J. Basic. Appl. Chem., **3(1)1-4, 2013**

ISSN 2090-424X
Journal of Basic and Applied Chemistry
www.textroad.com

Effect of Free Fatty Acid Content on the Yield of Biodiesel Derived from Neem Oil

Anya Uzo Anya, Chidimma Ugwumma, Oriah. V.N, Amaefuna Ifeanyi, Nwobia Chioma

National Research Institute for Chemical Technology (NARICT) Zaria,
Kaduna state, Nigeria

ABSTRACT

High free fatty acid content in vegetable oils affects the yield of biodiesel production. Various combinations of sulphuric acid and methanol to-oil ratio was use in the esterification reaction to produce different FFA values of 1.05mgKOH/g, 0.48mgKOH/g, 1.21mgKOH/g, 0.88mgKOH/g, and 1.53mgKOH/g from neem oil. While Keeping the following conditions constant, reaction and separation time at 1hr, temperature at 60^0c and agitation rate at 150rpm during the esterification process. Trans-esterification reaction was carried out on each pre-treated oil with various FFA value by using 20% methanol, $1\%^{W/}{}_{V}$ sodium hydroxide to oil volume, agitation rate 150rpm, reaction time of 45mins and separation time of 48hrs to evaluate the yield of neem oil methyl ester **(NOME)** at different FFA values.
KEYWORDS: Methyl ester yield; Trans-esterification; Esterification; High Free Fatty Acid.

INTRODUCTION

The advantage biodiesel has over petroleum–based diesel fuel cannot be over emphasized, its potentials of having renewable sources, biodegradability, sustainability and environmentally friendly was discussed by[1] , as a result biodiesel is receiving increasing attention as an alternative to fossil fuel. Vegetable oils are used as a feedstock for making biodiesel, it fatty acid methyl ester(FAME) is used as an alternative replacement for diesel fuel, the vegetable oil used could be waste cooking oil, edible oil, non-edible oil, animal fat etc. Vegetable oils are mainly triglycerides that are made of glycerine backbone, with each attached with different type of fatty acid, the percentage composition of the fatty acid type in vegetable oil varies from on one oil to another, some have high unsaturated fatty acid attached to the triglyceride, while some have low unsaturated fatty acid. It is more economically to produce biodiesel with low-cost feedstock such as non-edible oil as this will reduce competition with food, though most non-edible oils are associated with high FFA, examples include Jatropha (Jatropha curcas), Neem (Azadirachta indica), Karanja (Pongamia pinnata) etc. An increased FFA is undesirable as this will cause the loss of feedstock during it pre-treatment and hinder soap and glycerine separation. However some researchers have worked with feedstock with high FFA [2][3][4][5],in all, the idea was to either eliminate or reduce the FFA value, because of the effect it has during trans-esterification process. It is reported by [6]&[7] that oil should not contain more than 1% FFA for based-catalyzed trans-esterification, as this will generate moisture during the reaction that will hydrolyzed to form soap, hindering the separation of the glycerine from the methyl ester that affects the yield of the ester. The objective of this work is to examine the effect of FFA and reaction time during trans-esterification on the yield of neem oil methyl ester **(NOME)**. A study carried out by [8] to investigate the relationship between FFA level and triglyceride conversion. In the study, the free fatty acid content of Soybean oil was increased to between 5% & 33%, the conversion rate of soybean oil to it methyl ester dropped from 90.54% to 58.77%. [9] studied the production of biodiesel from high FFA rubber seed oil using two-step process, they observed that using molar ratio of 6:1 methanol to-oil with 0.5%v/v sulphuric acid during the esterification process, the maximum conversion efficiency was achieved.

Table 1: Composition of neem oil methyl ester (NOME)

FATTY ACID ESTER	SYSTEMATIC NAME	FORMULA	COMPOSITION
Palmitic acid methyl ester	Hexadecanioca cid methyl ester	$C_{17}H_{34}O_2$	16.72%
Oleic acid methyl ester	Methyl-3-octadecenoate	$C_{19}H_{36}O_2$	25.8%
Stearic acid methyl ester	16-methyl-heptadecanaote	$C_{19}H_{38}O_2$	12.9%
Ricinoleic acid methyl ester	Methyl ricinoleate	$C_{19}H_{36}O_3$	1.62%
Arachidic acid methyl ester	Methyl eicosanoate	$C_{21}H_{42}O_3$	7.24%
Behenic acid methyl ester	Methyl docosanoate	$C_{23}H_{46}O_2$	2.75%
Lignoceric acid methyl ester	Methyl tetracosanoate	$C_{25}H_{50}O_2$	2.47%

***Corresponding Author:** Anya Uzo Anya, National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna state, Nigeria. Email of corresponding author: anya_214@yahoo.com

MATERIAL AND METHODS

The crude neem oil was obtained from national research institute for chemical technology (NARICT) Zaria Nigeria. The following analytical grade reagents were use; sodium hydroxide, sulphuric acid and methanol. A round bottom flask was used as a laboratory scale reactor, hot plate with magnetic stirrer arrangement was used as a heating and stirring device, separating funnel and measuring cylinder.

EXPERIMENTAL PROCEDURES

One of the factor that affect the production of biodiesel is high free fatty acid content (FFA).This study looks at the influence of FFA and reaction time on the yield of methyl ester derived from neem oil, keeping the following conditions constant during oil pre-treatment (esterification), reaction and separation time of 1hr, temperature at 60^0c and agitation rate of 150rpm. Variation of methanol and sulphuric acid ratio to oil volume produces different FFA values.

ESTERIFICATION

A measured volume of neem oil was charged into a reactor flask and heated to 60^oc while stirring, 1.25%v/v H_2SO_4 to oil volume was poured into the heated oil and allow to stir for 5min before 0.63:1 methanol to oil ratio was added. The reaction was allowed for 1hr after which the mixture is transferred into a separating funnel and kept for another 1hr, a phase separation occur forming methanol-water layer at the top and the organic layer at bottom (esterified oil), the upper-layer consisting of the methanol-water was discarded.

This was repeated with the following combinations of sulphuric acid and methanol to- oil ratio; (0.75%v/v H_2SO_4 and 0.45:1), (0.5%v/v H_2SO_4 and 0.63:1), (1.0%v/v H_2SO_4 and 0.55:1), (0.5%v/v H_2SO_4 and 0.58:1), (0.75%v/v H_2SO_4 and 0.70:1), FFA value was determine on each combination which gives; 0.48mgKOH/g, 1.05mgKOH/g, 0.88mgKOH/g, 1.21mgKOH/g and 1.53mgKOH/g.

TRANS-ESTERIFICATION

Alkaline trans-esterification was carried out on each of the pre-treated oil to produce there various methyl ester , keeping temperature at 60^oc, agitation rate at 150rpm, reaction time at 45mins, separation time of 48hrs, using 1%w/v sodium hydroxide and 20% methanol to oil volume for the trans-esterification. Also keeping other conditions constant while varying the reaction time, the pre-treated oil with FFA of 0.48mgKOH/g was use for the trans-esterification process, the reaction time is stopped at the stipulated time, this was repeated with same pre-treated oil while varying the reaction time by 10, 15, 25, 35 and 45mins, after which each sample mixture is transferred to a separation funnel and allowed to stand for 48hrs, this was subsequently measured with the aid of a measuring cylinder to evaluate the effect of FFA values and reaction time on the yield of the product.

Analytical methods

Acid value (AV);

The acid value of the pre-treated oil was determined by acid/base titration method of AOCS(2001), using a standard solution of 0.1N of potassium hydroxide.

FFA= AV/2

INFLUENCE OF FFA ON METHYL ESTER YIELD

Studies was carried out on the influence of free fatty acid (FFA) on the yield of neem oil methyl ester**(NOME),** the pre-treated neem oil with the following free fatty acid content of 1.05mgKOH/g,0.48mg KOH/g,1.21mgKOH/g, 0.86mg KOH/g and 1.53mgKOH/g was use for trans-esterification which shows significant changes on the yield. A graph of the yield of neem oil methyl ester (NOME) was plotted against FFA value to ascertain the effect.

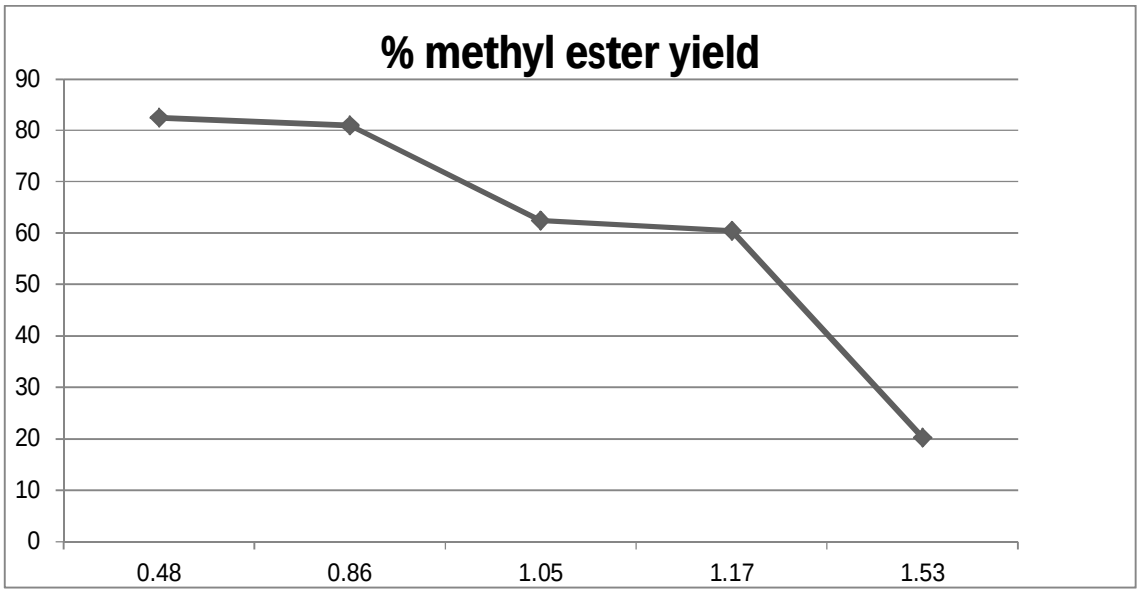

Figure 1; Graph of percentage yield of methyl ester against FFA values

INFLUENCE OF REACTION TIME ON THE YIELD

The pre-treated neem oil with FFA value of 0.48mgKOH/g was use for the trans-esterification process. Studies was carried out on the effect of reaction time on the yield of neem oil methyl ester**(NOME),** with reaction time set at 10, 15, 25, 35 and 45mins, results show a change in yield with respect to time. A graph of the product yield against time was plotted to evaluate results.

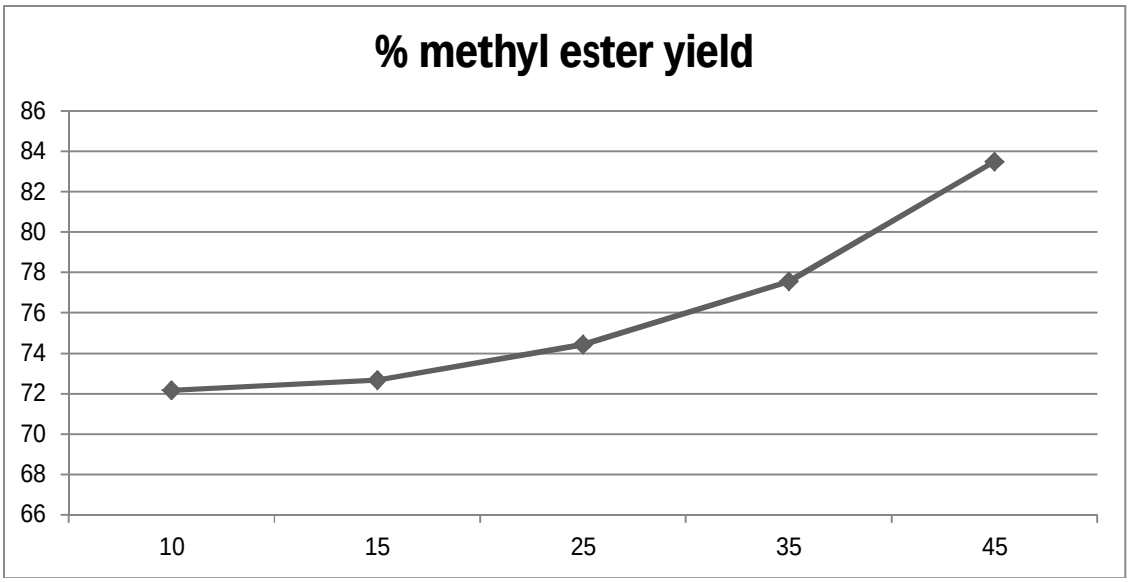

Figure 2; Graph of percentage yield of methyl ester against time

RESULT S AND DISCUSSION

Effect of free fatty acid (FFA) and reaction time

High free fatty acid content in vegetable oil and reaction time are some of the factors that affects the yield of biodiesel. Most non-edible oil have high FFA, as a result they are very difficult to produce biodiesel through direct alkaline-catalyzed trans-esterification. An FFA >1%$^{w/}_{w}$ will have significant effects on the trans-esterification of glycerides, this is because at FFA >1%$^{w/w}$, soap formation will occur which will inhibit the Separation of the products, thus resulting to low yield of methyl ester.**Figure1** shows the effect of FFA values

on the yield of neem oil methyl ester **(NOME)**, the result shows increasing yield with low FFA value. **Figure 2,** shows the effects of reaction time on the yield of the product, the result depicts that the yield is relatively stable at first 15mins and starts showing sharp increase after 25mins. This signifies that for separation of glyceride from methyl ester to occur fully, the reaction time most be optimized to further maximized methyl ester yield.

CONCLUSION

Neem oil methyl ester **(NOME),** its shows relative steady yield between 10 to 15min and increases it yield of conversion as reaction time increase to 45min. The effect of free fatty acid content and reaction time on the yield of biodiesel derived from neem oil was investigated in this study, with the objective of improving on the efficiency of production process. A two stage process; acid-catalyzed esterification (pre-treatment) followed by alkaline-trans-esterification was used to produce biodiesel from neem oil. Variation of methanol and sulphuric acid concentration during its pre-treatment gives FFA values of 0.48mgKOH/g, 0.86mgKOH/g, 1.05mgKOH/g, 1.17mgKOH/g and 1.53mgKOH/g .This study looks at effect of FFA values and reaction time during trans-esterification process on the yield of neem oil methyl ester **(NOME).** It's observed in figure (1) that the conversion efficiency is affected by the FFA value, with FFA of 1.53% and 0.48%, the alkaline catalyzed trans-esterification reaction yielded 20.2% and 82.2% neem oil methyl ester **(NOME).** Figure (2) depicts the effect of reaction time on the yield of neem oil methyl ester, thus this study also shows that optimization of reaction time and reduction of free fatty acid (FFA), will maximized the yield of neem oil methyl ester **(NOME).**

REFERENCES

(1) D. Puppan (2002). Environmental evaluation of biofuels , periodica polytechnica Series Social and management sciences **10 (**95-116)

(2) Freedman, B and E.H.Pryde (1984). Variables affecting the yields of fatty ester from transesterified vegetable oils JAOCS **61(10),(**1638-1643)

(3) Mittelbach.M and P.Tritthart (1988).Diesel fuel derived from vegetable oils;III.Emission tests using methyl esters of used frying oil JAOCS **65(7)**,(1185-1187)

(4) Mittelbach.M and B.Pokits (1992).Production and fuel properties of fatty acid methyl esters from used frying oil.In liquid fuels from renewable resources; proc of alternative Energy conference, st Joseph, Mich;ASAE (74-78)

(5) Wimmer. T (1995). Process for the production of fatty acid esters of lower alcohols. US Patent No 5399731

(6) Freedman, B and E.H.Pryde (1982).F atty ester from vegetable oils for use as a diesel fuel. In vegetable oils fuels; proc. Of the intl. conf. on plant and vegetable oils fuels st. Joseph, Mich; ASAE(117-122)

(7) Liu.K(1994).Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials JAOCS **71(11)**; 1179-1187

(8) Canakci. M and J.Van Gerpen (1999). Biodiesel production via acid catalysis. Trans. ASAE **42(5)**; 1203-1210

(9) Ramadhas. A.S, Jayaraj.S and Muraleedharan.C (2005). Biodiesel production from High FFA rubber seed oil Fuel. Elsevier science Ltd **84(4);** (335-340)