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Optimization of Biodiesel Production from Neem Seed Oil using Sulfated Zirconia and ZnO by two step Tranesterification

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ABSTRACT

In this work, two steps transeterification of neem seed oil was done using sulfated zirconia and ZnO catalysts with the aim of optimizing the process variables for higher yields. Sulfated zirconia catalyst was prepared by solvent-free method and ZnO by sol-gel method. Response surface methodology based on Box-behnken design was used to design the experiment and model factors yield relationship. Neem seed oil was extracted using soxhlet extractor apparatus and n-hexan as solvent. The results obtained showed oil yield of 40.64 ± 1.01 %. The empirical model obtained showed that reaction time and methanol were the most important variables that influenced biodiesel yield. The optimal process conditions were 60 °C, 98 minutes, 9:1 and 0.5 %, reaction temperature, reaction time, methanol to oil ratio and catalyst concentration are respectively. GC/MS showed that ester compounds were dominant over non-ester compounds. The fuel parameters were determined according to ASTM methods which were in conformity with ASTM D6751 requirements.

1. Introduction

Global energy crisis, unstable prices and depletion of petroleum fuels, environmental pollution arising from oil spillage and harmful gaseous emissions into the atmosphere are the major problems of conventional fossil energy source [Barnwal and Sharma, 2005; Amish et al., 2009].Thus, there is an urgent need to search for alternative, renewable and greener form of energy before the fossil oils supplies run dry. Nowadays, biomass has been focused as an alternative energy source since it maintains the level of carbon dioxide in the atmosphere constant through the process of photosynthesis. The carbon dioxide emitted during the combustion of biomass would be absorbed during the process of photosynthesis [Hossain, et al., 2008]. Bio-fuels are one of such alternative fuel that could minimize greenhouse gas emission as well as complimenting the fossil fuels [Rao, et al., 2010]. Biodiesel, which is proven as an alternative of fossil diesel is gaining ground as a biodegradable, nontoxic and environmentally friendly fuel to neat diesel, it is produced from local feedstock reducing the need for foreign oil imports, while boosting the local economy and supporting the agricultural community [Demirbas, 2008]. However, despite all these favorable attributes, the economic aspect of biodiesel production is the major barrier to its worldwide commercialization. The cost of biodiesel production is highly dependent on the cost of feedstock, which accounts for 60-80% of the cost of the finished product [Gui, 2008; Singh and Singh, 2010]. Exploring ways to reduce the cost of the raw material is of great interest. Consequently, an inedible oils are now being sought, from algae [Galadima, and Muraza, 2014] as well as other crops and sources such as Jatropha curcas [Tiwari et al., 2007; Berchmans and Hirata, 2008], Karanja [Naik et al .,2008], *Lagenaria vulgaris* [Sokoto et al., 2013], *Laganeria siceraria* [Muhammad et al., 2015], *Hevea brasiliensis* [Muhammad et al., 2016]. Currently, the main process for the production of biodiesel is the transesterification of vegetable oils using a strong base as homogeneous catalyst. However, this process presents some drawback, as it requires the use of relatively large amount of unrecoverable catalyst with consequent generation of waste/liquor which has to be treated and the purification of glycerine [Daud et al., 2015]. Free fatty acid (FFA) value of oil plays key role in the transesterification process. If free fatty acid content of the oil is lower than 3 mgKOH/g single step process (alkali transesterification) will be carried out. If it is greater than 3 mgKOH/g double step process (acid esterification and alkali transesterification) will be carried out [Selvankur et al., 2014].Therefore, this paper tends to exploit the potential of heterogeneous catalysts sulfated zirconia and ZnO in production of biodiesel from crude neem seed oil by two step transesterification process.

2. Materials and Methods

Sample preparation and oil extraction: The neem seeds was obtained from Bodinga Local Government area of Sokoto state, Nigeria. The seeds were sorted out, dehulled, ground into powder and the oil was extracted using soxhlet extraction method using n-hexane as solvent.

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$$\text{Crude lipid yield (\%)} = \frac{\textit{Weight of extracted oil}}{\textit{Weight of the sample}} \times 100 \quad (1)$$

2.1 Analyses of the Neem Seed Oil

The crude extracted seed oil was analyzed for its acid value, saponification value, free fatty acids content and iodine value according to ASTM methods.

2.2 Catalyst Preparation:

Two different catalysts were used in this research and they were prepared as described below.

Sulfated Zirconia

The solvent-free preparation of Sulfated zirconia (S-ZrO_2) was accomplished according to the procedure described by Sun *et al*.[2005]. $ZrOCl_2.8H_2O$ and $(NH_4)_2SO_4$ in a molar ratio of 1:6 was grounded in an agate mortar for 20 minutes at room temperature. After standing for 18 hour at room temperature in air, the sample was calcined for 5 hours at 600 °C.

Zinc (II) Oxide (ZnO)

Synthesis of ZnO nano powder is as follows: Zinc nitrate (0.5 M) and NaOH (1 M) solutions was prepared separately in standard flasks (100 cm^3). Sodium hydroxide solution was heated to 40 °C under constant stirring on the hot plate, the zinc nitrate solution was added slowly (drop wise for 30 minutes) to the NaOH solution. After 2 hours of stirring at 250 rpm, the white precipitate deposited at the bottom of the flask was collected and washed several times with absolute ethanol and distilled water. The dry $Zn(OH)_4^{2-}$ gel sample was obtained by dehydration of the precipitate in the oven at 85^{0}C for 8 hours. The obtained $Zn(OH)_4^{2-}$ gel was calcined at 400°C for 4 hours.

Catalyst Characterization:

Infrared spectroscopy and thermo gravimetric was used to characterize the catalyst prepared. The absorption peak at 748 cm^{-1} represent Zr-O_2 stretching vibrations and the absorption peaks at 1017 and 1140 cm^{-1} are due to stretching frequencies of O-S-O. The FT-IR spectrum of ZnO, the absorption peak at 435 cm^{-1} represent Zn-O stretching vibrations and absorption peak at 545 cm^{-1} are due bending vibration of O-H. The TGA and DTA curves of prepared of ZnO catalyst show a weight lost at a temperature of 100 ^{0}C due to evaporation of adsorbed water and at a temperature of 600 ^{0}C the compound decomposes rapidly. However, the TGA and DTA curves of prepared sulfated Zirconia catalyst show the weight loss at 100 ^{0}C and 750 ^{0}C due to loss of physically adsorbed water and SO_4^{2-} bounded to the surface of ZrO_2 respectively.

Pretreatment:

Response surface based on (Box-Beckhen) statistical experimental design was used to designed the experiment. Three independent variables namely temperature (40-65 ^{0}C), amount of methanol (6-12) molar ratio and catalyst concentration (1-2 %) at constant time 2 hours were selected based on literature survey. The runs were completely randomized to obtained a total of 15 runs. The acid value of the oil at the end of each run was determined by titrimetric method and FFA conversion were calculated using equation 2.6 below [Gore and Thomson, 1998].

Where xFFA is percentage conversion, a_i is initial acidity of the oil

$$\text{xFFA} = \frac{ai - at}{ai} \times 100 \quad (2)$$

and a_t is final acidity at time t.

Experimental Design

Response surface (Box-Behnken) statistical experimental design was employed in designing the experiments for determination of the optimal conditions for conversion of crude neem seed oil into biodiesel by two step transesterification using sulfated zirconia and ZnO as catalysts. Four independent variables including reaction time, methanol to oil molar ratio, catalyst concentration and reaction temperature, selected based preliminary experimental study, were investigated and optimized. Table 1 shows the levels of the factors employed in the design.

Each run was set in triplicate and all the runs were completely randomized to obtain a total of 54 runs (Table 2). The design and analysis, as well as optimization, of the results were done using MINITAB 17 statistical software.

Table 1: The Process Variables and their Levels

Factor	Lower level	Upper level
Temperature (0C)	60	70
Time (min)	60	120
Methanol / Oil (r)	6	12
Catalyst (%)	0.5	1.5

Table 2: Experimental design matrix and results (biodiesel yield) from the experimental runs

Std Order	Temp. (^{0}C)	Time (min)	Catalyst (%)	Met/ oil	% Yield
1	60	60	1.0	9	89.44
2	70	60	1.0	9	63.76
3	60	120	1.0	9	77.52
4	70	120	1.0	9	76.34
5	65	90	0.5	6	66.00
6	65	90	1.5	6	67.53
7	65	90	0.5	12	60.56
8	65	90	1.5	12	76.86
9	60	90	1.0	6	66.16
10	70	90	1.0	6	65.66
11	60	90	1.0	12	61.90
12	70	90	1.0	12	55.08
13	65	60	0.5	9	73.00
14	65	120	0.5	9	87.56
15	65	60	1.5	9	63.50
16	65	120	1.5	9	66.04
17	60	90	0.5	9	85.10
18	70	90	0.5	9	72.60
19	60	90	1.5	9	65.14
20	70	90	1.5	9	87.00
21	65	60	1.0	6	72.06
22	65	120	1.0	6	79.90
23	65	60	1.0	12	64.22
24	65	120	1.0	12	66.04
25	65	90	1.0	9	86.26
26	65	90	1.0	9	85.99
27	65	90	1.0	9	86.21
28	60	60	1.0	9	87.10
29	70	60	1.0	9	61.92
30	60	120	1.0	9	88.80
31	70	120	1.0	9	70.26
32	65	90	0.5	6	81.94
33	65	90	1.5	6	73.50
34	65	90	0.5	12	62.00
35	65	90	1.5	12	66.82
36	60	90	1.0	6	66.20
37	70	90	1.0	6	60.42
38	60	90	1.0	12	62.00
39	70	90	1.0	12	64.00
40	65	60	0.5	9	72.90
41	65	120	0.5	9	88.10
42	65	60	1.5	9	63.66
43	65	120	1.5	9	65.92
44	60	90	0.5	9	85.22
45	70	90	0.5	9	73.00
46	60	90	1.5	9	64.90
47	70	90	1.5	9	88.52
48	65	60	1.0	6	71.95
49	65	120	1.0	6	80.04
50	65	60	1.0	12	64.30
51	65	120	1.0	12	65.98
52	65	90	1.0	9	86.00
53	65	90	1.0	9	86.21
54	65	90	1.0	9	85.99

Description of experimental run (Transesterification):

The catalyst was added to the known amount of methanol mixed with neem seed oil (50 g) in flat bottom flask. The mixture was refluxed at constant stirring speed at a temperature and for a period of time as specified in the design matrix (Table 2). At the end of the reaction time, the biodiesel (yellowish upper layer) was recovered using a separating funnel after complete separation overnight under gravity. The spent catalyst was recovered from the bottom layer by centrifugation (4500 rpm, 10 min). The crude biodiesel in an evaporating dish, was heated on a water bath (90 °C, 30 min) to remove the residual methanol. It was further purified by neutralization with dilute phosphoric acid (pH 4.0), washed with hot distilled water until the washed water has a pH of 7.0 and the residual water was removed by drying at100 °C over anhydrous Na_2SO_4. The biodiesel yield was calculated from Eq. 3 as follows:

$$\text{Biodiesel yield (\%)} = \frac{Weight\ of\ Biodiesel}{Weight\ of\ oil} \times 100 \qquad (3)$$

3. Results and Discussion

Oil content of the plant seeds is one of factors for assessing the economic viability of a feedstock for biodiesel production. The results 40.64 ± 1.01 % indicate that the neem seed is good source of oil which could be used for biodiesel production.

Acid value is the measure in milligram of potassium hydroxide per gram required to titrate a sample to a specified end point. It is a direct measure of FFA present in the oil. Excess or higher acid and free fatty acid values of oil greater than 5% is not suitable for base catalyzed transesterification reaction [Rakesh et al., 2014]. The acid value 23.64±1.16 mg KOH/g as presented in Table 3, is comparable with 24.74 mg KOH/g reported by [Muthu et al., 2010]. But slightly lower 32.54 mg KOH/g obtained by [Aransiola et al.,2012].

Table 3: percentage crude lipid yield and properties of oil extracted from neem seed oil

Properties	Yield
Crude lipid yield (%)	40.64 ± 1.01
Acid value (mgKOH/g)	23.64 ± 1.16
Iodine value (gI_2/100g)	82.45 ± 1.60
Saponification value	190.74 ± 1.07
Free fatty acid (%)	11.82 ± 0.05

Mean ± SD

Main Effects Plot for FFA Conversion (Step 1)

The results presented in figure 3.1 infer that the highest FFA conversion of almost 92.65 % (from 23.64 to 1.81 mg KOH/g) could be achieved at 52.5 ^{0}C, 1.5 % and 9:1 temperature, catalyst and methanol to oil molar ratio respectively. The conversion efficiency for neem oil with SZ obtained is comparable to the results 92.33 % and 94 % obtained by [Hawash et al., 2014], and [Anton et al., 2006] respectively. However, the conversion efficiency of esterification reaction has less effect as the catalyst concentration is raised beyond 1.5 %.

Effect of Process Variables on the Biodiesel Yield (%)

Figure 2 gives a summary of the biodiesel yield obtained from the 54 experimental runs conducted at different levels of the four process variables investigated (see Table 2 for details). The biodiesel yield varies from minimum of 55% to maximum of 93%. Although, there is large variability in the biodiesel yield due to effect of other variables, there is clear increase in biodiesel yield with increase in reaction time. Notably, the yield also increased with an increase in methanol to oil ratio from 6 to 9, but then decreased when the methanol to oil was raised to 12. However, the yield decreases with increase in reaction temperature.

Table 5 shows the result of Analysis of Variance (ANOVA) of the experimental studies on the effects of temperature, time, catalyst concentration and methanol to oil ratio on the maximization of biodiesel production from the neem seed oil. The Response Surface Methodology that was used to model factors - yield relationship in this experiment is presented in the (Table 2). The significance of terms was evaluated by comparing the p- values with α – Value (0.05). The results of Analysis of variance in (Table 3.4), revealed that linear, quadratic and interaction terms of the model are all statistically significant ($p < 0.05$, at $\alpha = 0.05$). The high coefficient of variation (R^2= 64.98 %) shows that the model adequately account for the empirical relationship between biodiesel and process variables.

Table 4 shows the fuel properties, Iodine value is a measure of unsaturation level of fats and oils [Knothe, 2006]. Higher iodine values indicate higher unsaturation in fats and oils. Esterification process reduces the iodine value to a small extent [Asmare and Gabbiye, 2014]. This infers that the produced biodiesel may have higher oxidation stability due to the absence of polyunsaturated fatty acids methyl esters [Knothe, 2010].

$$\text{Yield} = -609 + 24.6r - 0.2208d^2 - 0.00500t - 19.00c - 1.516r + 3.81dc \qquad (4)$$

Table 4: Fuel properties of biodiesel produced

Parameter	Unit	Biodiesel ASTM D6751	Value
Acid value	mgKOH/g	0.5 max	0.03 ± 0.01
IodineValue	gI_2/100g	130 max	37.36 ±0.12
KinematicViscosity	Cst	1.9 – 6.0	4.32 ±0.04
Cetane Number	__	47 min	149.82 ±2.0
HighHeatingValue	MJ/kg	___	47.19 ± 045
Flash Point	^{o}C	93 min	110 ± 2.0
Pour Point	^{o}C	-15 – 16	3 ± 0.00
Specific Gravity	g/cm^3	0.86 – 0.9	0.74 ± 0.02
Water and Sediment	%	0.05 max	0.02 ±0.00

Table 5: Results of Analysis of Variance (ANOVA) for Neem Biodiesel Yield

Source	DF	Adj SS	Adj MS	F	P
Model	14	3760.63	268.62	5.17	0.000
Linear	4	743.35	185.84	3.58	0.014
Square	4	1996.83	499.21	9.61	0.000
Interaction	6	1020.45	170.08	3.27	0.011
Error	39	2026.85	51.97		
Lack-of-Fit	10	1623.78	162.38	11.68	0.000
Pure Error	29	403.08	13.90		
Total	53	5787.48			

On eliminating the insignificant terms from the model, the new regression model (Equation 4) with seven significant terms the model is slightly better than the previous model. The fitness of the model was further determined by coefficient of variation (R^2) and effects of terms were evaluated at 95% confidence level.

At a low reaction time and higher temperature (less than 70 minutes greater than 64 ^{o}C), the biodiesel yield was less than 70.0 %. Highest biodiesel yield greater 85 %, were obtained at reaction time greater than 80 minutes when reaction temperature was between 62 ^{0}C – 64 ^{0}C.

The amount of methanol appears to have more influence on the yield than the temperature. Higher yields greater than 85 % are only obtained when methanol to oil ratio is greater than 8:1 and reaction temperature is greater than 60 ^{o}C . Excess amount of alcohol increases conversion of oils into esters within a short time. Catalyst concentration and reaction time interact positively to influence biodiesel yield. When reaction time is less than 75 minute, the biodiesel yield is less than 75 % irrespective of the catalyst concentration.

Optimization of biodiesel yield:

Optimization of the biodiesel yield was carried out using Response Optimizer in MINITAB 17 statistical software. Four response variables (temperature, time, catalyst and methanol) were optimized in this study to determine experimental condition that is best for maximization of biodiesel yield thereby reducing the process cost and making it economically favorable. In this response optimizer identify the combination of process variables with objective of identifying a better process condition.

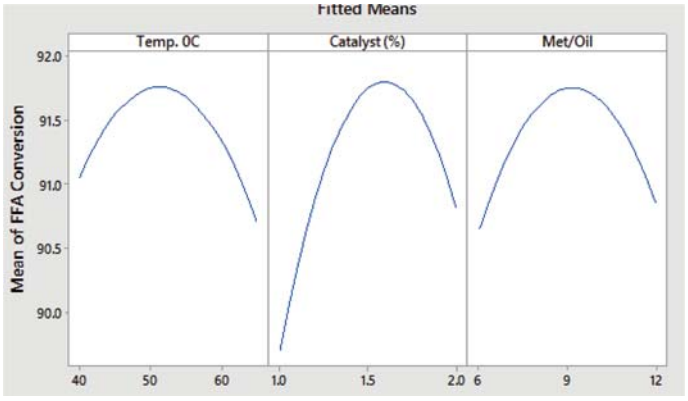

Figure 1: Main Effects Plot for Free Fatty Acid Conversion

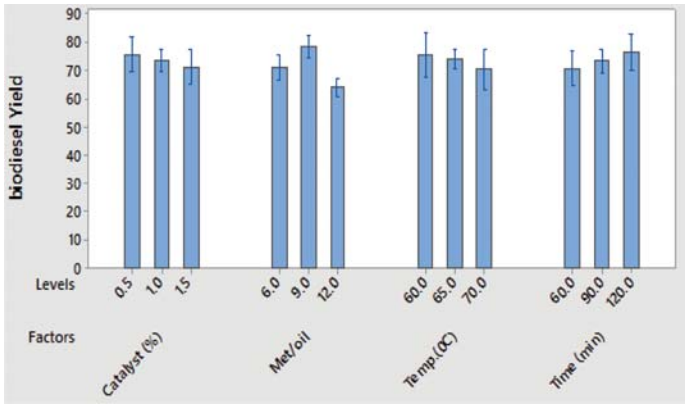

Figure 2 Summary of the effect of the reaction variables on the biodiesel

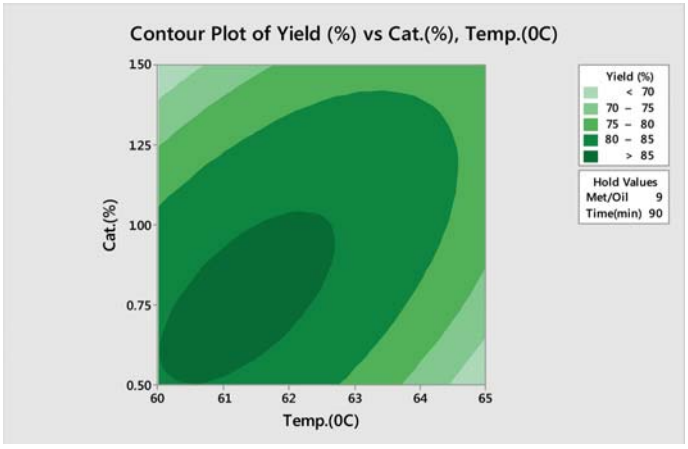

Figure 3a contour plot of cat vs temp when met/oil and time held constant

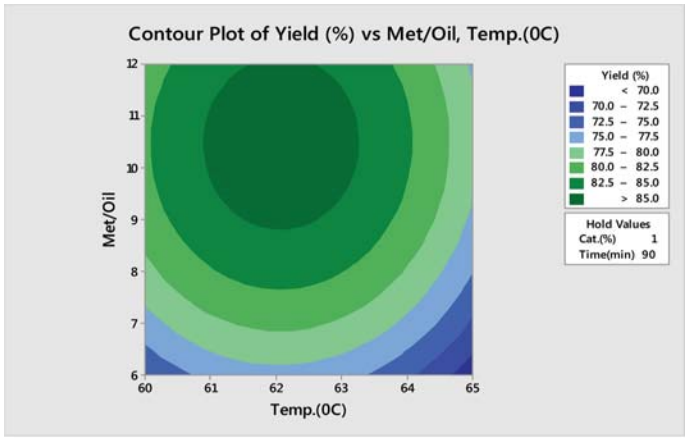

Figure 3b contour plot of met/oil vs temp. when cat and time held constant

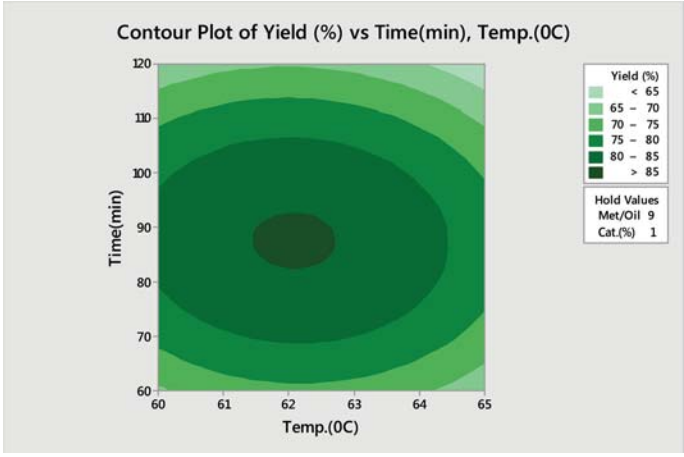

Figure 3c contour plot of time vs temperature when met/ oil and catalyst held constant

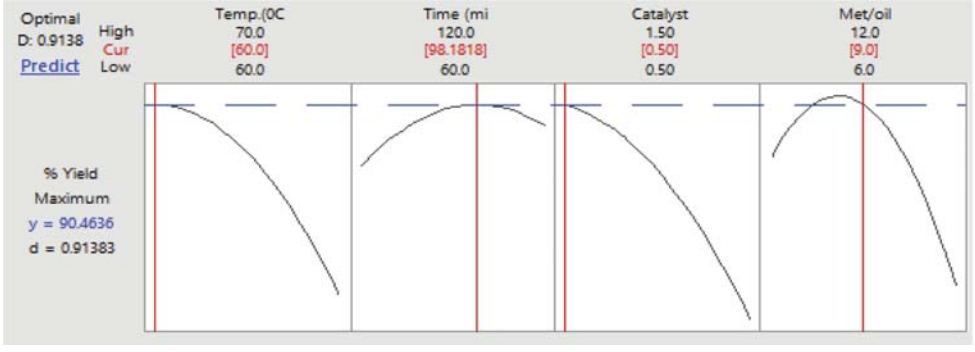

Figure 4: optimization plot

The optimal process condition was discovered to be when the temperature, time, catalyst and methanol to oil ratio are 60 ^{0}C, 98 min, 0.5 %, and 9:1 respectively and predicted 90.46 % yield of biodiesel and desirability of 0.91383.

Validation on the reliability of the conditions predicted by the response optimizer led to further experimental study. It was observed that the optimizer predicted and experimental validated results were 90.46 and 90.48 % respectively. Since the result of the validation experiment showed agreement with the predicted value, the model is reliable. The results were further compared statistically using one sample t-test. It showed that the tabulated t-value was greater than the calculated t-values. Thus, it can be concluded that the optimization model is reliable and can be applied on large scale production of biodiesel from neem seed oil.

The profile of fatty acids methyl esters in neem biodiesel shown in Table 6, indicates methyl 9Z,12(Z) - octadecadienoate (linoleic acid ester) as the dominant ester. This compound has two level of unsaturation which may accords it likelihood to undergo a peroxidation. Therefore, a biodiesel produced from this feedstock could deteriorate on long storage due its susceptibility to the attack of oxygen.

Table 6 Methyl Fatty Acids Esters (approximate wt %) of Biodiesel Produced from Neem Seeds Oils

Methyl esters	Molecular formula	wt %
Methyl hexadecanoate	$C_{17}H_{34}O_2$	8.96
Methyl-12-octadecenoate	$C_{19}H_{36}O_2$	33.62
Methyl eicosanoate	$C_{21}H_{42}O_2$	1.6
Methyl 9Z,12Z-octadecadienoate	$C_{19}H_{34}O_2$	54.20
Other non methyl ester	___	1.62

Conclusions

Two step transesterification was successfully used in converting crude neem seed oil to biodiesel. Process variables, including reaction temperature, reaction time, catalyst concentration and amount of methanol, were found to have significant effects on the biodiesel. Nevertheless, reaction time and methanol to oil ratio influence the maximization of biodiesel yield not temperature. Optimization of process variables show that yield greater than 90% can be obtained at 60 ^{o}C, 98 min, 0.5 % and 9:1 temperature, time, catalyst and methanol to oil molar ratio. However, economic analysis of the process and further investigation to find efficient method that could minimize the reaction cost are here by recommended.

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