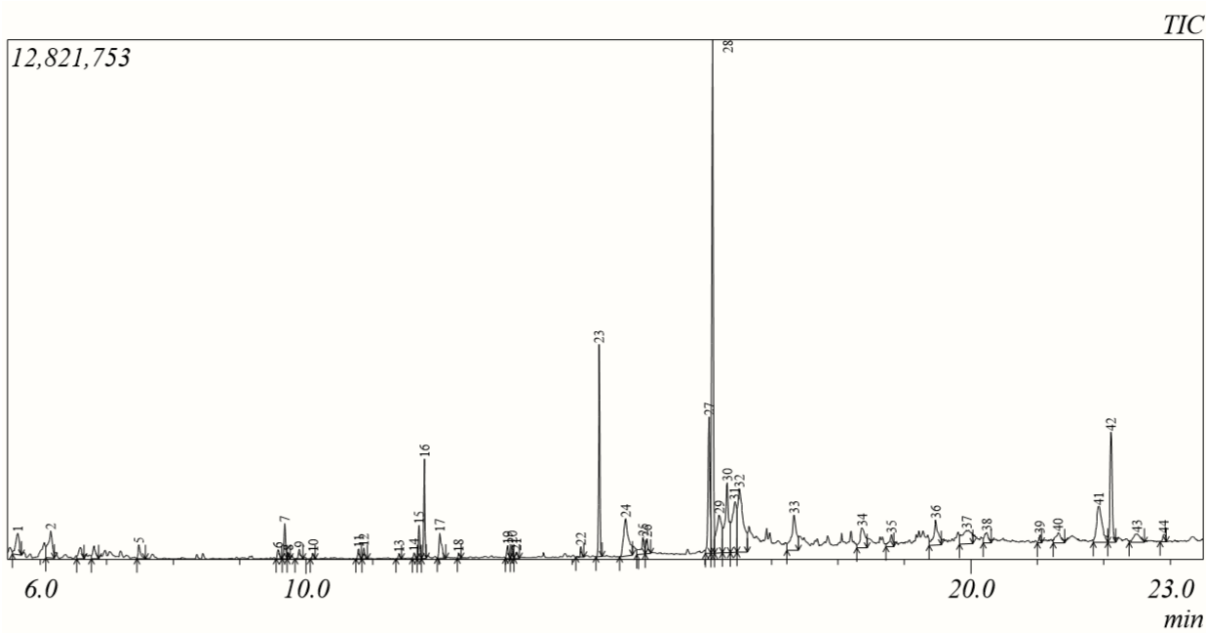

Fig. 1: GC-MS chromatogram of tiger nut oil biodiesel

Modeling

The ANOVA showed that the model has a high $F-value$ which implies that the model is significant (Wong *et al.*, 2015). The high F-value of the model led to the rejection of the null hypothesis and acceptance of the alternative hypothesis which implies that at least one of the variables studied significantly affect the yield of biodiesel produced using co-solvent technique. The P-value of 0.0001 implies that there is only a 0.01% chance that the large "F-value" obtained for the model is due to noise. Values of "Prob > F" less than 0.05 indicate model terms are significant at the 95% confidence level. "Prob > F" for each of the model terms less than 0.05 indicates that the terms in the model have a significant effect on the response. In this case A, B, C, D, A^2, B^2, C^2, D^2, AB, AC, AD, BC, BD, CD are significant model terms. The "Lack of Fit F-value" of 2.90 implies the Lack of Fit is not significant relative to the pure error. The "Prob > F" value associated with the lack of fit implies that there is a 12.22% chance that a "Lack of Fit F-value" this large could occur due to noise. The Non-significant lack of fit is good as it is desired for the model to fit the data well. The values of the

predicted biodiesel yield is compared to the experimental results and presented in the form of a plot shown in Fig. 2. The value of R^2 generated for the developed model Equation 2 was found to be 0.9991 which communicates a very strong relationship between the experimental and the predicted biodiesel yield. The standard deviation for the same model equation was determined to be 0.26. This also shows that the experimental values obtained for the biodiesel yield agrees reasonably well with the values suggested by the model. Furthermore, the effect of each variables on the biodiesel as they interact with other

variables can be deduced from the ANOVA. As seen from Table II, the reaction time had no effect on the biodiesel yield, i.e. its $p-value$ was greater than 0.05 implying that it is statistically insignificant from a standpoint of its interaction with the other variables in determining the yield of biodiesel. Other works have shown that other variables may become insignificant when a heterogeneous catalyst is used (Olutoye *et al.*, 2016). However, a combination of time and any other parameter becomes statistically significant as seen from the ANOVA table where they all have $p-value$ less than 0.05. Also, the predicted and experimental results show that the maximum yield obtained in this study was 89.3% and this corresponded to a methanol-to-oil volume ratio of 7:1, a catalyst loading of 1 % (w/w), a reaction temperature of 36 ℃ and a reaction time of 30 minutes. The primary objective for modelling the biodiesel production process is to obtain the optimum settings for the reaction process variables that would maximize the biodiesel yield. With respect to this need, the results obtained from modelling the reaction process that will achieve this objective are presented in the subsequent figures. Figure 3 displays a 3D response surface plot of the effect of varying two process parameters - time and temperature (while holding others constant) on the yield of biodiesel. The plot shows increased biodiesel yield upon an increase in the reaction time and the reaction temperature. From the figure, it can be seen that the maximum biodiesel yield of 88.75% was obtained when the reaction time was 60min and the temperature was 30^{o}C. An increase of temperature and time above these optimal values did not increase the biodiesel yield any further, on the contrary a decrease in yield was observed as the temperature and time were increased beyond these values. Other studies were

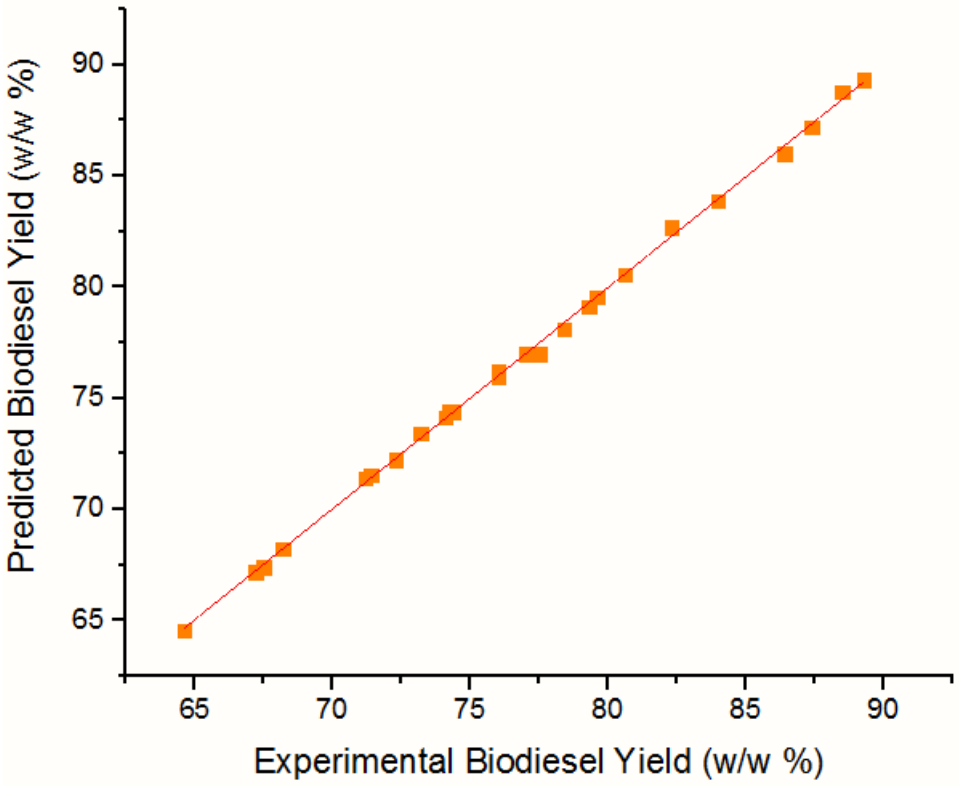

Fig. 2: Experimental vs. Predicted biodiesel yield

also made to see the simultaneous effects of two parameters on the biodiesel yield. Fig. 4 shows a similar plot for the effect of the catalyst weight and the methanol-to-oil ratio on the biodiesel yield. Like in the case of temperature and time, we see that increasing the methanol-to-oil ratio and the catalyst weight result to a corresponding increase in biodiesel yield until it reaches the maximum yield of 76.63%. The methanol-to-oil ratio and catalyst weight for

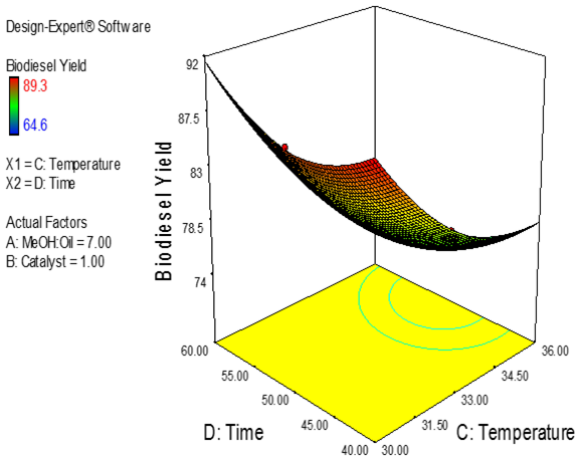

Fig. 3: 3D response surface plot for effect of time and temperature on biodiesel yield

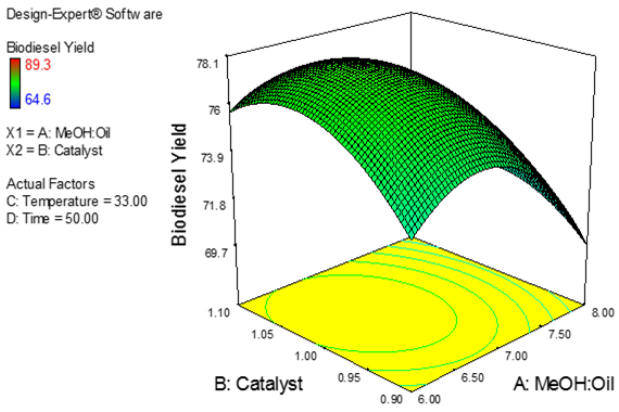

Fig. 4: 3D response surface plot for effect of catalyst and MeOH to oil ratio on biodiesel yield

any positive effect. In the case of the effect of reaction temperature and methanol-to-oil ratio, the maximum biodiesel yield of 84.21% was obtained when the temperature was 30.00^{o}C and methanol: oil ratio was 7:1. Temperatures above this and methanol: oil ratio above this, decreases of the biodiesel yield. While in the case of the effect of methanol-to-oil ratio and time, a maximum biodiesel yield of 80.13% was obtained when the time was 40 min and the methanol: oil ratio was 6.75:1.00. Using the mathematical model, the effect of all the four parameters were then combined and result showed that a maximum yield of 89.3% was obtained under the optimal transestrification conditions of methanol-to-oil volume ratio of 7:1, catalyst loading the maximum yield 76.63% are 7:1 and 1.00% (w/w) respectively. Other dual-parameter effects on the biodiesel yield that were studied include the combined effect of the reaction temperature and methanol-to-oil ratio, the reaction time and methanol-to-oil ratio, the reaction temperature and catalyst-weight and the time and catalyst weight. These all tended to increase the biodiesel yield to an optimum, and then further increase in value did not produce of 1.0 w/w %, temperature of 36 ^{o}C and reaction time of 30 minutes.

Conclusion

In this work, a co-solvent method was used to convert tiger nut oil to biodiesel. Furthermore, a statistical design of experiment was carried out to optimize the biodiesel yield. The model showed that the maximum biodiesel yield of 89.3% was obtained at a methanol-to-oil volume ratio of 7:1, a catalyst loading of 1.00 % (w/w), a reaction temperature of 36.00^{o}C and a reaction time of 30.00 minutes. Analysis of the biodiesel produced was carried out using GC-MS and the result confirmed the presence of methyl esters on the biodiesel sample. Also, characterization of the

biodiesel showed that it met ASTM specifications with respect to its FFA content (0.4908 wt %), kinematic viscosity (5.58 mm^2/sec), pour point (6 ℃) and cloud point (14 ℃). However its flash point (185 ℃) was quite elevated due to residual amount of methanol and the co-solvent (di-ethyl ether) left after washing of the biodiesel. Additional purification of the biodiesel using other separation techniques such as centrifugation could help further bring down the level of these residual impurities which would help improve the flash point.

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