1st INTERNATIONAL ENGINEERING CONFERENCE (IEC 2015)

SCHOOL OF ENGINEERING AND ENGINEERING TECHNOLOGY

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGERIA

Theme:

Security and Environmental Challenges: The Engineering Perspectives

1st - 3rd September, 2015

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Influence of catalyst concentration and temperature on Reactive Extraction of *Moringa oleifera* oil seed for biodiesel Production

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ABSTRACT

This paper presents the study of reactive extraction (in situ tranesterification) of moringa oleifera oil seed. In this study the effect of catalyst concentration (0.1–1.8 wt %) and reaction temperature (30–60 °C) on the synthesis of moringa methyl ester yield (MOME) via reactive extraction at a constant particle size, molar ratio of methanol to oil, reaction time and agitation speed of < 5 mm, 1:350, 60 minutes and 350 rpm, 60 respectively. Experimental results show that lower catalyst concentration promotes the methyl ester yield positively until an optimum of 1 wt % NaOH after which a decline in yield was observed. The reaction temperature exhibit small but noticeable effect on the reaction as the yield increases slightly with temperature increase. The optimum biodiesel yield of 80 % with a corresponding purity of 98.4 % against the European Union set limit of 96.5 wt % was obtained at a catalyst concentration of 1 wt % and a temperature of 60°C. The result of the characterization of the MOME biodiesel shows that it compares favorably with ASTM standard for biodiesel.

Keywords: Moringa *oleifera*, Reactive extraction, Biodiesel, *in situ* transesterification, catalyst, temperature characterization

1. INTRODUCTION

Biodiesel is a mono alkyl ester of fatty acid produced from the transesterification of vegetable oil/animal fat with an alcohol in the presence of a catalyst (Gerpen *et al.*, 2004). Biodiesel is presently enjoying wide popularity as a possible alternative to petroleum diesel due to ever increasing demand for energy resulting from population explosion, industrialization and the menace of environmental degradation largely attributed to the over dependency and usage of fossil derived diesel fuel (Madankar *et al.*, 2013). The fuel can be used in conventional diesel engines as a substitute for petro diesel (Musa and Aberuagba, 2012). It is known to be an attractive biofuel because it is essentially renewable, non toxic, biodegradable, emit less carbon, sulphur free, have high flash point, good lubricity, non flammable and miscible with petroleum diesel in all ratio (Musa *et al.*, 2014). The most prominent feedstock for biodiesel production are soya bean oil Silva *et al.*, 2011, palm oil , sunflower oil, canola (Musa *et al.*, 2014a) corn oil (Lu *et al.*, 2009), palm kernel oil (Alamu *et al.*, 2007) Jatropha curcas oil, castor oil, cotton seed oil, olive oil, , tallow, waste grease, peanut oil, madhuca indica, pongamia pinnala, fish oil, and linseed oil (Musa *et al.*, 2014b).

Transesterification is the most common technology employed for the production of biodiesel from vegetable oils (Abdulkareem *et al.*, 2011). Biodiesel production using these techniques involves a number of stages; such as extraction of oil from precursor, purification of the oil before esterification/transesterification. These multiple steps are reported to account for over 70 % of the total biodiesel production cost (Shuit *et al.*, 2010). In order to reduce the cost of biodiesel production a number of ways have been identified. According to Reefaat *et al.*, 2008, there is the need to minimize the cost of biodiesel

production by improving on the process technology through optimization of the process variables that affects the biodiesel yield and purity.

The development of *in situ* transesterification (reactive extraction) as a process of biodiesel production has the potential to drastically reduce the cost of biodiesel. This new technology differs from conventional transesterification process as it permits the synthesis of biodiesel from oil bearing seed directly through a single step process that involves in situ extraction and transesterification (Zakari and Harvey, 2011; Ponsak *et al.,* 2013). The technique essentially allows both extraction of oil from its seed and subsequent conversion to biodiesel to take place in one single step with the alcohol acting as a solvent for extraction and a reagent for transesterification (Shuit *et al.,* 2011). This makes both extraction and transesterification to take place simultaneously thereby eliminating the step of extraction, refining and further processing before tranesterification (Haas *et al.,* 2004, Georgogianni *et al.,* 2008). A number of study has been reported on the in situ transesterification of oil bearing seeds for biodiesel synthesis; some of seeds include rapeseed (Zakaria and Harvey, 2011), rice bran oil seed and rubber oil seed (Abdulkadir *et al.*, 2014) castor seed (Madankar *et al.,* 2011), Jatropha curcas seed (Shuit *et al.,* 2010) and cotton seed (Kazim and Harvey, 2011), Palm fruit (Ponsak *et al.,* 2013). Besides process optimization the present increase in human population and the current renewed interest in oleo-chemicals products and lipids derived fuels such as biodiesel has necessitate the need to search for new underutilized vegetable oils bearing seeds. Quite a number of this plants seed have been identified, however the dearth of information on their chemical composition has limited their applications as potential oilseed crop (Anwar and Rashid, 2007).

Moringa oleifera is a multi- purpose plant. The leaves, fruits, flowers and immature pods of this tree are edible and are part of traditional diets in many countries of the tropics and sub-tropic (Anwar and Rashid, 2007). Moringa *oleifera* is commonly known as Never Die tree, West Indian, Ben tree, Horseradish tree Drumstick tree and Radish tree In English. Moringa *oleifera* Lam belongs to an *onogeneric* family of shrubs and tree. Moringa seed kernels contain about 30 – 50 % oil (Zaku *et al.*,2012). The oil is commercially known as "Ben oil" or "Behen oil". Moringa seed oil content and its properties show a wide variation depending mainly on the species and environmental conditions (Anwar and Rashid, 2007). Moringa seed oil contains about 74 % oleic acid making it an ideal feedstock for biodiesel synthesis in term of improved oxidative stability (Anwar, 2005). One of the major threats against the use of vegetable oils for industrial purposes is the shortage of food supply. Abdulkareem *et al.,* (2011) reported that Moringa oleifera seed oil is not a popular edible oil in Nigeria and many other parts of the world; hence its usage for biodiesel production will not pose any food challenge. The author also establishes the potential of these oilseeds for biodiesel production

The objective of this work is to investigate the influence of in situ transesterification catalyst concentration and reaction temperature on the yield of moringa oleifera methyl ester (MOME) by reactive extraction for biodiesel production.

2.0 MATERIALS AND METHODS

2.1 Moringa *oleifera* seed

The oil seed was collected from Minna, Nigeria. These seeds were stored in very dark air tight container.

2.1.1 Preparation of Moringa *oleifera* seed

The seed including its shell were ground using a pestle and mortar in a fine particle of less than 5 mm and dried in an

oven (Dakai, Korea) for an hour at a temperature of 105 °C.

2.1.2 Determination of oil content

2g of the ground and dried moringa seed was weighed into thimbles. The thimbles were inserted in the soxhlet apparatus and the boiling flask was filled with 300 ml of n-hexane. The soxhlet apparatus was set up, powered and allowed to reflux for 6 hours. The thimbles were occasionally removed and weighed until a constant weight was observed. The thimbles were finally removed and the n-hexane was drained from the top of the apparatus. There liquid in the boiling flask was removed and oven dried at 105 °C to get rid of any trace of n-hexane. The sample was then cooled and weighed (Ibitoye, 2005).

$$\%\ Oil = \frac{weight\ of\ oil}{weight\ of\ sample} \quad (1)$$

2.2 Chemical and reagent

Methanol with a purity of 99.8%, NaOH, acetic acid, hexane were obtained from the Fisher scientific Co, U.S.A.

2.3 Reactive Extraction for Biodiesel Production

The reactive extraction experiments were conducted in a sealed conical flask. About 0.792g of sodium hydroxide (1% wt of oil) was first dissolved in 125.2 ml of methanol (i.e. alcohol to oil molar ratio of 1:350). This was then poured into the 500 ml conical flask and heated to a desired temperature of 60 °C. 20g of ground and dried moringa seed powder was poured into the alkaline alcohol and agitated for 60 minutes in a water bath agitator set to 60 °C. After 60 minutes, the agitation was stopped and a known amount of glacial acetic acid was poured into the mixture to stop further reactions. A funnel equipped with a filter paper was used to separate the liquid from the meal. Excess methanol was used to wash the residue to recover every methyl ester trapped in the meal. The excess methanol was recovered using a rotary evaporator equipped with a vacuum pump. The remaining mixture of glycerol and biodiesel was separated using a separating funnel. The mixture in the separating funnel formed two distinct layers; the biodiesel rich upper layer and the lower layer of glycerol which was further removed. An equal volume of warm acidified water was used to wash the biodiesel to increase its purity. The washed biodiesel was the oven dried (Kasim, *et al.,* 2012).

2.4 Biodiesel Analysis

2.4.1 Biodiesel yield

The biodiesel yield was calculated by dividing the mass of biodiesel obtained by the mass of oil in the moringa oilseed.

$$\text{Biodiesel yield (\%)} = \frac{weight\ of\ ester}{weight\ of\ raw\ oil} \times 100 \quad (2)$$

2.4.2 Characterization of Biodiesel

The flash point was determined in a Pensky–Martens closed-cup tester (ISL, Model FP93 5G2) using ASTM D 93. Cloud point and pour point determinations were determined using ASTM D 2500 and ASTM D 97. The kinematic viscosities were determined at 25 °C, using a Viscometer (Model VT-03) following the ASTMD 7042 procedure. The cetane index was calculated from the iodine value and saponification value as given by Krisnangkura below.

$$CI = 46.3 + \frac{5458}{SV} - \frac{0.225}{IV} \quad (3)$$

SV = Saponification value of ethyl ester; IV = Iodine value of ethyl ester.

The cetane number was therefore calculated from the cetane index as given by Patel in the equation below.

$$CN = CI - 1.5 \quad (4)$$

3.0 RESULT AND DICUSSIONS

3.2.1 Effect of Catalyst Concentration

The presence of catalyst is play a key role in reactive extraction of oilseed to biodiesel.

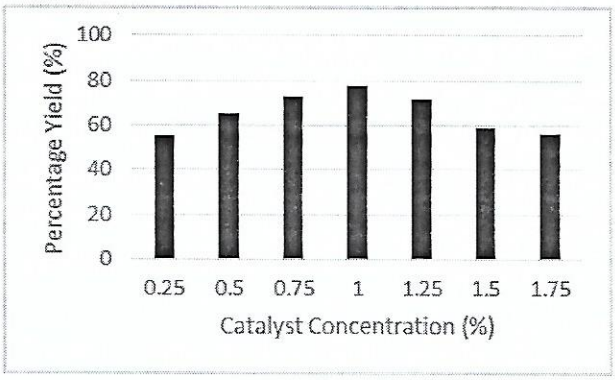

Figure 1: Effect of catalyst concentration on MOME yield

Different catalyst (NaOH) concentration (0.25, 0.50, 0.75, 1.0, 1.25, 1.50 and 1.75 %wt) other parameter such as temperature, molar ratio of methanol to oil, reaction time and agitation speed were kept constant at 50 ^{0}C, 1:350, 60 minutes and 300 rpm respectively. The result gave an average yield of 55.3, 65.3, 72.9, 77.9 71.6, 59.0 and 56.5 % with a corresponding methyl ester content (purity) of 83, 86.5, 93.1, 94, 90.5, 82.5 and 83.3 % respectively The clearly revealed that the methyl ester yield increased linearly with increase in catalyst concentration until an optimum of 77.9 % was obtained at 1 % wt catalyst concentration. The yield of methyl ester does not necessarily depend on high catalyst concentration but on a sufficient catalyst concentration required to penetrate the oilseeds and aid the oil extraction as well as methyl ester synthesis. Catalyst concentration below the optimal point (i.e. 1%) even under the same operating conditions of alcohol, temperature and time resulted into lower biodiesel yield. The result compares favourably with the work of Chandu *et al.,* 2012. The decrease in biodiesel yield at catalyst concentrations above 1 % can be attributed to increase in hydroxide ions which lead to side reactions such as soap formation.

3.2.2 Effect of Temperature

Generally temperature affects the diffusion of solvent into oil seed core and subsequent synthesis of the biodiesel (Zakaria and Harvey, 2012). The result of Figure 2 shows that the increase in temperature from 30 - 60 ^{0}C leads to an increase in biodiesel yield and purity

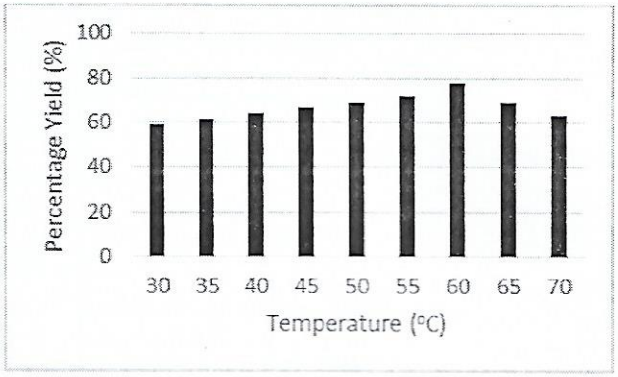

Figure 2: Effect of temperature on MOME yield

The highest yield of 80 % was obtained at a temperature of 60 °C beyond this point the yield began to drop. This result is in agreement with the report by Zakaria and Harvey, 2011, who reported that the solubility of the oil in the solvent into seed is usually increased at elevated temperature due to substantial decrease in parent oil viscosity which results higher diffusitivity of the solvent in to oilseed core. The findings from this work differ from the report of Chandu *et al.,* 2012 who reported the same yield at a temperature of 65 °C during the reactive extraction of castor methyl ester. Other researchers such as Kasim and Harvey (2011) have also reported insignificant effect of temperature beyond 30°C. According to Kasim *et al.,* 2010 the pronounced contradictions on the effect of temperature variation might probably be dependent upon the feedstock used, as different raw materials are characterized by different internal structures and effective diffusitivity.

3.3 3.1 Characterization of Moringa Oleifera seed oil Biodiesel

Table 3.4: Fuel properties of biodiesel

Fuel property	Experimental Values	Rashid *et al.*, 2008	European Norm (EN)	ASTM standard
Kinematic viscosity at 40°C (mm^2/s)	4.4667	4.83	3.5- 5.0	1.9 – 6.0
Specific gravity g/ml at 15 °C	0.88	-		0.88-0.93
Flash point (°C)	192	-	> 101	> 130
Cloud point (°C)	5	18		
Pour point (°C)	3	17		-15 – 10
Cetane number	66.8	67.07	> 51	> 47

The kinematic viscosity of any fuel is of utmost importance as it affects the atomization and distribution of the fuel (Gerpen *et al.*, 2004). According to ASTM D6751 the kinematic viscosity of biodiesel must be within the range of 1.9 - 6.0 mm^2/s. The kinematic viscosity of the biodiesel produced in this work is 4.4667mm^2/s at 40°C which is within the EN and ASTM D6751 standard and also shows close proximity to the report of Rashid *et al.*, 2008 as shown on Table 1. Excessive high kinematic viscosity will result in higher drag, higher pressures and higher injection volumes into the injection pumps particularly for engines under low temperature conditions (Sarada, 2011).

The flash point is the least temperature at which vapours of a fuel will be ignited by an applied ignition source. Flash point measures the tendency of a fuel to form flammable mixture with air (Gerpen *et al.*, 2004). The flash point of the moringa biodiesel was found to be 192 °C which is reasonably within the acceptable EN and ASTM D6751 standard. Biodiesels with higher flash points are safer to use. This makes moringa biodiesel a better option when compared to others like castor biodiesel with a flash point of 189.3 (Chandu *et al.*, 2012).

The cloud and pour point are important fuel properties which determine the use of that fuel for low temperature applications. The cloud and pour point of moringa biodiesel was determined to be is 5 °C and 3 °C respectively which were quite impressive when compared to 18 °C for cloud point and 17 °C for pour point reported by Rashid *et al*, (2008). The cloud point and pour point values of moringa biodiesel obtained present it as a very good fuel for low temperature applications.

The cetane number was found to be 66.9 which is just a little bit above the ASTM D6751 standard of 47-65 and slightly below the value of 67.07 reported by Rashid *et al.*, 2008 and this implies short delay in ignition and better ignition properties. This result confirms the report by Rashid et al, 2008 that moringa biodiesel has one of the highest Cetane numbers ever reported. When compared

with castor and jatropha, both with a cetane number of 52 (Mohammed, 2012; Salihu 2012).

The specific gravity was found to be 0.88 which is within the acceptable range of 0.88-0.93 by ASIM D6751 standard for biodiesel. This implies that moringa biodiesel is not only less viscous but also light. Comparing the specific gravity of moringa biodiesel with that of castor (0.89) and jatropha (0.91), moringa biodiesel have a lower specific gravity both castor and jatropha biodiesel.

The density of the diesel was also found to be 0.8837g/cm^3 as against the density of 0.9032g/cm^3 of the parent oil. The sharp change in this value is an indication of a decrease in the trigylceride content of the oil. The result of the characterization of moringa biodiesel obtained, the properties of the moringa biodiesel produced fall within EN and ASTM D6751 standard.

4.0 CONCLUSION

The study have attempted the reactive extraction (*in situ* tranesterification) of moringa oleifera oil seed studying the effect of catalyst concentration (0.1–1.8 wt %) and reaction temperature (30–60 °C) on the synthesis of moringa methyl ester yield (MOME) at a constant particle size, molar ratio of methanol to oil, reaction time and agitation speed of < 5 mm, 350 rpm, and 60 minutes respectively. The findings revealed an optimum yield of 80 % at 1.0 wt % catalyst concentration and a temperature of 60 ^{0}C. The characterization of the resultant biodiesel presents moringa oleifera oilseed as a good feedstock for biodiesel production as its properties conforms to the acceptable EN and ASTM standard. The innovation in this manuscript is that it is one of the very first attempt to document the reactive extraction of biodiesel from moringa oleifera oilseed.

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