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Biodiesel production from waste frying oil via heterogeneous transesterification: Optimization study

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ABSTRACT

This study deals with development of a new composite heterogeneous catalyst, anthill-eggshell promoted Ni-Co mixed oxides (NiCoAE). The catalyst was synthesized via co-precipitation and also characterized to evaluate its properties. The as-synthesized NiCoAE catalyst was thereafter tested for transesterification reaction. The effects of variables affecting the transesterification process, reaction temperature (50-70 ^oC), reaction time (2-4 h), catalyst loading (3-7 wt%) and methanol to oil ratio (6:1-12:1) were investigated using central composite design (CCD). The biodiesel yield of 89.23% was obtained at the following optimum reaction conditions; 70 ^oC of reaction temperature, 2 h of reaction time, 3 wt% of catalyst loading and methanol to waste frying oil ratio of 12:1. This indicates that NiCoAE as heterogeneous catalyst has potential to convert high FFA feedstock into biodiesel via single step transterification process

Keywords: *Anthill, eggshell, NiCoAE catalyst, transesterification, waste frying oil.*

1 INTRODUCTION

In last decade, significant concerns have been raised concerning the fossil fuel depletion and environmental degradation. To date, about one-fourth of the total pollutants emission results from power generation using fossil fuel are regarded as the main contribution to global warming (Quddus, 2013). Therefore, shifting from fossil fuel to biofuel is an antidote to all these menaces. Among all these alternative fuels, the features of biodiesel make it standout. Biodiesel is a mixture of alkyl ester of fatty acid which is often produced from vegetable oil or animal fat. Presently, industrial production of biodiesel is being done via homogeneous catalyzed transesterification that has some so many limitations. Those limitations include soap formation, waste water generation, inability to reuse catalyst because it is in the same phase with reactants. To this end, biodiesel could not compete with the petroleum based diesel. In this respect, heterogeneous catalyzed tranesterification process has received significant attention as a promising technique facilitating reuse of catalyst and reduction in biodiesel production cost. This non-convectional technique employs a solid catalyst to speed up the rate of reaction between vegetable oil/fat and monohydric alcohol. Therefore, the products and used catalyst are easily separable without any extra downstream processing cost involved in other available methods.

Various heterogeneous catalysts have been used for biodiesel production via transesterification process. The solid based catalysts include pure metal oxides, mixed metal oxides, alumina, silica and zeolite supported catalyst, sulphated-metal oxide and those ones derived from waste and naturally occurring materials. Vujicic *et al* (2010) investigated the transesterification of sunflower oil using CaO catalyst. Apart from that, Wen *et al*. (2010) studied the transesterification reaction between cotton seed oil and methanol using TiO-MgO as heterogeneous catalyst. Many more heterogeneous catalysts suitable for biodiesel production have been reported in literature (Jitputti *et al*., 2006; Peng *et al*., 2008; Kafuku *et al*., 2010; Olutoye and Hameed, 2013).

Meanwhile, It has been proven by many researchers that yield of biodiesel is found to be highly dependent on the transesterification process parameters such as amount of catalyst, reaction temperature, reaction time, alcohol to oil molar ratio and speed of agitation. These process parameters have to be varied to attain maximum methyl ester conversion (Muthu and Viruthagiri, 2015). In the past, most of the researchers made use of convectional one factor-at-a time method (OFAAT) to optimize alcoholysis process (Sharma *et al*., 2010; Tan *et al*., 2015). This method is so cumbersome, could not identify and quantify interactions between variables (Rutto, 2013). However, statistical design of experiments is now being used to accumulate and analyze information on the influence of process parameters on the yield of fatty acid methyl ester from oils, rapidly and efficiently using minimum number of experiments. This method is more powerful than one factor-at-a time method, because it can be used to test large number of process parameters and also identify the interaction between two or more variables (Yee and Lee, 2015).

In the current research, anthill-eggshell promoted Ni-Co mixed oxides (NiCoAE) was used as heterogeneous catalyst in transesterification reaction between waste frying oil and methanol. The as-prepared catalyst was characterized based on functional groups identification, as well as, surface morphology and topography. Moreover, various reaction parameters which affect the catalytic reaction were optimized using central composite design (CCD).

2 MATERIALS AND METHODS

Waste chicken eggshells and waste frying oil were collected from Students' Cafeteria 1, Afe Babalola University (ABUAD), Ado-Ekiti. Type II anthill situated at the back Department of Works and Maintenance, Afe Babalola University (ABUAD), Ado-Ekiti, was harvested. Synthesis grade methanol, sodium carbonate (Na_2CO_3), cobalt nitrate hexahydrate ($Co(NO_3)_2.H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) were purchased from Nizo Chemical Company Limited, Akure Nigeria. The free fatty acid (FFA) content of the waste frying oil (WFO) was determined by titration method and was found to be less than 2 wt.%.

2.2 CATALYST PREPARATION AND CHARACTERIZATION

The collected waste chicken eggshells were washed with water to remove white membrane, organic matter and impurities that adhered to it and then re-washed with deionized water. The washed eggshells were thereafter dried in an oven at a temperature of 110 ^{o}C for 2 h and the dried eggshells were ground into fine powder by mechanical grinder and later passed through 0.3 mm mesh to obtain particles less than 0.3 mm. The resulted fine eggshell powder was then kept in an enclosed container. Similarly, the harvested anthill clay

2.1 MATERIALS

was ground with the combination of mortar and pestle and screened with the same procedure earlier considered as with the eggshell. The procedure employed to prepare NiCoAE catalyst was referred to work reported by Sirichai *et al*. (2012). Based on preliminary experiment, the prepared eggshell powder, fine anthill clay, $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ were weighed and mixed in 69.7 wt%, 17.4 wt%, 8.6 wt% and 4.3 wt% proportion of eggshell, anthill, cobalt nitrate hexahydrate , nickel nitrate hexahydrate, respectively and fed into a beaker. Substantial amount of distilled water was added to the mixtures to form suspensions. The pH of the resulting slurry was adjusted to 8.0 by adding 0.1 M Na_2CO_3 solution and then age in a fume hood at 80 ^{o}C for 2 h with stirring. The solution was then filtered with filter papers and oven dried at 110 ^{o}C for 12 h. The resulting dried mixture was therefore calcined in a muffle furnace under static air conditions at a temperature of 1000 ^{o}C for 4 h. The heating rate used was 10 ^{o}C/min.

The Fourier Transform Infrared Radiation (FTIR) spectrometer (IRAffinity-1S, Shimadzu) was used to identify different functional groups present on the surface of the as-synthesized catalysts. Scanning Electron Microscope (SEM) was used on the as-synthesized catalysts to identify the surface topography or morphology.

2.3 DESIGN OF EXPERIMENTS

The design of experiment technique adopted in this study is central composite design (CCD) and the yield of biodiesel is the response measured. The effects of transesterification process variables, which included the reaction temperature, reaction time, catalyst loading and methanol to oil ratio, on the yield of biodiesel were investigated. The aforementioned independent variables were illustrated in Table 1. This table presented five level-four factor central composite design for waste frying oil (WFO) conversion via transesterification process. However, a total of thirty experimental runs were carried out. Out of which, six runs were for center points.

TABLE 1: LEVELS OF THE TRANSESTERIFICATION PROCESS PARAMETERS CONSIDERED FOR THIS STUDY

Variable	Factor coding	Unit	Level				
			-2	-1	0	+1	+2
Reaction temperature	x_1	^{o}C	40	50	60	70	80
Reaction time	x_2	h	1	2	3	4	5

Catalyst loading	x_3	wt.%	1	3	5	7	9
Methanol to oil ratio	x_4	-	3	6	9	12	15

In this present work, the main objective is to determine optimum values of process parameters that would provide maximum biodiesel yield. However, the response was determined via transesterification process and also used to develop a mathematical model, which correlate the biodiesel yield to those four independent variables considered through first order, second order and interaction terms, according to the Equation (2) (Yee and Lee, 2008).

2.4. TRANSESTERIFICATION REACTION STUDY

The transesterification of waste frying oil (WFO) into biodiesel using calcined NiCoAE catalyst was carried out in a batch reactor made up of a 250 mL one way round bottom flask fitted with a condenser and thermometer. The reaction was performed at different conditions, considering catalyst loading (3-7 wt%), reaction temperature (50-70 ^{o}C), reaction time (2-4 h), methanol/WFO molar ratio (6:1-12:1) and stirring rate constant. After the completion of reaction, the resulting mixture was filtered using white cloth in order to remove the spent catalyst and filtrate was then poured into a separating funnel and left there overnight to settle. During the process, two layers of liquid were observed, in which the upper layer was biodiesel and lower layer indicated glycerol. Thus, the biodiesel yield is determined theoretically by the Equation (2) given by Leung and Guo (2006). The biodiesel prepared under

$$Y = \alpha_o + \sum_{j=1}^{4} \alpha_j x_j + \sum_{i,j=1}^{4} \alpha_{ij} x_i x_j + \sum_{j=1}^{4} \alpha_{jj} x_j^2 \quad (1)$$

Where Y is the predicted biodiesel yield, x_i and x_j represents the process parameters, α_o is the offset term, α_j is the regression coefficient for linear term, α_{ij} is the regression coefficient for first order term and α_{jj} is the regression coefficient for quadratic effect.
the optimum reaction conditions was characterized by FTIR.

$$\text{Biodiesel yield (\%)} = \left[\frac{Weight\ of\ biodiesel}{Weight\ of\ WFO\ fed}\right] \times 100\% \quad (2)$$

3.0 RESULTS AND DISCUSSION

3.1 CATALYST CHARACTERIZATION

Scanning electron microscope (SEM) analysis was carried out to compare the surface structure and morphology of raw and calcined NiCoAE catalysts. Figure 1(a and b) show the SEM images of raw and calcined catalyst. The results depicted indicate that raw catalyst possessed irregular and undefined particles with the surface covered by adsorbed gases, volatile matters and moisture. This is attributed to why raw catalyst exhibited low surface area and level of its inactivity. Also, the particles that made up of uncalcined NiCoAE were combined and agglomerate into large particles as shown in Figure 1(a). The preparation method employed might be responsible for this observation.
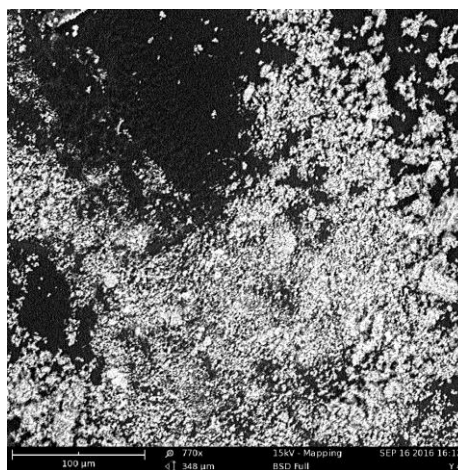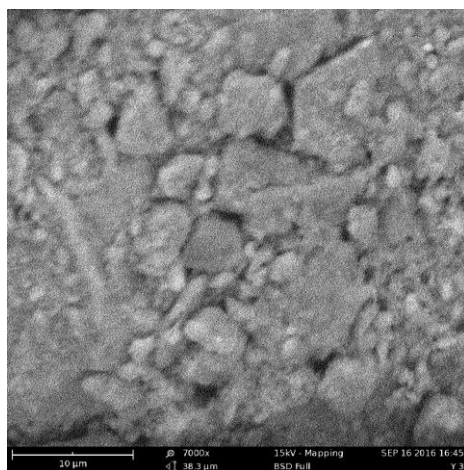
Figure 1: SEM images of (a) raw NICOAE; (b) calcined NiCoAE

Figure 1(b) shows the SEM images of calcined NiCoAE catalyst which was thermally treated at calcination temperature of 1000 ^{o}C. However, after calcination, the large and undefined particles present in raw NiCoAE split into smaller particles with high surface area and large voids. This observation is due to the changes in composition of the catalyst components as also revealed by FTIR analysis. Most of the essential metallic compounds contain in NiCoAE catalyst, have been decomposed into their corresponding oxides and carbon dioxide, CO_2 after calcination process (Tan *et al.*, 2015), thus, leaving cavities that indicate both solid rearrangement and the exit way of the eliminated components (Leofanti *et al.*, 1997). The result obtained herein agrees reasonably well with the finding of Buasri *et al.* (2013) who discovered that thermally activated carbonate based catalyst is made up of particles having tiny sizes and shape. The catalyst samples developed for this present study could be considered as porous materials.

The Fourier transform infrared (FTIR) characterization technique is employed to identify those functional groups contained in the as-synthesized catalysts. The FTIR analysis was carried out on both uncalcined and calcined NiCoAE and compared. The major absorption bands contained in displayed Figures 2(a) and (b) are thus interpreted in Table 2.

(a)
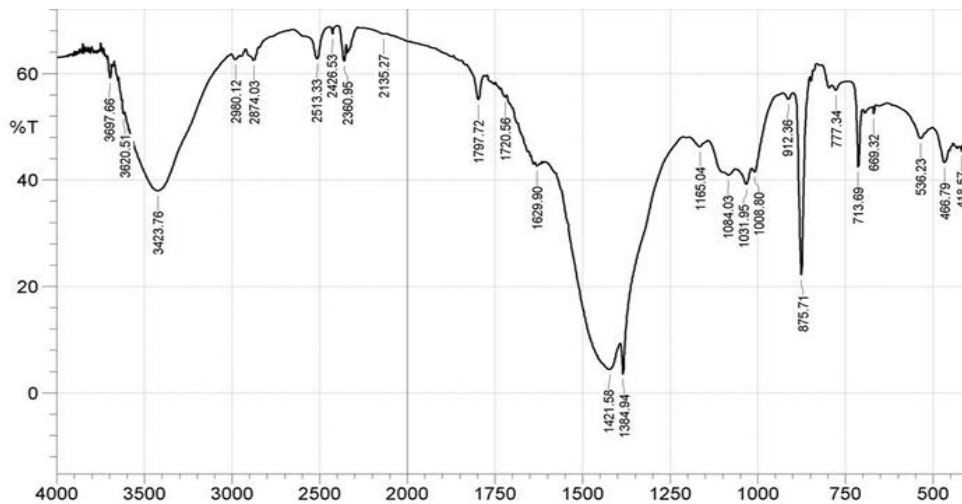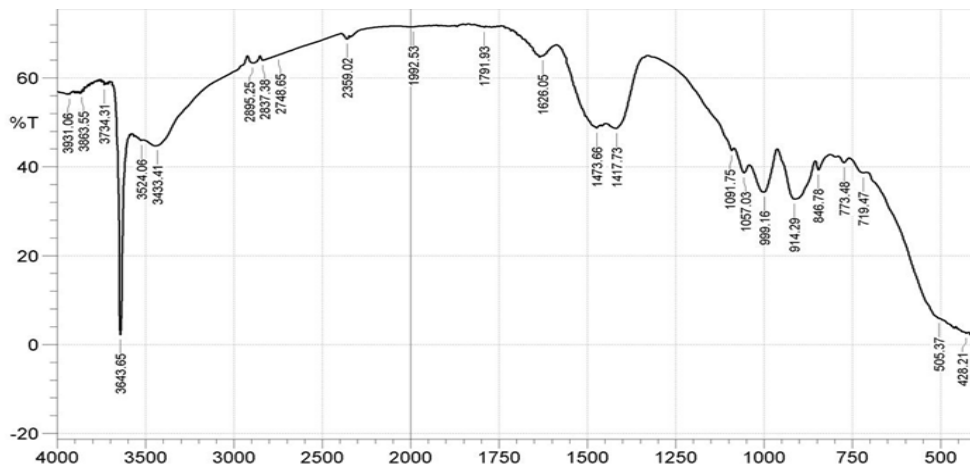
Figure 2: FTIR spectra for the (a) raw and (b) calcined NiCoAE catalyst

TABLE 2: THE MAJOR ABSORPTION BAND AND ASSIGNMENT FOR RAW AND CALCINED NICOAE CATALYST

IR Band	Wavenumber (cm^{-1})		Assignment
	Raw NiCoAE	**Calcined NiCoAE**	
1	3423.76	3643.65	Bonded O-H stretching vibration
2	2360.95, 2513.33	-	symmetric stretching of the C-H bonds
4	1797.72	-	C=O functional group contained in aldehydes
5	-	1473.66	CH$_3$ antisym deformation
6	1421.58	1417.73	Vinyl C-H in-plane bend
7	1384.94	-	C-CH$_3$ deformation
8	-	1057.03	P-O-C strongest band for aliphatic amines
9	-	999.16	C-H out of plane bend of alkenes
10	-	914.29	presence of silicate ion
11	875.71	-	C-O out of plane bend vibration modes of CO_3^{2-}
12	713.69	-	C-O in plane bend vibration modes of CO_3^{2-}
13	-	505.37	Al-OH stretching vibration or the sulphate vibration band width
14	-.	428.21	CaO vibration

The better performance of NiCoAE catalyst indicates that those aforementioned functional groups fully participated in transesterification reaction and this observation is in trend with the experimental result reported in the research carried out on active clay-based catalyst (Olutoye and Hameed, 2013) and CaO based catalyst synthesized from chicken and ostrich eggshells (Tan *et al*., 2015).

3.2 DEVELOPMENT OF REGRESSION MODEL

The whole design matrix couple with the values of the response obtained from the experimental works is presented in Table 3. The biodiesel yield was found to range from 17.51 wt% to 88.24 wt%. According to central composite design (CCD) embedded in response surface methodology (RSM). Several models were suggested, but the best model was selected based on the highest order polynomial in which the additional terms were significant and the model was not aliased (Tan *et al*., 2008). For response of biodiesel yield, the quadratic model was selected. However, the model equation in terms of actual factors including the non-significant terms for biodiesel yield is given by the following second-order polynomial Equation (3).

$Y = 16.77 + 0.92x_1 - 10.61x_2 - 14.59x_3 + 8.17x_4 - 0.38x_1x_2 - 0.13x_1x_3 - 0.17x_1x_4 + 0.02x_2x_3 - 0.62x_2x_4 - 0.42x_3x_4 + 0.02x_1^2 + 5.43x_2^2 + 2.31x_3^2 + 0.57x_4^2$ (3)

TABLE 3: EXPERIMENTAL DESIGN MATRIX AND RESPONSES

Run	Reaction temperature, x_1 (^{o}C)	Reaction time, x_2 (h)	Catalyst loading, x_3 (wt%)	Methanol to oil ratio, x_4 (mol/mol)	Biodiesel yield, Y (%)
1	60	3	1	9	87.76
2	70	2	7	6	58.29
3	60	3	9	9	54.94
4	60	1	5	9	72.65
5	50	4	3	6	39.43
6	60	3	5	9	35.88
7	60	3	5	15	88.24
8	60	5	5	9	39.35

Run	Reaction temperature, x_1 (^{o}C)	Reaction time, x_2 (h)	Catalyst loading, x_3 (wt%)	Methanol to oil ratio, x_4 (mol/mol)	Biodiesel yield, Y (%)
9	50	2	3	6	41.14
10	40	3	5	9	44.80
11	60	3	5	9	38.04
12	70	2	7	12	65.33
13	50	4	7	12	66.82
14	70	2	3	12	88.65
15	60	3	5	9	30.04
16	60	3	5	3	21.51
17	50	4	7	6	38.04
18	70	4	3	12	66.86
19	50	2	7	12	74.65
20	60	3	5	9	36.12
21	70	4	3	6	46.63
22	50	2	3	12	76.47
23	60	3	5	9	37.02
24	80	3	5	9	40.04
25	60	3	5	9	32.61
26	70	4	7	12	42.61
27	50	4	3	12	70.74
28	50	2	7	6	35.43
29	70	2	3	6	60.82
30	70	4	7	6	43.35

3.3 ANOVA ANALYSIS FOR TRANSESTERIFICATION PROCESS

In this case as well, the degree of accuracy of quadratic model connecting both dependent and independent variables was examined based on the values of correlation coefficient (R^2) and standard deviation suggested by the design expert software. The closer the value of correlation coefficient (R^2) to unity and the smaller the standard deviation, the more accurate the response could be well predicted by the model. The value of R^2 for developed model Equation (3) was obtained to be 0.9542. However, this value justified better correlation between biodiesel yield and transesterification variables.

The standard deviation for the same Equation (3) was 5.68. This indicates that the experimental values obtained for biodiesel yield agrees reasonably well with those values suggested by the model. The value of R^2 for the model was approximately 95% of unity, which indicates that only 5.0% of the total variations were not considered by the model. This discrepancy is attributed to the fact that not all the parameters considered in this study affected the yield of biodiesel. A similar observation has been reported by Ibrahim and Pillai (2011), in the optimization of process parameters for biodiesel synthesis from rubber seed oil using central composite design.

Furthermore, the adequacy of the developed model was evaluated using the analysis of variance (ANOVA). The ANOVA for fit of biodiesel yield from central composite design (CCD) is presented in Table 3. The larger the magnitude of the F-value and the values of prob>F less than 0.05 indicated that the model was significant and also, the model terms were significant (Tan *et al*., 2008; Chaisongkroh *et al*., 2012)

TABLE 4: ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL FOR BIODIESEL YIELD

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob>F
Model	10089.36	14	720.67	22.33	<0.0001
x_1	17.17	1	17.17	0.53	0.4770
x_2	974.10	1	974.10	30.19	<0.0001
x_3	724.46	1	724.46	22.45	0.0003
x_4	4332.52	1	4332.52	134.26	<0.0001
x_1x_2	232.41	1	232.41	7.20	0.0170

x_1x_3	102.72	1	102.72	3.18	0.0946
x_1x_4	402.80	1	402.80	12.48	0.0030
x_2x_3	0.018	1	0.018	5.648E-004	0.9814
x_2x_4	55.65	1	55.65	1.72	0.2088
x_3x_4	102.01	1	102.01	3.16	0.0957
x_1^2	114.24	1	114.24	3.54	0.0795
x_2^2	810.47	1	810.47	25.12	0.0002
x_3^2	2358.71	1	2358.71	73.09	<0.0002
x_4^2	728.77	1	728.77	22.58	0.0003
Residual	484.05	15	32.27	-	-
$R^2 = 0.9542; Adj - R^2 = 0.9115$					

As contained in Table 4, the model F-value of 22.33 indicated that the model is significant. However, only $x_1, x_3, x_4, x_1x_2, x_1x_4, x_2^2, x_3^2$ and x_4^2 were influencing

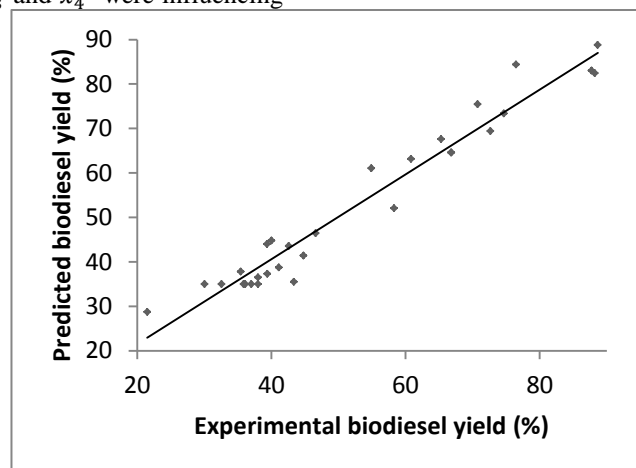terms, while the remaining terms as contained in Table 4 were insignificant.

Figure 3: Plot of predicted vs. experimental (actual) biodiesel yield (%

Therefore, from the statistical result obtained, it was found that the model is adequate to predict the response (biodiesel yield) within the range of transesterification parameters studied. The Figure 3 depicts a plot of predicted values versus experimental values over the observed values of biodiesel yield. It was revealed that there was closeness between predicted values and experimental values.

3.4 EFFECT OF INDIVIDUAL PROCESS PARAMETERS ON BIODIESEL YIELD

The influence of single variable was evaluated and plotted against the biodiesel yield while the other variables were kept constant. Base on the ANOVA result presented in Table 4, the catalytic reaction was significantly influenced by various linear and quadratic terms. However, significant individual process variables

that influence the transesterification reaction include reaction time (x_2), catalyst loading (x_3) and methanol to oil ratio (x_4). The result displayed the merit of applying design of experiment in identifying the significant parameters that influence the biodiesel production process.

3.4.1 EFFECT OF REACTION TEMPERATURE

As contained in Table 4, the reaction temperature has no effect on biodiesel yield, that is, its p-value was greater than 0.05. However, as shown in Figure 2, the yield of biodiesel slightly increases from 35.62% at 50 $^{\circ}$C to 36.01 at 70 $^{\circ}$C. As it has been well reported in the literature that higher reaction temperature enhances mass transfer of reactants involve and dispersion of the catalyst particles. High

temperature also favours high reaction rate, which eventually results in high conversion to biodiesel (Olutoye *et al*., 2015). Meanwhile, at lower reaction temperature, there would be poor interaction between methanol and catalyst particles, thus leading to poor slower reaction rate (Yee and Lee, 2008).
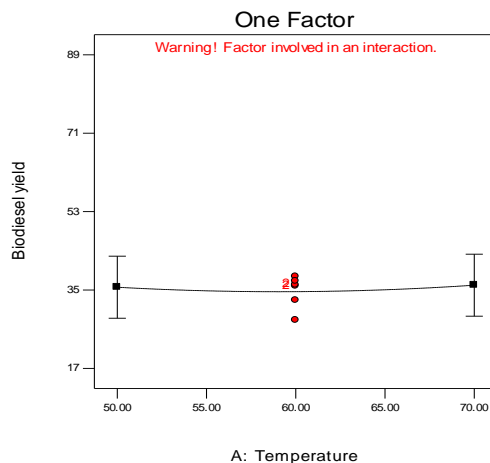

Figure 4: Biodiesel yield versus reaction temperature while other variables are constant

Relatively, either high reaction temperature or reaction time is needed to achieve a maximum yield of biodiesel in most of the heterogeneous catalyzed transesterification reaction (Yee and Lee, 2008). This is attributed to why maximum biodiesel yield was attained at reaction temperature of 70 ^{o}C. However, with reaction temperature above 70 ^{o}C, that is 80 ^{o}C, lower yield was recorded. This is due to liquid methanol in the reaction medium that had been totally gasified, therefore favouring the formation of glycerol over biodiesel (Tan *et al*., 2015).

3.4.2 EFFECT OF REACTION TIME

As depicted in Figure 5, it was observed that the biodiesel yield decreases as the reaction time increases. However, the effect of reaction time on the biodiesel yield was significant as contained in Table 3, that is, the p-value of reaction time was less than 0.05. The possible cause for the higher yield of biodiesel at lower reaction time might be due to the reaction temperature. The reaction rate increases with reaction temperature. In most of the heterogeneous transesterification reactions, high temperature or time is required to achieve high conversion of triglyceride (Olutoye and Hameed, 2013).
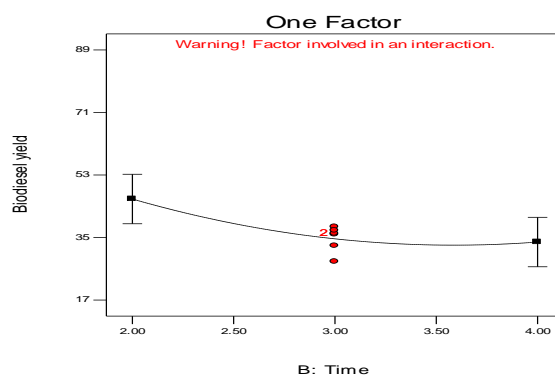

Figure 5: Biodiesel yield versus reaction time while other variables are constant

Meanwhile, higher reaction temperature and time is not beneficial in maximizing the yield of biodiesel. In this present study, the maximum biodiesel yield was achieved at lower reaction time of 2 h. This is due to the fact that the experimental run that provided the maximum yield was carried out at higher reaction temperature of 70 ^{o}C.

3.4.3 EFFECT OF CATALYST LOADING

In order to investigate the influence of catalyst loading on the yield of biodiesel, the optimization of transesterification of waste frying oil was carried out with various catalysts loading ranging from 1.0 wt% to 9.0 wt% of oil. As shown in Figure 6, biodiesel yield decreases as the catalyst loading increases. Maximum biodiesel yield was obtained at catalyst loading of 3.0 wt%. This result implied that catalyst loading equivalent to 3 wt% of waste frying oil is sufficient enough to provide required absorption sites for methanol on catalyst surface, in which O-H functional group split into methoxide anions and proton, thus leading to complete conversion of the triglycerides into biodiesel (Chorkendoff and Niemantsverdriet, 2003).
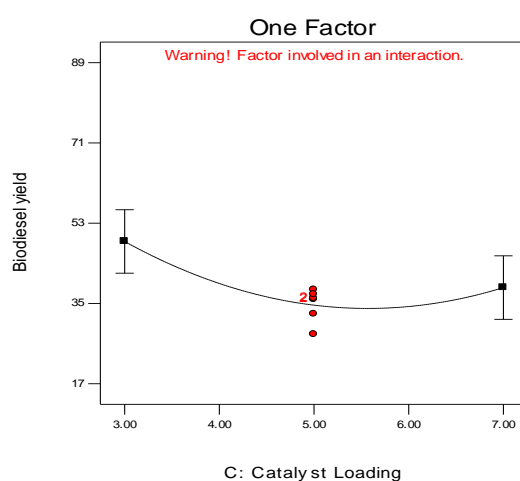
Figure 6: Biodiesel yield versus catalyst loading while other variables are constant

However, when the catalyst was loaded in large amount, the reaction contents became more viscous, thereby reducing the interactions between them and at same time, favoured the formation of glycerol over biodiesel. This finding can be explained from the point described by Olutoye *et al*., (2015) who concluded that excess catalyst loading resulted to undesired saponification reaction.

3.4.4 EFFECT OF METHANOL TO OIL MOLAR RATIO

Figure 4 shows the effect of methanol to oil ratio (6:1-12:1) on the yield of biodiesel. The relationship between methanol/oil ratio and biodiesel yield was found to be linear. As can be seen from Figure 7, the yield of biodiesel increases significantly from 26.7% at ratio of 6:1 to 51.45% ratio of 12:1. However, the effect of molar ratio of methanol to oil (x_4) was highly significant as confirmed in Table 1. The increase in the yield of biodiesel at higher molar ratio of methanol to oil is due the shifting of reaction equilibrium to the forward direction, in the sense that the transesterification is a reversible process (Tan *et al*., 2015).
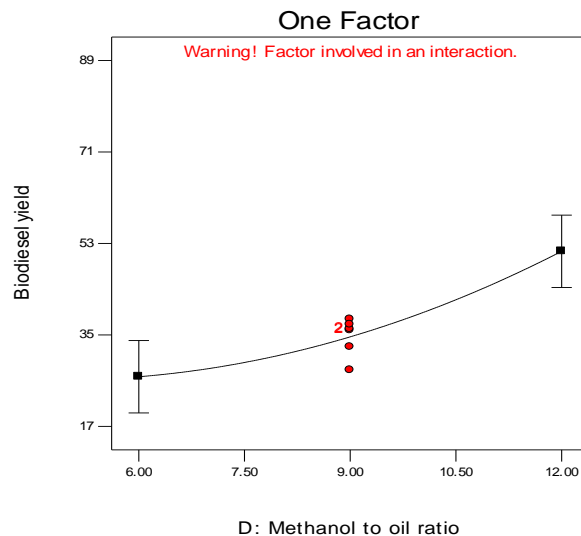
Figure 7: Biodiesel yield versus methanol to oil ratio while other variables are constant

Besides, at higher molar ratio, the oil molecules interact strongly with excess methanol (Olutoye *et al*., 2015). Meanwhile, too much quantity of methanol could hinder the separation of products, thus affecting the final yield of biodiesel (Ghoreishi and Moein, 2013). The

3.5 PROCESS VARIABLE OPTIMIZATION

The results presented above have proven that transesterification process parameters have influence on biodiesel yield. Having obtained this fact, the optimum process parameters were then selected based on the

methanol to oil ratio of 12:1 showed the highest biodiesel yield, so it was chosen as the optimum molar ratio and employed for further investigation in the present study.

experimental run which showed maximum biodiesel yield and the developed model regression (Equation 3) was used to estimate the predicted yield as well. However, the optimum predicted variables for highest biodiesel yield is presented in Table 5.

TABLE 5: OPTIMUM NUMERICAL SOLUTION FOR TRANSESTERIFICATION PROCESS

Temperature, x_1 (^{o}C)	Time, x_2 (h)	Catalyst loading, x_3 (wt%)	Methanol/oil ratio, x_4	Biodiesel yield (%)	
				Predicted	**Experimental**
70.00	2.00	3.00	12.00	88.42	89.23

The optimum transesterification process variables contained in Table 4 above, suggested that a biodiesel yield of 88.42% could be predicted. Experiments were conducted at these optimum reaction conditions, to check if the experimental value is in accordance with the predicted value. In most of the reported research findings, a relatively high reaction temperature or time has been recommended as crucial factor in obtaining a high biodiesel yield in a heterogeneous catalyzed transesterification reaction. However, in this present study, the reaction conditions to achieve maximum biodiesel yield can be easily achieved at reaction conditions of 70 ^{o}C temperature, 2 h time, 3 wt%

catalyst loading and 12:1 methanol/oil ratio. This trend is in agreement with the results of Lin and Hsiao (2013). From here, it can be concluded that anthill-eggshell promoted Ni-Co mixed oxides (NiCoAE) is a highly active solid catalyst for conversion of waste frying oil into biodiesel via single-step transesterification.

3.6 ANALYSIS OF BIODIESEL

3.6.1 FOURIER TRANSFORMS INFRARED (FTIR) ANALYSIS ON BIODIESEL

The composition and functional groups of biodiesel prepared under optimum reaction conditions (70 °C reaction temperature, 2 h reaction time, 3 wt% catalyst loading and 12:1 methanol/WFO molar ratio) were confirmed by FTIR spectrum (Figure 8).
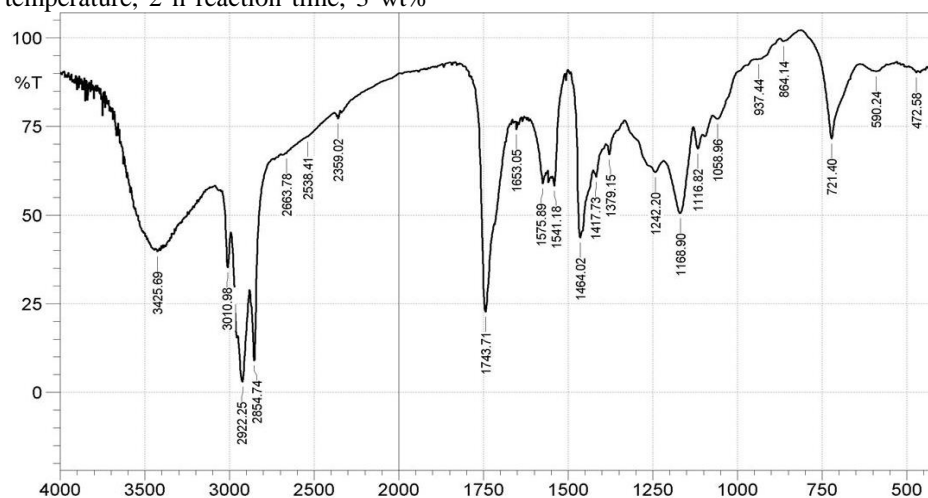

Figure 8: FTIR spectrum of biodiesel produced under optimum conditions

As shown in Figure 8, the broad absorption band at 3425. 69 cm^{-1} is attributed to O-H stretching vibration. A sharp band at 2922.25 and 2854.74 cm^{-1} are due to C-H stretching vibrations of methylene groups. Absorption band at 1743.71 cm^{-1} is assigned to C=O stretching vibration of ester carbonyl, while 1464.02 cm^{-1} is as a result of C-H bends of CH_2 and CH_3

aliphatic hydrocarbons. More so, bands at 1168.90 cm^{-1} and 721.40 cm^{-1} are attributed to C-O vibration stretching of fatty acid methyl esters and $C-H_2$ methylene rock, respectively. The presence of these functional groups confirmed the quality of the produced biodiesel and this observation is in trend with the experimental data reported by Yadav et al. (2010).

3.6.2 DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES

The biodiesel prepared under the optimum reaction temperature of 70 °C, catalyst loading of 3 wt%, reaction time of 2 h and methanol to WFO molar ratio of 12 was characterized based on its physicochemical and fuel properties. Table 6 shows the properties of the WFO-biodiesel. However, these properties were compared with that of ASTM/EN standard for biodiesel. Some of these properties were found to be comparable and in reasonable agreement with ASTM/EN standard for biodiesel.

TABLE 6: WFO-BIODIESEL PHYSICO-CHEMICAL AND FUEL PROPERTIES

Parameter	Waste frying oil-biodiesel	Biodiesel standard ASTM/EN
Specific gravity	0.886	0.86-0.90
Kinematic viscosity at 40°C (mm^2/s)	3.58	1.9-6.0
Acid value (mgKOH/g)	0.92	>0.8
Flash point (°C)	148	100-170
Cloud point (°C)	-9	-
Pour point (°C)	-12	-15-10
Lower heating value (MJ/kg)	37.49	40.13

4 CONCLUSION

In this work, anthill-eggshell promoted Ni-Co mixed oxides (NiCoAE) was successfully developed and used for converting waste frying oil (WFO) into fatty acid methyl ester (biodiesel). The SEM analysis revealed that the developed catalyst is made of small particles which enhance adsorption of reactants on its

surface and also, FTIR result revealed various functional groups on the catalyst surface. The influence of process variables on the catalytic reaction was investigated. The obtained data showed that the maximum biodiesel yield of 89.23% was achieved at reaction temperature of 70 ^{o}C, 2 h reaction time, 3 wt% catalyst loading and methanol/WFO of 12:1.

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