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Optimization, Kinetics and Thermodynamics Study of Transesterification of Neem Oil Using Heterogeneous Catalyst Derived from Waste of Goat Bones

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ABSTRACT

In this study, calcium oxide (CaO) derived from waste bone (from goat) was used as catalyst for the transesterification of neem seed oil (NSO). The catalyst was characterized using scanning electron microscope (SEM).The transesterification was optimized using response surface methodology (RSM). Under the optimal conditions of methanol to oil molar ratio of 8:1, catalyst concentration of 4.0wt %, reaction temperature of 55^{0}C, reaction time of 4hr and agitation speed of 400rpm, 92.0% biodiesel was achieved. The reaction kinetics conforms to a pseudo-second order rate law with reaction rate constants of 1.96E-5, 2.17E-5 and 5.18E-5, at 45, 50 and 55^{0}C, respectively. Activation energy (EA) for the reaction was 90.98 kJ/mol and pre-exponential factor of1.46E10dm^{3}mol-^{1}min-^{1}.Thermodynamic parameters calculated for the reaction show the enthalpy and entropy for the process to be 90.98 kJ mol-^{1} and 0.195 kJ mol-^{1} respectively. The Gibbs free energy was calculated to be -28.63, 28.84 and 26.95 kJ mol-^{1} at 45, 50 and 55^{o}C, respectively.

INTRODUCTION

Fast depletion of world's petroleum reserves and increasing ecological concerns has created a great demand for environmentally benign renewable energy resources (Ashish et al., 2010). There is an increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources. For this reason the possibility of developing alternative energy source to replace traditional fossil fuels has been receiving a large interest in the last few decades (Vicente et al., 1998). Biodiesel is considered as a possible alternative and future fuel for diesel engine due to the predicted shortage of fossil fuels and increase in the price of the petroleum.

It is biodegradable, renewable, non-toxic, environmentally-friendly, and has high flash point, better lubrication, high cetane number and has quite resemblance in regard with physical and chemical characteristics with that of conventional diesel fuel (Sanjay, 2013; Demirba2003; Kaya et al., 2009; Hetsi et al., 2009). Biodiesel is the mixture of mono alkyl esters that can be continuously derived from vegetable oils or animal fats and therefore it is termed as renewable energy (Lin et al., 2006). Several studies have shown that biodiesel is a better fuel than fossil based diesel in terms of engine performance, emissions reduction, lubricity, and environmental benefits (Canakci et.al., 1997; Peterson et al.,1997).

Different types of catalysts such as base, acid or lipase are used in transesterification for biodiesel synthesis but the base-catalyzed reaction is the most common in the industry due to easier, faster and cheaper processing (Hassan et al., 2013). The conventional catalysts used for transesterification are homogeneous and heterogeneous catalysts. The biodiesel industry is dominated by application of homogeneous catalysts (such as KOH, NaOH and CH$_3$ONa) because of their easy usage and short time required for conversion of triglycerides to biodiesel (Demirbas 2008; Sharmaet al., 2011).

However, the use of homogeneous catalysts requires neutralization and separation from the final reaction products leading to a series of environmental concerns such as production of waste water and corrosion problems (Georgogianni et al., 2009).

Among heterogeneous catalysts which have been researched, calcium oxide a solid base catalyst shows high potential/promising result in transesterification process with oil conversion of more than 95% (Liu et al., 2008). This catalyst is low cost, low methanol solubility, non-corrosive, environmental friendly and able to be reused for several times (Boey et al., 2011).There are various processes/techniques that have been adopted in production of biodiesel from vegetable oils and animal fats namely: dilution, micro-emulsification, pyrolysis and transesterification process/ technique (Demirbas et al., 2009; Aderemi et al., 2010; Leng et al., 1999; Jabalu et al., 2009). Among these methods, transesterification is the key and foremost important process to produce the cleaner and environmentally safe fuel (Younis et al., 2009; Atlanatho et. al., 2004). Biodiesel is produced through a chemical process known as transesterification of different vegetable oil or animal fat with a short chain alcohol, in which one mole of glyceride reacts with three moles of alcohol in the presence of appropriate amount of catalyst to form mono methyl ester and glycerol (Balat et al.,2010; Demirbas 2009; Ghanei et al.,2011;Helwani et al.,2009; Moradi et al.,2012).Transesterification of vegetable oils with low molecular weight simple alcohols (methanol, ethanol, propanol, butanol and amyl alcohol) has been established as the best option to reduce the high viscosity, low volatility, heavy engine deposits and toxic substance formation associated with the direct use of vegetable oils (edible, non-edible, animal fats and used cooking oil) Schwab et.al.,(1987); Tesser et.al., (2005).

The most common alcohols widely used are methyl alcohol and ethyl alcohol. Methanol, found frequent application in the commercial uses because of its low cost and its physical and chemical advantages (Demirbas, 2005). Another advantage of using methanol is the separation of glycerine, which can be obtained through simple decantation (Nagi et. al., 2008).

The current feed stocks for production of biodiesel or mono-alkyl ester are vegetable oil, animal fats and micro algal oil. In the midst of them, vegetable oil is currently being used as a sustainable commercial feedstock. There are number of edible oil available in market i.e. Sunflower oil, Soyabean oil, cotton seed oil, coconut oil, ground nut oil etc. from which preparation of biodiesel can be achieved. But use of edible oil is generally used for cooking purpose. Similarly if edible oil is used for biodiesel production it can cause the shortage of oil for cooking and the cost of oil may go high (Hanumanth et al., 2012). However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel. In order to overcome these disadvantages, many researchers are interested in non-edible oils which are not suitable for human consumption because of the presence of some toxic components in the oils (Patni Neha et al., 2013).

The various non-edible oil which can be used for the preparation of biodiesel are jatropha oil(*J. curcas*), karanja oil(*P. pinnata*), Beef tallow oil, used frying oil, other waste oil and fats, *Pongamia pinnate oil*, *Kokum oil*, *Mahua oil* (*M. indica)*, Simarouba oil, willed apricot oil, Jojoba oil, Tobacco seed oil (*N. tabacum L.*), rice bran, mahua rubber plant (*H. Brasiliensis*), castor oil, linseed oil, and microalgae, Kusum oil, Neem oil (*A. indica*) and sal oil but the use of these oils as a feed stock for production of biodiesel varies as per their availability in different parts of the world.

Different researchers synthesized and used different kinds of solid wastes based catalysts (such as mollusk shells, eggshells, calcined fish scale, sheep bone, calcined waste bone etc.) in order to produce cost effective catalysts and biodiesel (Viriya-Empikul et al., 2010; Jiang et al; 2015). Obadiah et al. (2012) worked on the biodiesel production from palm oil using calcined waste animal bone as catalyst. The biodiesel yield was 96.78 % under optimal reaction conditions of 20 wt% of catalysts, 1:18 oil to methanol ratio, and 200 rpm of stirring of reactants and at a temperature of 65^{0}C.

Among these solid wastes, animal bone is one of the best solid wastes that are easily and abundantly available all over the world. Although, the waste bone derived catalysts have shown a reasonable performance and constancy in the reaction, however these catalysts are required in high amount, high methanol/oil molar ratio with longer time for the reaction to occur. All these disadvantages make waste bone derived catalysts practically and economically unsuitable. To overcome these difficulties, it would be imperative to impregnate waste animal bones with other catalysts such as NaOH to make waste animal bone derived catalyst more active and to boost the surface chemical properties. Waste animal bones have proved to be highly effective as a catalyst support. The properties of calcined bone make it advantageous for use as catalyst support in transesterification reaction. It contains hydroxyapatite $[Ca_{10} (PO4)_6(OH)_{2}]$, that is highly porous and also has a large surface area which allows catalyst to disperse over it largely and effectively. Calcined bones can also be used in high pressure and temperature reaction conditions. The main influential parameters of transesterification of vegetable oils are as follows: molar ratio of alcohol to oil, catalyst amount, reaction temperature, mixing intensity, and reaction time has been widely studied and optimized.

In this study, goat waste bone activated by chemical means (alkaline) were used as catalyst for the transesterification of neem seed oil (NSO). The transesterification was optimized with response surface methodology (RSM) using central composite design (CCD). The use of RSM addresses optimization by providing an understanding of how the test variables affect the selected process response, determining the interrelationships between the test variables, and characterizes the combined effect that all the influential test variables may have on process response. The kinetics of the reaction were studied at the optimal conditions and the thermodynamic properties were also evaluated.

MATERIALS AND METHODS

The non-edible neem seed oil was purchased from National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna state, Nigeria and the waste bones was sourced from a local market (Kubwa village market), Kubwa, Abuja. The physico-chemical properties of the Neemseed oil are shown in Table 1. The chemicals used include methanol, potassium hydroxide and benzene. They were all of analytical grade. The equipment used include Petri dish, various sizes of beaker, different sizes of measuring cylinders, thermometer, pipette hot plate with magnetic stirrer arrangement used as a heating and stirring device, separating funnel, digital weighing balance, stop watch, laboratory oven, filter paper, cotton wool, masking tape, conical flasks.

Catalyst Preparation/Activation

The catalyst (waste animal bones) from goats was sourced from a local market in Kubwa, Abuja. The sourced waste bones was soaked in boiling water for several hours (6-8 hours) at about 75^0C to remove tissues and fats in the bone and then rinsed with distilled water for 3-4 times to remove dust and impurities. The waste bones were dried in the drying oven at 110^0C for 4hours to remove water and moisture before being ground finely to a <2mm particle size powder using a hammer mill. The crushed and powdered catalysts was sieved using various mesh sizes (100-200) to get particle of uniform size of mesh screens. They were stored in a desiccator in the presence of silica and KOH pellets in order to avoid water and CO_2 (reaction with air)contact with the catalysts prior to further usage because the CaO catalyst will be reacted with CO_2 and converted into$CaCO_3$, thus reducing its activity as a catalyst.

Catalyst Activation

Sample of the crushed/powdered waste bone was impregnated with concentration of NaOH at different mass solution on weight basis by dissolving the sodium hydroxide with deionized water in the ratio of 2:1. The crushed/powdered waste bone was impregnated with the prepared NaOH at different ratios of 1:2 to 1:6 (w/v) by stirring vigorously. After the completion of the impregnation process, it was dried at a temperature of 110^OC for 24hours then cooled to room temperature and was washed with distilled water and dried for 4 hours in an oven at 120^oC.

Characterization of Catalyst

Scanning Electron Microscope

The surface morphology of the prepared catalyst from waste bone was observed under a scanning electron microscope (SEM) using a Phenom Prox working at an accelerated voltage of 15kV.Micrographs were observed at $80\mu m$and 100 μm at magnification of 100x and 500x, respectively.

Transesterification Reaction Procedures

The transesterification reaction was carried out in a three necked 250 ml round bottom flask fitted with a thermometer, condenser and a mechanical stirrer whose speed was also controlled The neemseed oil reacts with methanol in the presence of catalyst derived from waste of animal bone to produce methyl esters of fatty acids (biodiesel) and glycerol. The refined neemseed oil (30ml) was quantitatively transferred into a flat bottom flask placed on a hot magnetic stirrer.

Then specific amount of catalyst (by weight of refined neemseed oil) dissolved in the required amount of methanol was added. The reaction flask was kept on a hot magnetic stirrer under constant temperature with defined agitation throughout the reaction. At defined time 1-2 hours, sample was taken out, cooled, and the biodiesel (i.e. the methyl ester in the upper layer) was separated from the by-product (i.e. the glycerol in the lower layer) by settlement overnight under ambient condition. The percentage of the biodiesel yield was determined by comparing the weight of layer biodiesel with the weight of refined neemseed oil used.

The percentage conversion of each sample was calculated from the below equation (Yusuf and Sirajo, 2009).

$$\text{Yield (\%)} = \frac{\text{weight of methylester}}{\text{weight of oil used}} \text{ x } 100 \qquad (1)$$

Design of experiments

The experimental design for optimization was done by applying response surface methodology (RSM) with central composite design (CCD) to investigate the influence process conditions. Design Expert software (version 10.0.6.0) was used in this study to design the experiment and to optimize the reaction conditions. The 2-level -5- factor fractional factorial experimental design was employed in this study requiring 32 experiments consisting of 16 factorial points, 10 axial points and 6 center points. The level of each was chosen based on the importance to the experiment.

The following five parameters (catalyst concentration (A),methanol to oil molar ratio (B), and reaction temperature (C) reaction time (D) and agitation speed (E) were varied in order to maximize the biodiesel yield. The experimental range and level of independent variables of the central composite design for the optimization of the transesterification process are shown in Table 2

Table2. *Experimental range and levels of the independent variables*

Independent variable	Units	Low level (-1)	High level (+1)	-α	+α	0 level
Catalyst conc. (A)	Wt%	3(-1)	5(+1)	2(-2)	6(+2)	4
Methanol, (B)	Mol/mol	6(-1)	10(+1)	4(-2)	12(+2)	8
Temperature, (C)	°C	45(-1)	65(+1)	35(-2)	75(+2)	55
Reaction time (D)	Hours	3(-1)	5(+1)	2(-2)	6(+2)	4
Agitation speed (E)	Rpm	300(-1)	500(+1)	200(-2)	600(+2)	400

A quadratic polynomial equation by central composite design was developed to predict the response as a function of independent variables and their interaction (Razali et al., 2010). A mathematical model, following a second –order polynomial which includes interaction terms was used to calculate the predicted response (Yasin, 2012).The response for the quadratic polynomials is described below (Montgomery 2001):

$$Y= \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X^2{}_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \qquad (2)$$

Where Y is % methyl ester yield, xi and xj are the independent study factors(coded variables), and β_0 , $\beta_{i,}\beta_{ii}$ and β_{ij} are constant co-efficient, regression co-efficient of the linear terms, regression co-efficient of the quadratic terms, and regression co-efficient of the interaction terms, respectively, and k is the number of factors studied and optimized in the experiment (number of independent variables). The Design–Expert 10.0.6.0 software package was used for regression analysis and analysis of variance (ANOVA).

Table3. *Experimental design matrix for 2-level 5 factors response design and the experimental values and predicted values for biodiesel production from neem seed oil*

Run order	Catalyst conc. (wt %) A		Methanol/Oil molar ratio(mol)B		Temperature (^{o}C) C		Time (Hours) D		Agitation Speed (Rpm) E		Expt.Yield (%)	Pred. Yield (%)
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real		
1	-1	3.0	-1	6:1	-1	45.0	-1	3.0	+1	500.0	43.00	41.88
2	+1	5.0	-1	6:1	-1	45.0	-1	3.0	-1	300	63.00	57.88
3	-1	3.0	+1	10:1	-1	45.0	-1	3.0	-1	300	70.00	62.88

4	+1	5.0	+1	10:1	-1	45.0	-1	3.0	+1	500	80.00	72.79
5	-1	3.0	-1	6:1	+1	65.0	-1	3.0	-1	300	60.00	56.88
6	+1	5.0	-1	6:1	+1	65.0	-1	3.0	+1	500	53.00	49.79
7	-1	3.0	+1	10:1	+1	65.0	-1	3.0	+1	500	53.00	47.79
8	+1	5.0	+1	10:1	+1	65.0	-1	3.0	-1	300	70.00	60.79
9	-1	3.0	-1	6:1	-1	45.0	+1	5.0	-1	300	60.00	61.88
10	+1	5.0	-1	6:1	-1	45.0	+1	5.0	+1	500	60.00	61.79
11	-1	3.0	+1	10:1	-1	45.0	+1	5.0	+1	500	33.00	33.79
12	+1	5.0	+1	10:1	-1	45.0	+1	5.0	-1	300	27.00	23.79
13	-1	3.0	-1	6:1	+1	65.0	+1	5.0	+1	500	33.00	36.79
14	+1	5.0	-1	6:1	+1	65.0	+1	5.0	-1	300	50.00	49.79
15	-1	3.0	+1	10:1	+1	65.0	+1	5.0	-1	300	77.00	74.79
16	+1	5.0	+1	10:1	+1	65.0	+1	5.0	+1	500	63.00	60.71
17	-2	2.0	0	8:1	0	55.0	0	4.0	0	400	60.00	61.29
18	-1	6.0	0	8:1	0	55.0	0	4.0	0	400	57.00	66.46
19	0	4.0	0	4:1	0	55.0	0	4.0	0	400	53.00	50.29
20	0	4.0	+2	12:1	0	55.0	0	4.0	0	400	43.00	55.46
21	0	4.0	0	8:1	-2	35.0	0	4.0	0	400	53.00	57.29
22	0	4.0	0	8:1	+2	75.0	0	4.0	0	400	57.00	62.46
23	0	4.0	0	8:1	0	55.0	-2	2.0	0	400	63.00	79.29
24	0	4.0	0	8:1	0	55.0	+2	6.0	0	400	73.00	67.46
25	0	4.0	0	8:1	0	55.0	0	4.0	-2	200	50.00	59.29
26	0	4.0	0	8:1	0	55.0	0	4.0	+2	600	47.00	48.46
27	0	4.0	0	8:1	0	55.0	0	4.0	0	400	82.00	90.38
28	0	4.0	0	8:1	0	55.0	0	4.0	0	400	85.00	90.38
29	0	4.0	0	8:1	0	55.0	0	4.0	0	400	93.00	90.38
30	0	4.0	0	8:1	0	55.0	0	4.0	0	400	92.00	90.38
31	0	4.0	0	8:1	0	55.0	0	4.0	0	400	92.00	90.38
32	0	4.0	0	8:1	0	55.0	0	4.0	0	400	91.00	90.38

The fitness of the model and the statistical significance was evaluated using analysis of variance (ANOVA). ANOVA was also used to determine the significance of the individual terms, interacting terms and also the quadratic terms.

RESULTS AND DISCUSSIONS

Characterization of the catalyst

Scanning Electron Microscope Analysis

The SEM images of the activated catalyst at different magnifications are shown in Fig.1.The morphology of the alkaline activated waste bone at magnifications of 1000xhas smooth surface with little cavities which result from evaporation of the activating agent (NaOH).The surface morphology with magnifications of 500x has smooth surface with no cavities and hair line cracks. This could be as a result of the activation process which might have filled up the holes thereby giving it a smooth surface.

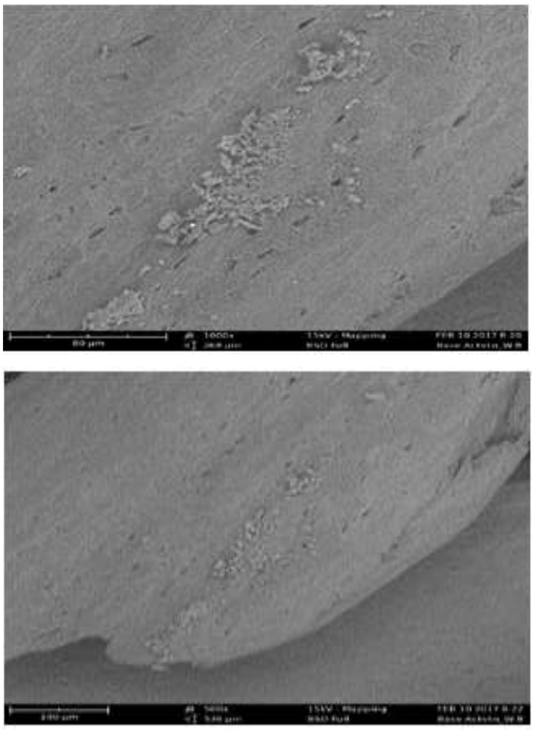

Figure1. *SEM images of alkaline waste bone at different magnifications*

Modelling and optimization of the transesterification reaction

Development of regression model

The regression equation as a function of the selected variables for FAME yield (%) is given by:

$$\text{Yield}=+90.38+1.29*A+1.29*B+1.29*C-2.96*D-2.71*E-1.44*AB-0.69*AC-2.69*AD+9.31*AE+5.06*BC-3.44*BD+1.81*BE+3.81*CD\;3.19*CE+0.56*DE-6.62*A^2-9.38*B^2-7.63*C^2-4.25*D^2-9.18*E^2. \qquad (3)$$

where "Y" is the response, that is the conversion to biodiesel, and A, B, C,D and E shows the values of the test variables, catalyst concentration, methanol to oil molar ratio, temperature, reaction time and agitation speed respectively.

The Positive sign in front of the terms indicates synergistic effect in increase FAME yield.while negative sign indicates antagonistic effect of the factor (Shuit et al. 2010). The model regression equation(equation 3) indicated that the positive coefficients indicated linear to increase the FAME yield.Although,the quadractic termshad negative effects that decrease the FAME yield. Hence, the model reduces to equation 4 after eliminating the insignificant coefficients.

$$Y=+90.38+1.29*A+1.29*B+1.29*C+9.31*AE+5.06*BC+1.81*BE+3.81*CD+0.56*DE \qquad (4)$$

The result of statistical analysis of variance (ANOVA) which was carried out to determine the significance and fitness of the quadratic model as well as the effect of significant individual terms and their interaction on the FAME is presented in Table 4.The Model F-value of 168.19 and Prob>F of < 0.0001 implied that the model is significant at 95% confidence level.The Prob>F or p-value (probability of error value) is a tool used to determine the significance of each regression coefficient as well as interaction effect of each cross product.

The smaller the p-value, the bigger the significance of the corresponding coefficient is (Chen et al. 2008).In this case, the p-values less than 0.05 indicated that the particular term is statistically significant.The value of regression coefficient R^2 for the model is 0.9967, indicating the good fitness of the model. High values of predicted R^2 (0.9906) and adjusted coefficient of determination (R^2 Adj:0.9908) and low value of coefficient of variation (C.V) (2.71%), are an indication of precision of fitted model.(Rashid et al.,2009).

The "Lack of Fit F-value"of 0.06 and p-value of 0.998 implies the lack of fit is not significant relative to the pure error. Insignificant lack of fit is good as sufficiently good model fitting is desirable.There is a 99.81% chance that lack of fit F-value could occurdue to noise.

Table4. *Analysis of variance (ANOVA) for the fitted quadractic polynomial catalyzed by alkaline activated waste bone methyl ester from neem seed oil*

Source	Coefficient estimate	Degree of freedom	Sum of square	Mean squares	F-value	P-value (Prob>F)
Model	90.38	20	9683.83	484.19	168.19	< 0.0001 significant
A	1.29	1	40.04	40.04	13.91	0.0033
B	1.29	1	40.04	40.04	13.91	0.0033
C	1.29	1	40.04	40.04	13.91	0.0033
D	-2.96	1	210.04	210.04	72.96	< 0.0001
E	-2.71	1	176.04	176.04	61.15	< 0.0001
AB	-1.44	1	33.06	33.06	11.48	0.0060
AC	-0.69	1	7.56	7.56	2.63	0.1333
AD	-2.69	1	115.56	115.56	40.14	< 0.0001
AE	9.31	1	1387.56	1387.56	482.00	< 0.0001
BC	5.06	1	410.06	410.06	142.44	< 0.0001
BD	-3.44	1	189.06	189.06	65.67	< 0.0001
BE	1.81	1	52.56	52.56	18.26	0.0013
CD	3.81	1	232.56	232.56	80.78	< 0.0001
CE	-3.19	1	162.56	162.56	56.47	< 0.0001
DE	0.56	1	5.06	5.06	1.76	0.2117

A^2	-6.62	1	1287.46	1287.46	447.22	< 0.0001
B^2	-9.38	1	2578.13	2578.13	895.56	< 0.0001
C^2	-7.63	1	1705.46	1705.46	592.42	< 0.0001
D^2	-4.25	1	529.83	529.83	184.05	< 0.0001
E^2	-9.13	1	2442.46	2442.46	848.43	< 0.0001
Residual		11	31.67	2.88		
Lack of fit		6	2.17	0.36	0.061	0.9981 Not significant
Pure error		5	29.50	5.90		
Cor Total		31	9715.50			

Std Dev. = 1.70, Mean =62.63, C.V% =2.71,Press =91.65, R^2*=0.9967, Adj* R^2 *=0.9908, Pred* R^2 *=0.9906, Adeq precision =48.442*

Effect of Independent Variables on the Biodiesel Yield (3D Response Surface Plots)

The interaction effects of variables on biodiesel production are studied by plotting the three dimensional response surfaces with the vertical axis representing biodiesel conversion (response) and two horizontal axes representing the coded levels of two independent variables, while keeping other variables at their central level (0).In figure 2 the three dimensional surface plot shows that increase inreaction time and catalyst weight leads to a corresponding increase in yield. The increment of catalyst weight caused significant increase in biodiesel yield at low reaction time. However, the biodiesel yield was slightly infuenced by the rise of catalyst at higher reaction time. It was observed that the yield became steady, when these parameters were increased further.This might indicate that the transestrification reaction has reached equilibrium condition, and further increase may lead to reverse reaction and thus reduce the biodiesel yield.

The 3D plot shown in figure 3 shows that increase in catalyst weight and agitation speed leads to an increase in biodiesel yield. Further increament of catalyst weight beyond 4wt% and agitation speed of 400rpm leads to decrease in biodiesel yield.This may be attributed to the apperance of emulsion. Figure 4 shows the response surface plot of reaction time and methanol to oil ratio on yield. When the other factors were kept constant, increase in methanol/ oil ratio and reaction time leads to a higher yield. In other words, increase in time with a corresponding increase in methanol/oil ratio gives high yield. Higher production of methyl ester is strongly favored when high molar ratio is employed for a certain time of reaction and catalyst weight (Silva et al.,2010).Figure 5 shows the response surface plot for the interaction effect between reaction time and reaction temperature on biodiesel yield.The surface response indicates that increment of reaction temperature from low level to a higher level leads to an increase in yield of biodiesel under reduced reaction time. It was also observed that increase of reaction time does not improve catalytic activity at low reaction temperature. The reaction processes was in agreement with Lee's study in which high temperature improved the dispersionof catalyst in the liquid medium with better mass transfer between the reactant.

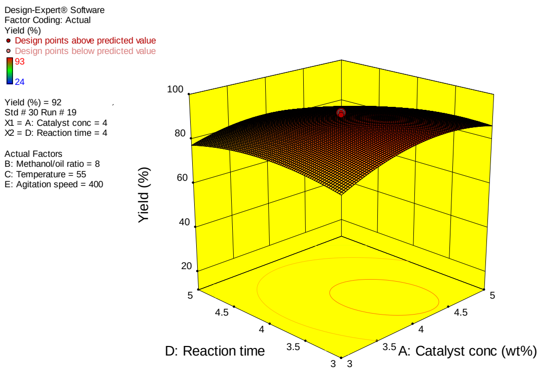

Figure2. *3D response surface plots for the interaction effect of catalyst concentration (A) and reaction time(D) against yield (%)*

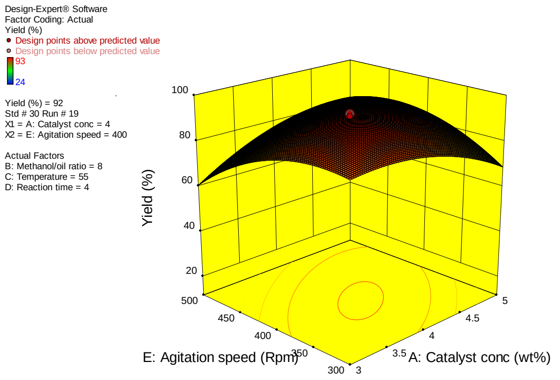

Figure3. *3D response surface plots for the interaction effect of catalyst concentration(A) and agitation speed (E) against yield (%)*

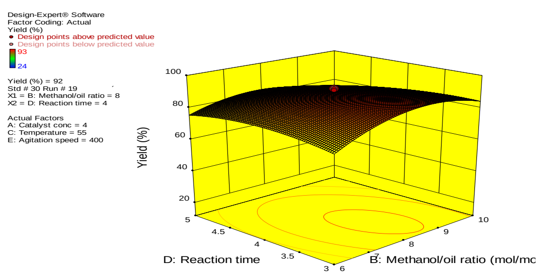

Figure4. *3D response surface plots for the interaction effect of methanol/oil ratio (B) and reaction time(D) against yield (%)*

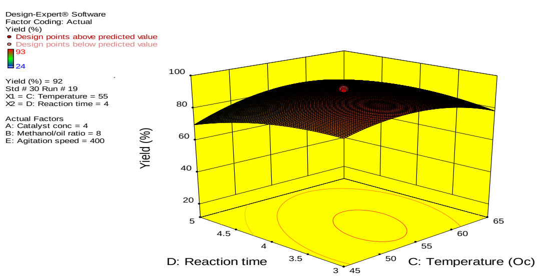

Figure5. *3D response surface plots for the interaction effect of reaction temperature (C)and reaction time(D) against yield (%).*

Validation of the Optimization result

Optimization study was carried out to obtain the optimum combination of operating conditions at which the maximum biodiesel yield is achieved. In this study, biodiesel yield was set to maximum value, while the other reaction parameters were set in a range between high and low levels as shown. The experimental conditions with the highest predicted biodiesel yield were selected for further validation. The result of model validation is shown in Table 5. The optimum biodiesel yield of 93% was obtained by transesterifying neemseed oil with 4wt. % of catalysts and methanol to oil molar ratio of 8:1 at 55^{0}C for 4 h. The predicted biodiesel yield was 94.3%. This means that the experimental yield obtained was in good agreement with the predicted yield, with relatively small percentage error (1.3 %). This indicated that the proposed statistical model was suitable for prediction of optimized biodiesel yield and for optimization of transesterification process.

Table5. *Results of the model validation at optimum conditions catalyzed by alkaline activated waste bone*

Catalyst conc.(wt) A	Methanol/oil (mol/mol) B	Temperature (^{o}C) C	Time(Hour) D	Agitation speed (rpm) E	Experimental Yield (%)	Predicted yield (%)	(%) error
4	8	55	4	400	93.0	94.3	1.3

Kinetics of the transesterification Reaction

Transesterification reaction is a consecutive and reversible reaction being driven by excess alcohol and a catalyst. The reaction can be represented as follow (Freedman et al., 1986; Wenzel et al., 2006; Leevijit et al., 2006; Gemma et al., 2005 and 2006 and Noureddini and Zhu, 1997):

$$TG + A \underset{K_2}{\overset{K_1}{\leftrightarrow}} DG + BD \qquad (5)$$

$$DG + A \underset{k_4}{\overset{k_3}{\leftrightarrow}} MG + BD \qquad (6)$$

$$MG + A \underset{k_6}{\overset{k_5}{\leftrightarrow}} G + BD \qquad (7)$$

The overall reaction is: $TG + 3A \rightleftharpoons 3BD + GL$

Where k_1, k_3 and k_5 are rate constants for forward reactions; k_2, k_4 and k_6 are rate constants for reverse reactions (backward reaction rate). The lowest value of k is believed to be the rate determining step of the reaction. Triglyceride is TG, diglyceride is DG, monoglyceride is MG, glycerol is G and fatty acid methyl ester (biodiesel) is BD and A is the concentration of alcohol.

The kinetics study of the neem seed oil FAME production using activated waste bone was done using Langmuir-Hinshelwood-Hougen-Watson (LHHW) reaction mechanism. The rate and equilibrium constants were determined by using genetic algorithm (GA) to solve the objective functions developed with concentration of various species in the reaction obtained by GC-MS analysis. From the rate and equilibrium constants obtained at different temperatures, it could be observed from the rate and equilibrium constants that for all the temperatures considered, the rate constant for adsorption of triglyceride was lowest and it increases as temperature increased. This can be considered as rate determining step (RDS). The rate determining step is defined as the reaction step with the highest activation energy.

The net chemical reaction can only proceed at the rate of the slowest reaction step. It is this rate determining step that is responsible for the rate equation of an overall reaction. The triglyceride adsorption reaction has activation energy, 90.98 kJ/mol. The activation (Ea) energy (90.98kJ/mol) of the rate determining step and the pre-exponential factor, A (1.46×10^{10} dm^3 $mol^{-1}min^{-1}$) was calculated from Arrhenius plots using figure12.

The high value indicates that triglyceride adsorption was slow and needed high energy and catalyst to break the energy barrier. The variation of concentration with time at temperatures of 45^{0}C, 50^{0}C, and 55^{0}C are shown in figures 6, 7 and 8, respectively. It could be observed that concentration decreases as time increases for triglyceride, diglyceride, monoglyceride and methanol showing they were consumed to produce biodiesel and glycerol with biodiesel been dominant.

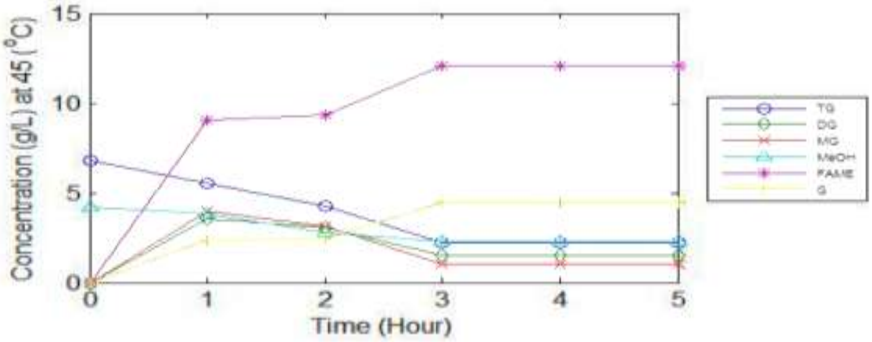

Figure6. *Variation of reaction time on concentration of TG, DG, MG, ME, FAME and GL at 45^{o}C*

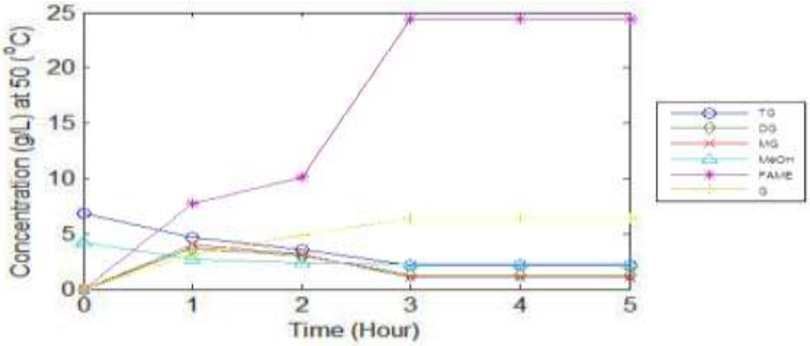

Figure7. *Effectof reaction time on concentration of TG, DG, MG, ME, FAME and GL at 500C*

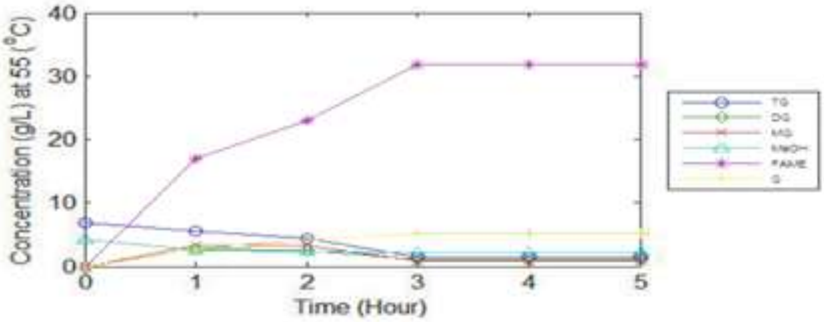

Figure8. *Effect of reaction time on concentration of TG, DG, MG, ME, FAME and GL at 550C*

Thermodynamics Properties

The thermodynamic parameters: the standard free energy (ΔG°), enthalpy (ΔH°), and entropy change (ΔS°) was estimated to evaluate the feasibility and endothermic nature of the transesterification process.

The value of ΔS° and ΔH° were calculated from the intercept and slope of the plot of 1n $K_f$versus 1/T for transesterification catalyzed by acid activated waste bone.

The calculated values of ΔH^o, ΔS^o and ΔG^o are listed in Table 7. As seen from the results, the inverse of K_f values increased with increase in temperature and decreases which resulted to a shift of equilibrium to the left that is production of methyl ester was favored at high temperatures.

The positive values of ΔH^o indicated the endothermic nature of the transesterification. The transesterification reaction for the endothermic processes could be due to the increase in temperature and increase in the rate of diffusion between the three-interphases.

The positive values of ΔS^o showed the affinity of the catalysts for methanol and the increasing randomness at the solid-solution interface during the transesterification process.

The negative values of ΔG^o indicated the feasibility of the process and the spontaneous nature of the transesterification reaction. The results showed that the transesterification process was more favorable at high temperature, due to the endothermic nature of the transesterification system

Table6. *Data for determination of Arrhenius parameters*

Temp.(Kelvin)	Rate constant (K) TG adsorption	$\ln K_f$	1/T(1/K)
318	1.96E-5	-10.83	0.00314
323	2.17E-5	-10.74	0.00315
328	5.18E-5	-9.87	0.00305

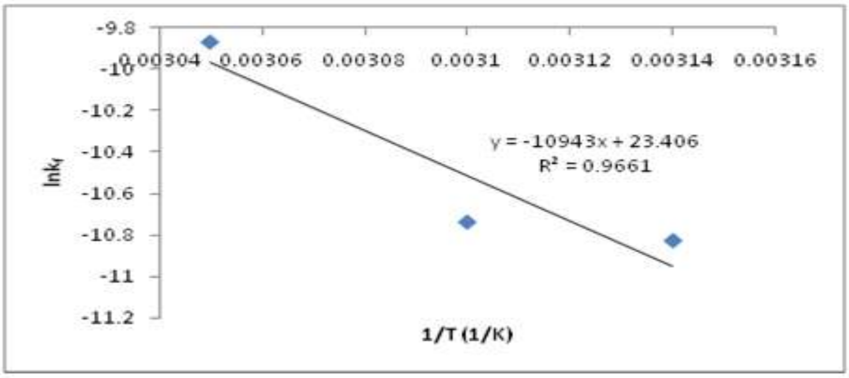

Figure8.*Arrhenius plots of the rate determining step*

Table7. *Transesterification thermodynamic results*

Catalyst	Temp. (K)	$\ln K_f$	ΔG^o(kJ/mol)	ΔH^o(kJ/mol)	ΔS^o(kJ/mol)
	318	-10.83	-28.63	90.98	0.195
	323	-10.74	-28.84		
	328	-9.87	-26.92		

CONCLUSION

Calcium oxide derived from waste goat bone was used as catalyst for the transesterification of Neemseed oil in this study. SEM, analysis was carried out to determine the morphological structure/microscopic characteristics of the catalyst. Optimization of transesterification process of NSO was achieved by five-factorial CCD using RSM in 32experimental runs. A second-order model was obtained to predict the NSOB yield as a function of process variables. Transesterification of NSO using the CaO derived from waste of goat bone was optimized using RSM in combination of central composite design (CCD) and the optimal conditions were found to be catalyst weight 4wt%,methanol to oil ratio 8:1, reaction temperature 55^0C,reaction time 4hr and agitation speed 350rpm to achieve a biodiesel yield of 93.0%. Based on the ANOVA results, the reaction time and agitation speed was the most significant factor affecting the transesterification process. The regression model was found to be highly significant at 95% confidence level as correlation coefficients for R-Squared (0.9967), adjusted R-Squared (0.9908) and predicted R-Squared (0.9906) was very close to 1 hence an indication of good correlation and predictive capabilities. The best fit for experimental data was the second order kinetic model.

The triglyceride adsorption reaction has activation energy, 90.98 kJ/mol. The activation (Ea) energy (90.98kJ/mol) of the rate determining step and the pre-exponential factor, A (1.46×10^{10} dm^3 $mol^{-1}min^{-1}$). The high value indicates that triglyceride adsorption was slow and needed high energy and catalyst to break the energy barrier. The positive ΔH, positive ΔS and the negative ΔG indicate that this process are endothermic, irreversible, and spontaneous.

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