Advances in Energy Research, *Vol. 1, No. 2 (2013) 147-163*
DOI: http://dx.doi.org/10.12989/eri.2013.1.2.147

Optimization and characterization of biodiesel produced from vegetable oil

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(Received March 5, 2013, Revised October 14, 2013, Accepted November 4, 2013)

Abstract. The world faces several issues of energy crisis and environmental deterioration due to over-dependence on single source of which is fossil fuel. Though, fuel is needed as ingredients for industrial development and growth of any country, however the fossil fuel which is a major source of energy for this purpose has always been terrifying thus the need for alternative and renewable energy sources. The search for alternative energy sources resulted into the acceptance of a biofuel as a reliable alternative energy source. This work presents the study of optimization of process of transesterification of vegetable oil to biodiesel using NaOH as catalyst. A 2^4 factorial design method was employed to investigate the influence of ratio of oil to methanol, temperature, NaOH concentration, and transesterification time on the yield of biodiesel from vegetable oil. Low and high levels of the key factors considered were 4:1 and 6:1 mole ratio, 30 and 60^{o}C temperatures, 0.5 and 1.0 wt% catalyst concentration, and 30 and 60 min reaction time. Results obtained revealed that oil to methanol molar ratio of 6:1, tranesetrification temperature of 60^{o}C, catalyst concentration of 1.0wt % and reaction time of 30 min are the best operating conditions for the optimum yield of biofuel from vegetable oil, with optimum yield of 95.8%. Results obtained on the characterizzation of the produced biodiesel indicate that the specific gravity, cloud point, flash point, sulphur content, viscosity, diesel index, centane number, acid value, free glycerine, total glycerine and total recovery are 0.8899, 4, 13, 0.0087%, 4.83, 25, 54.6. 0.228 mgKOH/g, 0.018, 0.23% and 96% respectively. Results also indicate that the qualities of the biodiesel tested for are in conformity with the set standard. A model equation was developed based on the results obtained using a statistical tool. Analysis of variance (ANOVA) of data shows that mole ratio of ground nut oil to methanol and transesterification time have the most pronounced effect on the biodiesel yield with contributions of 55.06% and 9.22% respectively. It can be inferred from the results various conducted that vegetable oil locally produced from groundnut oil can be utilized as a feedstock for biodiesel production.

Keywords: vegetable oil; biodiesel; optimization; alternative energy; characterization

1. Introduction

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http://www.techno-press.org/?journal=eri&subpage=7 ISSN: 2287-6316 (Print), 2287-6324 (Online)

Petroleum (fossil fuel) is today the most important energy source; demand is ever-increasing worldwide yet petroleum resources are finite, and non-renewable (Nakpong and Wootthikanokkhan 2009). The formation of fossil fuels takes millions of years and are very limited (Sharma and Singh 2008). Also, emissions from combustion of fossil fuels constitute severe health and environmental implications, creating a serious global environmental problem (Gerpen 2004). Hence, environmental pollution is a major problem emanating from over dependence on fossil fuel. In line with the global depletion of the non-renewable energy sources, the Energy Commission of Nigeria's long term (2016 – 2025) plan on the nation's energy requirements is completely non-fossil. Thus, locally produced oils are currently being investigated as alternative sources of diesel fuel amongst other efforts at executing the country's renewable energy master plan (Alamu *et al*. 2008).

The depletive nature of fossil fuel had increased energy demand for both domestic and industrial uses, and global warming problems are some of the factors that prompted the quest for an alternative renewable energy source that can be domestically produced and are not as harmful as petroleum to the environment (Lang *et al*. 2001, Freedman *et al*. 1986). Different renewable sources of energy have been tried to reduce over-dependence on fossil fuels. Among these alternative sources, the use of vegetable oils has gained considerable attention (Nakpong and Wootthikanokkhan 2010). Renewability, availability and non polluting nature of vegetable oils favor their choice as a feedstock for biodiesel production (Shuguang 2011). It has been reported that biodiesel has significantly lower emission when compared to petrol diesel when used for combustion either in a blended or pure form (Shuguang 2011). The production of carbon monoxide, hydrocarbon emissions and particulates proves minimal (El-Diwani *et al*. 2009). Biodiesel has advantages of bio-degradability, high combustion efficiency, renewability, low aromatic and sulphur content (Shah baz *et al*. 2010). Biodiesel which is described as a non-toxic, biodegradation and renewable energy source that can be obtained from different feedstocks such as fresh vegetable oil, waste vegetable oil, fats from animal and seed of plants. Blends of bio-diesel reduce engine wear and help in increasing the life span of fuel injection system (Emil *et al*. 2009). In addition, it has high lubricity than any other fuel (El-Diwani and El-Rafie 2008) and high cetane numbers (El-Diwani *et al*. 2009). Despite the vast benefits of bio-diesel as an alternative energy source to fossils fuels, high price has been identified as the major factor that militate against commercialization of biodiesel (Silva *et al*. 2011). Optimization of process variables that influence the yield and purity of biodiesel is a sure way of addressing the higher priced hurdle (Refaat *et al*. 2007). As elucidated earlier, renewability and less polluting nature of biodiesel as compared to petrol diesel are the major attributes of biodiesel, hence influence of the process parameters via optimization method is worthy of investigation continually (Meher *et al*. 2006). It is also worth of mentioning that much work has been done and reported in open literature on the production of biodiesel from different feedstocks, but little has been done so far on the production of biofuel from locally produced groundnut. It has been reported that the nature of feedstock utilized in the production biodiesel greatly affect the price of biodiesel and has been identified as a major factor that militate against availability of biodiesel in commercial quantity in developing country like Nigeria. Hence, the need to study the effectiveness of locally produced groundnut oil as a feedstock for the production of biodiesel. Literature also revealed that Nigeria is the 4th largest producer of groundnut oil with estimated production rate of 1.55 million metric tons per year; hence utilization of groundnut oil for biodiesel production will not affect food supply in the country. This study seeks to optimize the process of producing the biodiesel from groundnut oil that is locally produced without refinement. This will involve investigating the effects oil to methanol ratio, concentration of catalyst, temperature and time the production of biodiesel from vegetable oil with NaOH as catalyst. The focus of this research can be achieved through the following objectives;

a. To pre-treat and characterize the vegetable oil to determine its density, saponification value, iodine value, acid value, refractive index, viscosity, unsaponifiable matter, protein content and moisture content.

b. To conduct investigation on the influence of time, temperature, concentration of catalyst and alcohol-to-oil ratios on the yield of bio-diesel from vegetable oil through 2^4 factorial experimental design

c. To characterize the bio-diesel produced to determine its specific gravity, flash point, cloud point, distillation characteristic, ash content, cetane number, total glycerine, water content, and acid value and compare with the set standard.

d. To analysis the experimental data obtained for the purpose of theoretical studies on the yield rate of oil and statistical analysis.

2. Material and methods

The vegetable oil used as a feedstock in this study was sourced locally. Anhydrous ethanol (C_2H_5OH- 99.8%) and Sodium hydroxide (NaOH- 95% - analytical reagent grade), both manufactured by EMD Chemicals Inc., Darmstadt, Germany, was purchased from Nahson Chemicals, Minna, Niger state. Sulphuric acid, H_2SO_4 (98% - analytical reagent) manufactured by EM Science, Darmstadt, Germany, was gotten from WAFT laboratory, FUT Minna. The sodium hydroxide was used as catalyst (96% Analar BDH). Other chemical used in this study are carbon tetrachloride (96% Analar BDH), Wijs solution (Hopkins and Williams), potassium hydroxide pellet (Burgoyne and co, Mubai), petroleum ether (95% Analar BDH), potassium iodide solution (92% M&B England), sodium thiosulphate (95% M&B England, hydrochloric acid (Analar BDH) and potassium iodide pellet (95% M&B England). Prior to the production of biodiesel, the feedstock (vegetable oil) was analysed to determine the physico-chemical properties. Basic properties tested include Specific gravity (or density), kinematic viscosity, refractive index, acid value, iodine value, pH, moisture or water content, saponification and unsaponifiable matter. Prior to the production of biodiesel, the feedstock (vegetable oil) was analysed to determine the physico-chemical properties. Basic properties tested include Specific gravity (or density), kinematic viscosity, refractive index, acid value, iodine value, pH, moisture or water content, saponification and unsaponifiable matter.

2.1. Transesterification of vegetable oil

This is considered as a pre-treatment method as stated by Gerpen (2006) for the crude oil in order to reduce its water content which is the main cause of soap formation and subsequently, reduce its FFA. 50 ml of GNO was measured and transferred into the conical flask where the reaction is taken place. The GNO in the conical flask was then pre-heated to the desired temperature of 50^{o}C with hot plate.. The sulphuric acid-ethanol solution was prepared by adding 1.0% (wt/wt oil) H_2SO_4 to 30% v/v ethanol and heated to 60^{o}C. The ethanoic acid was then added to the crude GNO in the reaction flask and was vigorously stirred using a magnetic stirrer for a period of one hour. At the end of the reaction, the mixture in the conical flask was then transferred into the separating funnel and allowed to settle for a period of one hour, after which two layers was formed. The top layer consists of unreacted ethanol, sulphuric acid and impurities. The lower layer which is the oil phase was utilized for alkali catalyzed transesterification.

Table 1 Experimental design of 2^4 factorial

Run	Oil to Methano ratio	Esterification on Temperature (^oC)	Concentration of Catalyst (wt %)	Time (min)
1	4:1	30	0.5	30
2	4:1	60	0.5	30
3	4:1	30	0.5	60
4	4:1	60	0.5	60
5	4:1	30	1.0	30
6	4:1	60	1.0	30
7	4:1	30	1.0	60
8	4:1	60	1.0	60
9	6:1	30	0.5	30
10	6:1	60	0.5	30
11	6:1	30	0.5	60
12	6:1	60	0.5	60
13	6:1	30	1.0	30
14	6:1	60	1.0	30
15	6:1	30	1.0	60
16	6:1	60	1.0	60

2.2. Alkali catalysed trasesterification

The lower phase content of the previous experiment was transferred to a conical flask and preheated until the required temperature is attained. A known amount of NaOH was then dissolved in ethanol in a separate flask; the solution formed was then preheated to the required temperature. The solution formed was then transferred into the flask that contained esterifies GNO. The transesterification was conducted on the hot plate to maintain the reaction temperature and stirring speed of (100 rpm). At the end of the reaction time, the mixture was transferred into a separating funnel and allowed to settle gravitationally for about 8 – 20 hrs. After settlement, the bottom layer (glycerol) was drained off and the top layer (ethyl esters) was collected in a clean beaker. Same procedure was followed for the optimization process of biodiesel production from groundnut oil as shown in Table 1.

Purification processes, which include washing and drying, were used in treating the ethyl esters (biodiesel) produced because the biodiesel produced contains soap, glycerol, unreacted ethanol and glycerides. Water wash method (warm distilled water) was continually used to wash the biodiesel in a separating funnel until the washing water became clear. After washing, the bio-diesel was collected in a beaker and dried on a hot plate at about 100^oC until all the water molecules present in it were evaporated.

The biodiesel produced was then characterized for their physico-chemical properties. The qualities of the biodiesel determined were density, viscosity, cloud point, flash point, cetane number, distillation characteristics, sulphur content, diesel index, free glycerine, total glycerine, acid value and kinematic viscosity.

Table 2 Measured physiochemical properties of vegetable oil

S/No	Properties	Unit	Experimental Value	AOCS Standard Value (1941)	Ibeto *et al*. (2011)
1.	Protein	%	7.793		
2.	Specific Gravity (S.G) at 30^{o}C	-	0.912	0.910 - 0.915	0.93
3.	Density (ρ)	g/ml	0.918	-	-
4.	Moisture Content	%	11.0	-	0.09
5.	Acid Value (A.V)	mgKOH/g	2.93	0.72 - 3.0	2.61
6.	Saponification Value (S.V)	mgKOH/g	189.29	188 - 195	148.67
7.	Iodine Value (I.V)	gI_2/100g	133	84 - 100	89.46
8.	Free Fatty Acid (FFA)	%	1.46	< 1%	1.31
9.	Ref. Ind. (R.I) at 30^{o}C	-	1.467	1.467 – 1.470	1.463
10.	Viscosity (v) at 30^{o}C	mm^2/s	35.0	-	32.66
11.	Unsaponifiable Matter	%	2.06	1 % max.	-

3. Results and discussion

This study is focused on the optimization and theoretical kinetics study of biodiesel produced from vegetable oil obtained locally from Minna, Niger State, Nigeria. The vegetable oil used as a feedstock was characterized and the results obtained are summarized in Table 2.

Saponification value indicates the percentage of fatty acids in the crude vegetable oil sample. High saponification values indicate high percentage of fatty acids which might lead to soap formation and thus low biodiesel yield (Cynthia 2011). Saponification value is described as the tendency of oil to form soap during transesterification reaction (Al-Zahrani 2005). It is also described as the number in milligram of potassium hydroxide (KOH) that is required to saponify 1g of fat. In the present study, saponification value of 189.29 was obtained for the sample of crude vegetable oil. This falls within the range 188 - 195 recommended by AOCS standard but higher than 148.67 reported for the variety used by Ibeto *et al*. (2011). Also tested for and reported is the Iodine Value (IV) of vegetable oil which is described as the measured in grams, absorbed by 100 grams of given oil (Abdulkareem *et al*. 2013). The iodine value is expressed in grams of iodine for the amount of halogens linked with 100 g of the test sample, and is used as degree of unsaturated bond of fats and oils. Iodine values are used to classify oils as either drying oil (>130), semi-drying oil (115 - 130) and non-drying oil (<115) (Othmer 2011). The oil used in the present study has iodine value of 133 gI_2/100 g, higher than 89.46 gI_2/100 g reported for the groundnut oil sample used by Ibeto *et al*. (2011) and the 84 - 100 gI_2/100 g range recommended by AOCS standard. Based on this value, the present oil in use can be classified as drying oil. Unsaponifiable matter is another quality of the crude vegetable oil tested for and it describes as substances that are soluble in fatty acids and drying oils that cannot be saponified when treated with caustic but are soluble in fat solvents. The unsaponifiable value for the oil sample used oil was 2.06% which is higher than the 1% maximum recommended by AOCS standards. The high value of the unsaponifiable matter can be attributed to the production process of the vegetable oil. The acid value (AV) which described as an important factor that determines the quality of vegetable oil is also measured in this study. Al-Zahrani (2005) classified vegetable oils with high acid value as

inedible while those with low acid value are classified as edible oils. An acid value of 2.93 mgKOH/g was obtained for the oil sample used in the present study. This value falls within the 0.72 - 3.0 mgKOH/g reported in the AOCS standard and higher than the 2.61 mgKOH/g obtained by Ibeto *et al*. (2011).

Also measured in this study is the Free Fatty Acid (FFA) of the vegetable oil and the results obtained as presented in table 2 indicate that the Free Fatty Acid (FFA) of the vegetable oil is 1.46 %, which is higher than the AOCS limits having its FFA value as <1%. On the contrary, Cynthia (2011) reported that for groundnut oil to be used for biodiesel production, its free fatty acid content should be <2% so as to enable efficient conversion of the oil. Also, Ibeto *et al*. (2011) obtained a free fatty acid value of 1.31%, which is slightly less than the 1.46% obtained in the present work. This high value necessitates the need for pre-treatment of the crude vegetable oil before being used for biodiesel production. Kinematic viscosity which is a quality that measures the oil thickness and it is function of temperature. Hence the temperature at which the kinetic viscosity was measured need to be stated, otherwise the value becomes meaningless. The oil sample used shown a kinematic viscosity of 35.0 mm^2/sec at 30^0C, which is slightly lower compared to 32.66 mm^2/sec obtained by Ibeto *et al*. (2011) at 30^0C. The purpose of transesterification of vegetable oils and animal fats is to reduce the kinematic viscosity because high viscosity causes poor combustion; increases exhaust smoke and deposits in the fuel injectors of diesel engine (Roseli *et al*. 2011). Results as presented also indicate that the specific gravity of the crude vegetable oil is 0.912 falling within the range of AOCS specification and less than 0.93 reported by Ibeto *et al*. (2011). Hence, the oil can be used for biodiesel production. The moisture content in the oil sample used was found to be 11.0% and much higher compared to 0.09% reported for the oil sample used by Ibeto *et al*. (2011). The 11.0% value obtained is also higher than the value recommended by ASTM (D 6571) and the <3% moisture content suggested for all raw materials to be used in the production of bio-diesel by Cynthia (2011). This is because moisture content greater than 3% will decrease the efficiency of the transesterification reaction due to possible deactivation of catalyst active sites and soap formation. To this problem, pre-treatment was carried out to greatly reduce the moisture content to <3, the recommended value. Refractive index at 30^0C for the crude vegetable oil sample was 1.467 which was within the recommended AOCS standard index of 1.467 - 1.470 and also compared well with 1.463 reported by Ibeto *et al*. (2011)

3.1 Optimization of biodiesel production

Table 3 summarises the result obtained on the influence of process parameters such as temperature, time, catalyst weight and ratio of oil to methanol on the yield of the biodiesel from groundnut oil.

3.1.1 Influence of ratio of methanol to vegetable oil

Mole ratio of methanol to oil is considered as one of the most valuable factors that affects production of biodiesel from different feedstocks. According to the transesterification reaction one mole of triglyceride and three moles of alcohol give three moles of fatty acid alkyl esters (biodiesel), which is the main product and one mole of glycerol (Gerpen 2004). Since the reaction is an equilibrium reaction, there is the need for excess alcohol to move the reaction to the product site. In this study, the influence of ratio of methanol to vegetable oil was conducted at two different ratios of 4:1 (low level) and 6:1 (high level). The best yields ranging from 80 - 96% (Fig. 1) were obtained at molar ratio of 6:1. As elucidated earlier, the reaction of biodiesel production is an

Table 3 2^4 factorial design transesterification of vegetable oil

Run	Mole Ratio (wt/wt)	Temperature (^oC)	Catalyst Conc. (wt %)	Time (min)	Crude Yield (%)	Refined Yield (%)
1	4:1	30	0.5	30	75	72
2	4:1	60	0.5	30	82	76
3	4:1	30	0.5	60	86	82
4	4:1	60	0.5	60	84	80
5	4:1	30	1.0	30	73	70
6	4:1	60	1.0	30	76	72
7	4:1	30	1.0	60	81	78
8	4:1	60	1.0	60	88	84
9	6:1	30	0.5	30	92	88
10	6:1	60	0.5	30	89	86
11	6:1	30	0.5	60	97	94
12	6:1	60	0.5	60	94	90
13	6:1	30	1.0	30	86	80
14	6:1	60	1.0	30	99	96
15	6:1	30	1.0	60	85	82
16	6:1	60	1.0	60	91	86

equilibrium reaction; hence lower oil to methanol molar ratio may result in an incomplete, while an increase in molar ratio will shift the reaction to the biodiesel production direction (Alamu 2007). It is worthy of mentioning also that excess molar ratio will favour conversion of triglycerides to diglycerides and then monoglycerides and possibility of recombination of esters and glycerol to monoglycerides since their concentrations will be increasing during the course of the reaction (Cynthia 2011). Excessive methanol in the reaction medium with one polar hydroxyl may act as emulsifier which increases the solubility of glycerol in the ester phase, the situation that makes the separation to be difficult. There is also the possibility of the glycerol that remained in the solution to drive the equilibrium back to the left, thereby reducing the esters conversion (Cynthia 2011). It can be observed from Fig.1 that there is an increase in biodiesel yield for both 0.5 wt% and 1.0 wt% catalyst concentration as the molar ratio was increased from 4:1 to 6:1 at constant temperature and time. The experimental result obtained is in agreement with Cynthia (2011) who studied the effect of ground nut oil to ethanol using a molar ratio from 1:4 to 1:6.

3.1.2 Influence of transesterification temperature

Depending on the type of oil used, transesterification can take place at different temperatures. Ma and Hanna (1990) proposed that the temperature range should be from 25^{o}C to 120^{o}C and they also suggested that 60oC is the required temperature for transesterification reaction to take place. It is also worth of mentioning that nature of catalyst also influences the extent of conversion of oil to biodiesel at different temperature, hence the need to optimize the temperature at which the process was carried out. The two levels of temperatures used in the present study were 30^{o}C for the low level and 60^{o}C for the high level. These chosen values are both less than the boiling point of methanol (65^{o}C) so as to avoid loss of the solvent by vaporization during heating operation. The

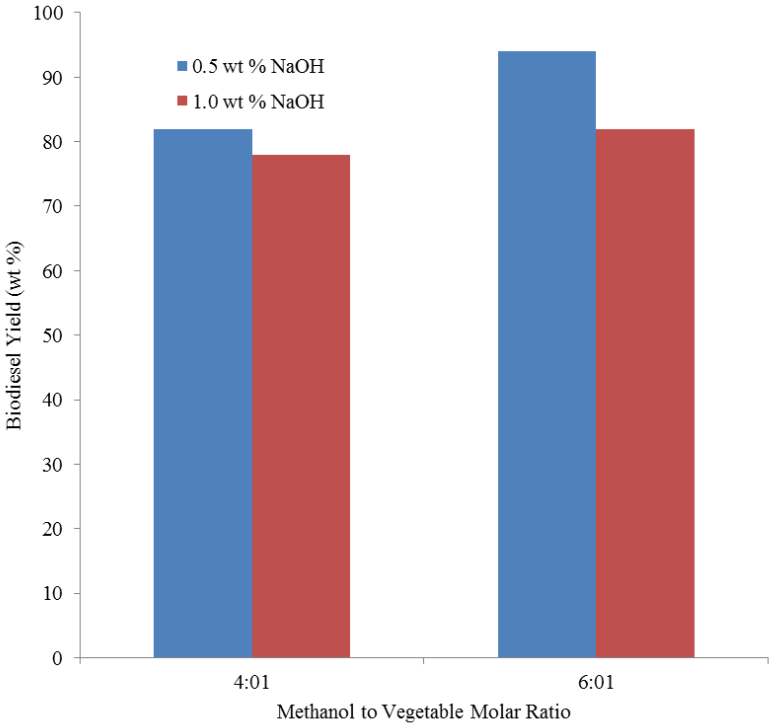

Fig. 1 Influence of Molar Ratio of Methanol to Oil on the yield of Biodiesel (at 30^{o}C and 60 minutes) reaction

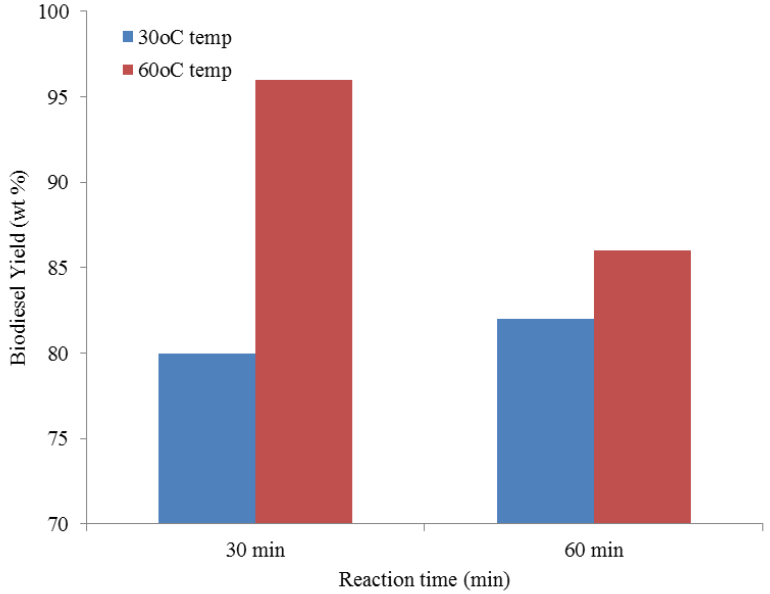

Fig. 2 Influence of Temperature on the yield of Biodiesel (at 6:1 Molar ratio and 1.0 wt % NaOH)

best yields were obtained at the high temperature (60°C) and this is in agreement with the work of Ahmad *et al*., (2009) whose optimal temperature for base transesterification of groundnut oil was also 60°C, using methanol. It can be observed from Table 3 that at operating temperature of 60°C, the biodiesel yields produced were greater than those produced at 30°C (Fig. 2). This is because at 60°C, the molecules of the triglyceride have higher kinetic energy and thus increases collision rate and therefore, improves the overall process by favouring the formation of methyl esters while at the lower temperature, there was lesser collision of reacting molecules and hence, reduced biodiesel yield.

3.1.3 Influence of Catalyst Concentration (NaOH)

Another variable that affects transesterification process is the amount of catalyst used. Though, catalyst determines the rate of reaction, it could also favour the process of hydrolysis and saponification which are known to affects the process of separating the glycerol rich phase and and purification of methyl esters (Issariyakul *et al*. 2006). The two levels of catalyst concentration (NaOH) used in the present study are 0.5 wt% for the low level and 1.0 wt% for the high level as shown in Fig. 3. It can be observed from the results presented in Table 3 that the best yield (96 %) was obtained at 1.0 wt % NaOH. Though, 0.5wt % NaOH also gave 94% yield, and the lowest yield was achieved at 1.0 wt% (70%), the low yield obtained at catalyst concentration of 1.0wt% was influenced by low amount of methanol (4:1), low temperature (30°C) and low reaction time (30 min). Results presented in Fig. 3 indicate that though, catalyst concentration affects the yield of biodiesel, operating conditions combination also play an important role. For instance a yield of 70% at 0.5 wt% is favoured by high molar ratio (6:1) and longer reaction time (60 min).

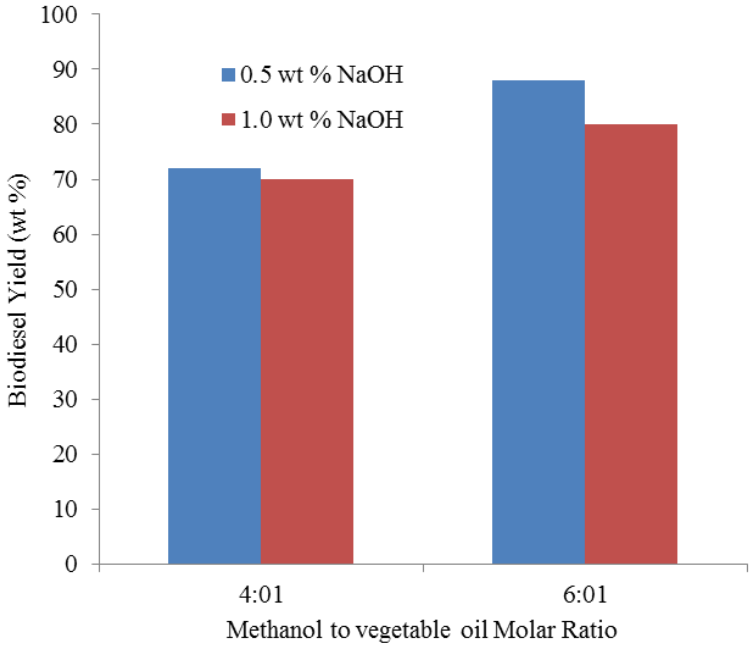

Fig. 3 Influence of Catalyst Concentration on the yield of Biodiesel (at 30°C reaction temperature and 30 minutes reaction time)

Fig. 4.2 indicates that the biodiesel yield was higher at 60^{o}C than at 30^{o}C for 1.0 wt% catalyst concentration and molar ratios of 4:1 and 6:1. This pattern of results can be attributed to the fact that the process of conversion of oil to biodiesel is endothermic in nature as reported by Abdulkareem *et al*. (2013) in their work. This implies that higher temperature will favoured the endothermic reaction and thus increase the reaction rate.

Based on the result presented, it can be deduced that the biodiesel yield is higher at catalyst concentration of 0.5 wt % than at 1.0 wt % (Fig. 3). This observation is in contrary to reported work by Cynthia (2011) who studied catalyst concentrations of 0.5 wt % and 1.0 wt % of KOH in transesterifying ground nut oil and the optimum value she found was 1.0 wt % KOH. But it was also observed that at conditions other than the optimal conditions of 1:6 molar ratio, 60^{o}C and 90 minutes reaction time, 1.0 wt % catalyst weight gave improved yields in some runs than the 0.5 wt % for same conditions.

3.1.4 Influence of transesterification time

The time required for conversion of oil to biodiesel is also identified as an important factor that influences transesterification reaction. Freedman *et al*. (1984) reported in their work that rate of conversion of oil to biodiesel increases with increase in temperature. The group utilized peanut, cotton seed, sunflower and soybean oil as feedstocks for production of biodiesel under the transesterification condition of methanol to oil ratio of 6:1, 0.5 wt% catalysts and temperature of 60^{o}C. Two levels of reaction time were used in the present work, 30 minutes for low level and 60 minutes for the high level. Contrary to the work of Ahmad *et al*. (2009) and Cynthia (2011), an optimum yield of 96% was achieved at 30 minutes. This was favored by high reaction temperature

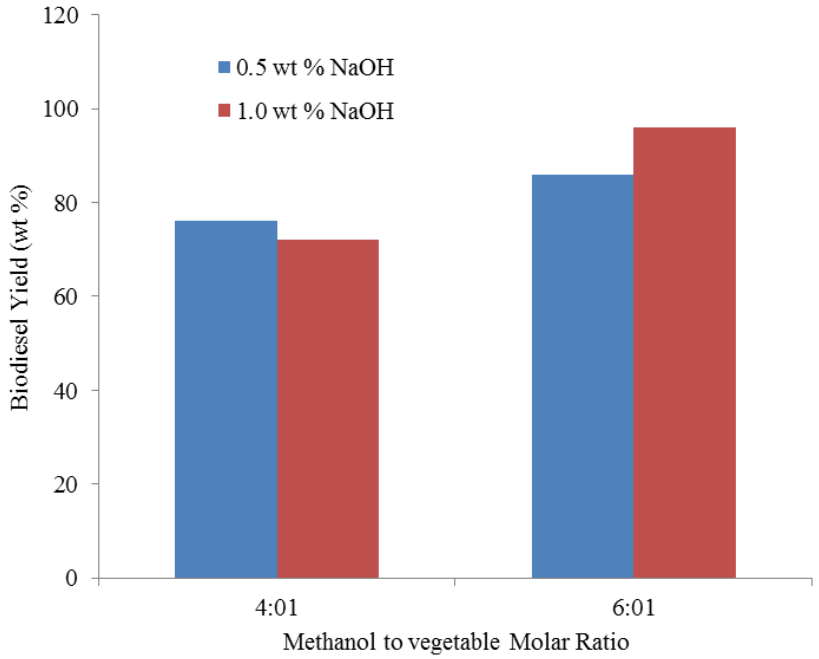

Fig. 4 Influence of Time on the yield of Biodiesel (at 60^{o}C reaction temperature and 30 minutes reaction time)

(60^oC) and high catalyst concentration (1.0 wt%). The maximum biodiesel yield was 96wt% at 30 minutes which was higher than 90wt% obtained at same reaction conditions but at 60 minutes reaction time as shown in Fig. 4. Generally, there is an increase in biodiesel yield as reaction time increases. Hence, from the experimental matrix shown in Table 3, it can be inferred that the optimum conditions for the production of biodiesel from the vegetable oil are methanol to oil molar ratio of 6:1, reaction temperature of 60^oC, catalyst concentration of 1.0 wt% NaOH and transesterification time of 30 minutes.

3.2 Statistical Analysis

Results obtained on the influence of operating parameters on the yield of biodiesel from vegetable oil were statistically analyzed using analysis of variance (ANOVA). The effects of the four key factors on biodiesel production and their interaction effect were estimated and the results obtained are presented in Tables 4 and 5. Results as presented indicate that the four reaction parameters: molar ratio, temperature, concentration of catalyst and transesterification time had different degrees of effects on the biodiesel yield with percentage contributions of 55.06%, 4.10 %, 2.84 % and 9.22% respectively (Table 4).

Table 4 Factor effects and contribution

Term	Effect	Sum of Square	% Contribution
A-Molar Ratio	11	484	55.0626
B-Temperature	3	36	4.09556
C-Catalyst	-2.5	25	2.84414
D-Time	4.5	81	9.21502
AB	0.5	1	0.113766
AC	-1	4	0.455063
AD	-4	64	7.281
BC	4	64	7.281
BD	-2	16	1.82025
CD	-1.5	9	1.02389
ABC	2.5	25	2.84414
ABD	-1.5	9	1.02389
ACD	-3	36	4.09556
BCD	0	0	0
ABCD	-2.5	25	2.84414

Where:
A is the Molar Ratio
B is the traestericatión temperature
C is the concentration of catalyst
D is the tranesetrification time

Table 5 Summary of ANOVA on the 2^4 transesterification experiment

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	878.00	14	62.71	62.71	0.0987
A-Molar Ratio	484.00	1	484.00	484.00	0.0289
B-Temperature	36.00	1	36.00	36.00	0.1051
C-Catalyst	25.00	1	25.00	25.00	0.1257
D-Time	81.00	1	81.00	81.00	0.0704
AC	4.00	1	4.00	4.00	0.2952
AD	64.00	1	64.00	64.00	0.0792
BC	64.00	1	64.00	64.00	0.0792
BD	16.00	1	16.00	16.00	0.1560
CD	9.00	1	9.00	9.00	0.2048
ABC	25.00	1	25.00	25.00	0.1257
ABD	9.00	1	9.00	9.00	0.2048
ACD	36.00	1	36.00	36.00	0.1051
BCD	0.000	1	0.000	0.000	1.0000
ABCD	25.00	1	25.00	25.00	0.1257
Residual	1.00	1	1.00		
Cor Total	879.00	15			

It can be inferred from Table 4 that molar ratio has the highest effect on bio-diesel yield with percentage contribution of 55.06% while catalyst concentration has the lowest effect (-2.5) percentage contribution of 2.84%. Also, it can be observed from the results presented that there are significant interactive effects between the factors investigated. For instance, interactions between two factors such as molar ratio - time (A*D) had the lowest effect of -4 with the highest percentage contribution (7.28%) while molar ratio - temperature (A*B) had an effect of 0.5 with the lowest percentage contribution of 0.113766%. For interactions between three factors for instance, molar ratio – transesterification temperature – concentration of catalyst (A*B*C) had the highest effect (2.5) with percentage contribution of 2.84%, while molar ratio-catalyst concentration-reaction time (A*C*D) had the lowest effect of -3 with the highest percentage contribution of 4.09556%. In concise, all four factors were seen to have positive effects with the exception of catalyst concentration which had a negative effect while all interactions also had positive effects with the exception of (A*C), (A*D), (B*D), (C*D), (A*B*D) and (A*C*D) which had negative effects. However, according to Cynthia (2011), the negativity of temperature-time (B*D) and (A*B*D) interaction effects is probably due to side reactions such as soaps formation.

Results as presented in Table 5 indicate that the model F-value is 62.71,which implies that the model is significant. Analysis of results also show that there is 0.1% chances that f-values of the model could be influence by noise. Results presented also indicate that the model terms are significatnt with 95% confidence level, whivh implies that the values of Prob > F is less than 0.0500. Which is an indication that the factors A, B, C, D and interaction factors AD BC and BD are significant model terms. On the other hand, values greater than 5 % is an indication that the model terms are not significant. S.D. = 1.00; Mean = 82.25; C.V.% = 1.22; R^2 = 0.9989; R^2_{ADJ} =

0.9829; R^2_{PRED} = 0.7088; PRESS = 256.00; Adequate Precision, which measured the ration of signal to noise is equal to 26.853, and adequate precission greater than 4 is desirable. Hence, ratio of 26.853 indicates an adequate signal. C.V. is the coefficient of variation for this model. It is the error expressed as a percentage of the mean. It is computed as

$$\frac{\text{Standard Deviation}}{Mean} \times 100 \quad (1)$$

The R^2_{PRED} of 0.7088 obtained is not close to the R^2_{ADJ} of 0.9829 as expected, this pattern of result could be attributed to effect of large block and possibility of problems with data and model. To annul these effects, it is essential to consider the possibility of reduction in the model reduction and transformation response. From ANOVA, it can be concluded that A, B, C and D are significant factors. Hence, the mathematical model equation for predicting average biodeisel yield is

Y = 82.25 + 5.50*A + 1.50*B - 1.25*C + 2.25*D - 0.50*A*C - 2.00*A*D + 2.00*B*C -1.00 * B * D- 0.75 *C*D + 1.25*A*B*C - 0.75*A*B*D - 1.50 *A*C*D + 0.000B*C*D

-1.25*A*B*C*D

It is a Rule of Thumb that values of $R^2_{ADJ} > 0.8$ indicates that the developed model is a good fit model; otherwise, there will be a need to fit the data into a second order model (Rao 2009). The R^2_{ADJ} of the first order regression model above is 0.9829 which is greater than 0.8 and this means the first order model obtained above is adequate enough to completely describe the system.The R^2_{ADJ} of 0.9829 reveals that the developed model will predict 98.29% of the variance and 1.71% of the total variance could not be explained through the developed model. Using the developed first degree mathematical model, bio-diesel yields were predicted at same reaction conditions as the experimental matrix. A comparison between the predicted and the experimental (actual) show that both are relatively proximal and this therefore proves the fitness of the model in describing the entire system.

3.3 Characterization of the biodiesel produced

The produced bio-diesel from groundnut oil at optimum conditions was characterized to determine its qualities and compared with the standard. Results obtained on various properties tested for, are summarised in Table 6.

Kinematic viscosity is described as one an important quality of fuel with respect to fuel atomization and also with the fuel distribution. It has been reported that fuel with high viscosity resulted into a higher drag in the injection pump which resulted into higher injection volume and pressure especially when the engine is operating at low temperature (Cynthia 2011). Viscosity is also an indication of fuel aging during storage as it increases due to polymerization induced by oxidative degradation (Canakci *et al*. 1999). If biodiesel is to be utilized as alternative to petrol diesel, the values of kinematic viscosity must be in the range of 1.9 and 6.0 mm^2/s at 40^oC as recommended by ASTM D 6751. The kinematic viscosity of the biodiesel produced is 4.83 mm^2/s as shown in Table 6 and this value is within the stated ASTM D 6751 standard and compares well with the one obtained by Ibeto *et al*. (2011). The reduction in the viscosity of the parent oil from 65.1 to 4.83 mm^2/s is an indication of increment in flow capability of groundnut oil after transesterification process, which is also an indication of the produced biofuels ability to flow with complete burning without ignition delay. Also tested for and presented in Table 6 is the sulphur

content of biodiesel produced. Sulphur in the atmosphere has been associated with negative impacts on human health and on the environment. Mutagenic potentials have been ascribed to sulphur dioxide and particulate matters emitted by automobiles operating on high sulphur containing fuels. As a result of these reasons, there is currently a strict tightening of international limits. Biodiesel fuels have traditionally been acknowledged as sulphur free and this has been taken as one of its greatest advantage over fossil diesel. The result obtained in this work has shown that the produced biodiesel is "sulphur-free" having a very low value of 0.0087 wt%. This is low when compared to ASTM 6751 maximum limit of 0.050 wt% and ASTM D 975 maximum limit of 0.5 wt%.

Also tested for is the boiling point of the biodiesel produced, which is describes as the temperature at which heated liquid changes to a gas (Abdulkareem *et al*. 2013). Pure substances boil at a particular temperature, for a diesel fuel which is a mixture of hydrocarbon components, each of the components of diesel fuel will boil at a different range of temperature. Tested for in this study are the initial boiling point (IBP) and temperature of boiling which correspond to increment in the volume of the distilled (5%, 10%, 30%, 50%, 70% and 90%). The corresponding

Table 6 Measured properties of biodiesel produced

TEST	Value	ASTM biodiesel standard (ASTM D 6751)	ASTM fossil diesel standard (ASTM D 975)	Ibeto *et al*. (2011)	Galadima *et al*. (2008)
1. Specific Gravity	0.8898		0.95 max	0.88	0.84
2. Cloud point ^{o}F	4	-3 to 12	-15 to 5	-	-
3. Flash Points (^{o}F)	139	100 – 170	60 - 80	395.6	-
4. Sulphur (% wt)	0.0087	0.050 max	0.50 max	-	-
5. Viscosity @ 40^{o}C	4.83	1.9 - 6.0	1.9 - 4.1	5.16	-
6. Diesel Index	25	-	-	-	-
7. Cetane Number	54.6	48 - 60	40 - 55	-	-
8. Acid value mgKOH/g	0.228	0.5 max	-	4.96	0.45
9. Free Glycerine	0.018	0.02 max	0.02	-	-
10. Total Glycerine (%mass)	0.23	0.24 max	0.24	-	-
Distillation (^{o}C)					
IBP	256	-	-	-	-
5 %	322	-	-	-	-
10 %	328	360 max	70 max	-	-
30 %	332	-	-	-	-
50 %	334	360 max	125 max	-	-
70 %	336	-	-	-	-
90 %	340	-	-	-	-
95 %	-	-	-	-	-
EBP	342	-	-	-	-
T/R	96	-	-	-	-

values are 322^{o}C, 328^{o}C, 332^{o}C, 334^{o}C, 336^{o}C and 340^{o}C respectively. These values are within the acceptable ASTM D 6751 maximum of 360^{o}C and are also in agreement with the results of Cynthia (2011). Another property of the biodiesel tested for is the acid value, which is the free fatty acids and mineral acid contents of biodiesel. This value is dependent on a number of factors which include the nature of the feedstock utilized for the production of fuel, production process and degree of purification (Ahmad *et al*. 2009). Result obtained as presented indicate that the acid value of the biodiesel produced was 0.228 mgKOH/g which fall within the acceptable ASTM D 6751 standard limit of 0.5 mgKOH/g but less than values of 0.45 and 4.96 mgKOH/g reported by Galadima *et al*. (2008) and Ibeto *et al*. (2011) respectively. Presented in Table 6 also is the cetane number of the produced biodiesel. The most pronounced change brought about by transesterification of vegetable oil other than substantial reduction in viscosity is an increase in the cetane number of the vegetable oil (Gerhard *et al*. 2002). Gerpen (2004) in his work described cetane number as important parameters for controlling combustion thereby improve the performance and cold start that give rise to less exhaust. The cetane number of the bio-diesel which was estimated as cetane index in this work was found to be 54.6, a little above the ASTM D 6751 acceptable minimum of 48. The cetane number obtained for the bio-diesel produced is 54.6, which is within the range set by the ASTM biodiesel standard. Also presented in Table 6 is the flash point of the biodiesel produced which is used in determining the flammability of a fuel. Results obtained as presented indicate that the flash point of the produced biodiesel was 139^{o}F which is within the range of 100–170^{o}F specified by ASTM D 6751 but considerably small when compared to the 395.6^{o}F reported by Ibeto *et al*. (2011). Cloud and pour point of the produced biodiesel was also tested for and the results obtained are presented in Table 6. It has been reported that both the cloud and pour points are important properties of fuel when the fuel is to be utilized at low temperature. Operating at low temperature will resulted in formation of solid wax crystal nuclei that is invisible to human eye, further decrement in temperature will cause the crystals to grow and become visible human eye and the temperature at which this phenomenon takes place is referred to as the cloud point (Cynthia 2011). At temperatures below the cloud point, larger crystals fuse together to form large agglomerates that can restrict flow through fuel lines and filters and cause start-up and performance problems (Roseli *et al*. 2011). The temperature at which crystal agglomeration is extensive enough to prevent free pouring of fluid is called its pour point (Roseli *et al*, 2011). In this work, the cloud point of the biodiesel was determined as 4^{0}F and is in accordance with the ASTMD 6751 and ASTM 975 standards. The total and free glycerin determined for the biodiesel produced are 0.23wt% and 0.18wt% respectively and both values are seen to be within the acceptable standard of ASTM D 6751 as shown in Table 6. Based on the general analysis of the characterization result of the produced biodiesel, it can be inferred that the biodiesel produced from crude vegetable oil can be safely run in a diesel engine since it has successfully passed all major requirements set by ASTM D 6751 that will deem it fit to be used as fuel in a diesel engine.

4. Conclusions

In this study, biodiesel was successfully produced from vegetable oil by transesterification process. The physico-chemical properties of the bio-diesel (ethyl ester) produced showed that the bio-diesel met the requirements of ASTM D 6751 and hence can be effectively used in a diesel engine. With an optimum biodiesel yield of 96%, it can be inferred that vegetable oil is a good

feedstock for biodiesel production based on the fact that the obtained fuel properties of the biodiesel such as kinematic viscosity (4.83 mm^2/s), flash point 139^oF (95^oC), cetane number (54.6), total sulphur content (0.0087 wt%) were within the standard ascribed by ASTM D 6751.From the analysis of variance conducted at low and high levels of the key factors (4:1 and 6:1 mole ratio, 30 and 60^oC temperature, 0.5 and 1.0 wt% catalyst concentration, and 30 and 60 min reaction time), it can be concluded that mole ratio of methanol to ground nut oil and time has the highest effect on the biodiesel yield with contributions of 55.06% and 9.22% respectively. Hence, the statistical model developed can be used to predict the yield of biodiesel from groundnut oil at different operating conditions.

Acknowledgements

The research described in this paper was financially supported by the STEP B programme of Federal University of Technology, Minna, Niger State Nigeria.

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