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Biodiesel Production from Neem (*Azadirachta indica*) Seed Oil

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Abstract:

Biodiesel was produced from non-edible neem seeds. Due to its high FFA content, a two step acid-base transesterification approach was applied using $H_2SO_4 - NaOH$. In the first approach (esterification), H_2SO_4 was applied to reduce acid level to $<1mgKOH/g$ while the followup step involved direct conversion to fatty acid methyl ester using 1% NaOH as catalyst. The results revealed optimum conditions of biodiesel at 1% NaOH catalyst amount, $60^\circ C$ reaction temperature, 1:6 oil to methanol molar ratio and 70 min reaction time for the two step acid – base transesterification method. These optimum parameters produced a maximum biodiesel yield of 92.0%.

The fuel properties of the biodiesel produced compared favorably with recommendations by the American Standard Testing Method (ASTM D6751), European Standard and Ghana Standard Authority

Keywords: Biodiesel, Transesterification, esterification, homogeneous, heterogeneous, Neem, characterization, methanol, free fatty acid

1. Introduction

The depletion of fossil fuel, the resulting high price and its adverse effects on the environment has encouraged successive governments and researchers in recent times to consider alternative renewable sources of fuels. Renewable and clean energy fuel can be produced from different bio based raw material as a substitute for petro based products. Production of biofuels from renewable feed stocks can improve energy security and reduce greenhouse emissions. In the wake of this phenomenon, demand for energy and its security by various countries has shot up globally (Radha & Manikandan, 2011).

The term biodiesel refers to a clean burning alternative fuel, produced from domestic, renewable resources like vegetable oils, recycled cooking oils, or animal fats (Sivaramakrishnan & Ravikumar, 2012). Because plants produce oils from sunlight and air, and can do so year after year on cropland; these oils are best described as renewable. Animal fats are produced when the animal consumes plant oils and other fats, and they too are renewable. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (CI-diesel) engines with little or no modifications. Short chain alcohols such as methanol, ethanol, and butanol are very often used in the production of biodiesel. The selection of an alcohol is premised on several factors including cost effectiveness and performance considerations. Ethanol and methanol are much preferred among the most used alcohols (Saraf & Thomas, 2007). Whereas methanol is less costly with desirable physical and chemical attributes, ethanol is environmentally friendlier since it is sourced from renewable agricultural materials thus, making the transesterification process a total independence from petroleum-based alcohol (Saraf & Thomas, 2007). The high cost of edible plant and vegetable oils as raw materials used for biodiesel production is the major setback which greatly retards its widespread application. Thus, biodiesel production has not yet been commercialized all over the world (Yan et al., 2010). One way of reducing the cost of biodiesel is to employ low quality feedstocks such as waste or used vegetable oils, non-edible oils and soap stock (by-product of vegetable oil refinery), which are cheaply available and can be regarded as attractive feedstocks for biodiesel production (Canakci & Sanli, 2008).

Transesterification is the most common method for biodiesel production due to its simplicity, thus this method has been widely used to convert vegetable oil into biodiesel (Helwani et al., 2009). The transesterification process or methanolysis (alcoholysis), which refers to a catalyzed chemical reaction involving vegetable oil and MeOH to yield fatty acid methyl ester as the main product and glycerol as a by-product (Huber, O'Connor & Corma, 2007), is shown in the equation below;

Where TG, MeOH and ME denote triglyceride, methanol and methyl esters respectively.

Methods such as; conventional, non-catalytic supercritical, microwave and ultrasound are also employed in biodiesel production (Teixeira et al., 2009; Azcan & Danisma, 2008; Georgogianni, Kontominas, Pomonis, Avlonitis, & Gergis, 2008). Among these methods, conventional stirring and ultrasonication are much preferred and widely studied with different feedstocks (Marchetti, 2007). However, conventional stirring is preferred in most cases because of its convenience, easy and simple nature of application.

According to Meher, Vidya, Sagar, and Naik, (2006) the majority of feedstock currently used are obtained from edible agriculture resources. Biodiesels from edible oils are currently affected by concerns bordering on cost because of the competition that exists between food and fuel from edible oils; a major factor fuelling the change in narrative for more non-edible low-cost alternative feedstocks. According to Radha and Manikandan. (2011) neem is a viable alternative to *Jatropha* and *Castor*. Neem seed can be a potential and promising feedstock for biodiesel production with extra environmental and socioeconomic importance. Neem tree is available in virtually all the ten (10) regions of Ghana. Currently the tree doesn't have any significant use except for shade and in rare cases for medicinal purposes (Workneh, 2011).

Neem (*Azadirachta indica*) is a fast growing tree, easily cultivable, drought resistant, grows under poor soil conditions, has less annual rain fall requirement (not more than 200 mm), and other agricultural activities such as crop growing or livestock rearing can be carried out along with a neem tree plantation. In addition, the by-product like the seed cake can be used for soil conditioning; leaf extract can be used for waste water treatment and for production of pesticide and insecticide. The aforementioned importance and other significant multi benefits make the tree attractive for biodiesel production.

Firstly, a two step acid-base transesterification process is adopted to convert the high free fatty acid (FFA) oils to its mono-esters. Step one involves, acid catalyzed esterification to reduce the free fatty acid (FFA) content of the oil to less than 2%, followed almost immediately with a second step, entailing alkaline catalyzed transesterification process to convert the products obtained in step one to its mono-esters and glycerol.

The objectives of this work were to evaluate and optimize the transesterification of neem seed oil using a two step acid-base transesterification method using H_2SO_4 – NaOH and to compare yield/quality with international standards. The obtained results can be used to predict a conversion yield of neem oil transesterification going forward.

2. Materials and Method

2.1. Materials and reagents

Chemicals including methanol, NaOH, H_2SO_4 , KOH, petroleum ether (60-90 °C), hydrochloric acid (HCL) and tetradecane (internal standard for GC) were obtained from the school of biological sciences (UCC) and were all of analytical reagent (AR) grade.

2.2. Apparatus

The apparatus used in this study include, Oven, heating mantle, crucible, thermometer, desiccators, centrifuge, mortar and pestle, mill, rotary evaporator, 250ml two neck reaction flask, separating funnel, hot plate, condenser, magnetic stirrer, water bath, micropipette, Gas chromatograph (GC) (Agilent Technology Inc. USA).

2.3. Procedures

2.3.1. Acid Pre-Treatment (Acid Catalyzed Esterification)

The extracted crude neem oil was first weighed, heated at 60°C for about 10 min and mixed with 45.0 ml of methanol (4.5 : 1 methanol to oil ratio). 0.5% w/w of concentrated H_2SO_4 was added to the mixture. The obtained resulting mixture was then stirred with the aid of a magnetic stirrer on a plate for 50 min at 60°C, after which it was allowed to settle for 2 hours. The acid treated oil is separated from the methanol - water mixture with the aid of a separating funnel.

2.3.2. Base Catalyzed transesterification

These laboratory scale experiments were carried out batch wise in a 250 ml conical flask containing 25g of pre-treated neem oil. These were done with a magnetic stirrer on a plate at a temperature of 60°C, varying oil to alcohol ratio from 1:4, 1:6, 1:8 to 1:10. The acid treated oil was poured into the reaction flask and heated. A solution of NaOH in methanol (1%) was dissolved at room temperature and the pre-treated oil was added. The reaction time spanned through various periods of 50, 60, 70 and 80 min. The reaction condition of 60°C and 1% NaOH catalyst was maintained as reported previously (Aransiola et al., 2010; Muthuet al., 2010). The resulting mixture was poured into a separating funnel and allowed to settle under gravity for 24 hours. The rather heavier glycerol settled in the lower layer and was tapped off before the biodiesel layer which was subsequently washed with warm water three times and dried over anhydrous calcium chloride. The viscosity value recorded for the biodiesel produced was adopted as a proxy estimation of the extent of reaction with reference to ASTM standard which served as an indicator of completeness of the transesterification reaction. The aforementioned approach has been used in the literatures (Aransiola et al., 2010). The procedure employed in this study was repeated varying catalyst amount, temperature and reaction time constant and mole ratio in the quest to yield optimum reaction conditions. The biodiesel produced was analyzed for various parameters including: density, acid value, ash content, pour point, flash point, cloud point, water content, colour, density, and kinematic viscosity at 40°C.

2.4. Analysis of FAME Yield

The analysis for the composition of the oil sample was carried out with the aid of a 7890B GC-MS (Agilent Technology Inc. USA) according to ASTM D6584. The GC-MS was equipped with a thermal conductivity detector (TCD) and a high-polarity general purpose column recommended for Free Fatty Acid and Phenols (15% FFAP, Chromosorb W, A/W 80/100, Length of 2m). Helium at high purity 99.9999% was used as the carrier gas. Column operation temperature range of 50°C-250°C and sample inlet temperature of 200°C were used. The temperature of the oven was initially held at 60°C for 5min and then increased to 220°C at 10°C/min for 10min. Sample inlet pressure (Carrier gas 20mL/min) and total pressure with makeup (Carrier gas and makeup 21mL/min) were used. Temperature of the detector was 250°C.

The neem oil was analyzed for characterization. Standard ASTM D6751 methods were being used to determine, at kinematic viscosity 40°C (ASTM D445-06), density at 15°C (ASTM D4052-96) acid value (ASTM D664-06), saponification value (GB/T5534-08), FFA (ASTM D5555-95) and water content (ASTM D2709-96).

The yields of the biodiesel samples were determined from the content of the esters using the equation below;

$$\text{Me yield (\%)} = \frac{\% \text{ FAME area from GCMS} \times \text{weight of product}}{\text{weight of oil sample}} \times 100\% \quad (\text{Omar \& Amin, 2011})$$

All data points were presented as means of triplicate for both experimental and GC analysis.

3. Results

3.1. Esterification of Neem Oil Using Sulphuric Acid

Free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. Feed stocks with high free fatty acid (> 1%) are not easily converted by base catalyzed transesterification processes because of the occurrence of concurrent soap formation, which has a potential of reducing catalyst efficiency, increase viscosity and glycerol separation difficulty. To avoid the above problems, obtained free fatty acids were pre-treated via sulphuric acid treatment into esters with methanol as shown in the equation below:

3.2. Methanol: Oil Molar Ratio

As can be seen in figure 1, holding catalyst amount at 0.5wt.%, reaction temperature at 60 °C and reaction time at 40 min, the increase in methanol-to-oil molar ratio proportions from 3.5:1 to 4.5:1, correspondingly increased yield from 80% to 90.2%. The last two of the series being, 5.0:1 and 5.5:1 produced only a slight decline when methanol: oil molar ratio further increased.

Figure 1: Effect of Methanol on Conversion Efficiency

3.3. Catalyst Amount

Amount of acid catalyst variation affects the conversion efficiency. Sulphuric acid proportions when varied from 0.25, 0.5, 0.75 to 1% v/v H₂SO₄ (holding Molar ratio at 4.5:1, reaction temperature at 60 °C and reaction time at 40 min). Maximum conversion efficiency is observed at 0.5 % v/v H₂SO₄ (90.2%) as can be seen from Figure 2, a decline is observed as the catalyst amount increased.

Figure 2: Effect of Acid Catalyst Amount on Conversion Efficiency

3.4. Reaction Temperature

Maintaining methanol: oil molar ratio at 4.5:1, catalyst amount at 0.5 %v/v.H₂SO₄ and reaction time at 40 min, the increase in temperature from 40 °C to 60°C resulted in an increase in conversion efficiency from 80% to 90%. Optimum temperature was achieved at 60°C as can be seen from Figure 3.

Figure 3: Effect of Temperature on Conversion Efficiency

3.5. Reaction Time

As can be seen from Figure 4, the maximum conversion efficiency (90.1%) was achieved in 50min. The excess reaction time (after 50min) resulted in slight reduction in conversion efficiency possibly due to the reversibility of the reaction.

Figure 4: Effect of Time on Conversion Efficiency

In this experiment, 4.5:1 methanol to oil molar ratio, 50min reaction time, 60°C reaction temperature and 0.5wt.% catalyst amount were finally selected as the attained optimum reaction conditions for the esterification of neem oil.

3.6. Alkali transesterification using NaOH

3.6.1. Methanol: Oil Molar Ratio

Effect of methanol on the biodiesel yield was studied at constant temperature, time and catalyst to oil weight ratio that is, 60°C, 70min and 1%, respectively. As can be observed from Figure 5, the increase of methanol: oil molar ratio from 1:4 to 1:6, increases biodiesel yield from 87.43% to 90.33%. However, further increase in methanol: oil molar ratio reduced the yield.

Figure 5: Effect of Methanol on Yield

3.6. Catalyst Amount

Figure 6 shows that, the increase of catalyst amount has a significant positive effect on FAME yield. It can be observed that maximum yield (92.3%) was achieved when the catalyst dose was increased from 0.5wt.% to 1wt.%, a further increase resulted in yield decline.

Figure 6: Effect of Catalyst on Yield

3.7. Reaction Temperature

The effect of reaction temperature variation on yield is shown in figure 7. Temperature was varied in four different levels that is; 50, 60, 70 and 80°C. Amongst these, 70°C reaction temperature gave the maximum methyl ester yield of 92.6%.

Figure 7: Effect of Reaction Temperature on Yield

3.8. Reaction Time

The effect of reaction time variation on the conversion efficiency is shown in Figure 8. It can be seen that, increase in reaction time from 50min to 60min increased FAME yield from 87.0% to 92.5%. A further increase in reaction time led to a slight decline in yield.

Figure 8: Effect of Reaction Time on Yield

From the experiment, it was determined that the optimum parameters for transesterification of Neem oil using NaOH after the pre acid treatment with H_2SO_4 are 6:1 methanol:oil molar ratio, 1wt% catalyst loading, 60°C reaction temperature, and 70min reaction time. These optimum parameters for transesterification of neem oil produced the highest methyl ester yield of 92.0%.

3.9. Characterization of the Methyl Esters

The chromatogram of methyl ester produced from NaOH catalyzed transesterification is presented in Figure 9. Analysis in this study was mainly carried out to confirm the conversion of oil to methyl ester. The methyl ester eluted at a retention time of 2.310 minutes was a little lower than that of the standard (2.460 minutes). The difference may be due to instrumental and/or experimental error.

Figure 9: Chromatogram of the Methyl Ester

From table 1, all properties of the methyl ester obtained from NaOH catalyzed transesterification were within the standard limits, thus, making the biodiesel suitable for use.

Property	Acid Treated Oil	Akali FAME	ASTM Standard D6751	EN Standard	Ghana Standard Authority
Density, kg/m ³	910	890	870 - 900	860– 900	-
Kinematic Viscosity(mm ² /s), 40 OC	27.4	4.68	1.9 – 6.0	3.5 – 5.0	1.5 – 6.5
Iodine Value (g/ 100g)	70	52.62	-	≤ 120	-
Acid value (mg KOH/g)	0.7508	0.31	≤ 0.8	≤ 0.5	≤1.0
Saponification value	222.2	148.6	-	-	-
(mgKOH/g)	0.00	0.01	-	-	≤0.1
Ash content (%)	-	+3	-	-	-
Cloud point (OC)	-	180	≥ 120	≥ 130	66min
Flash point (OC)	-				

Table 1: Properties of the Methyl Ester Compared to International Standards

4. Discussions

4.1. Esterification of Neem Oil Using Sulphuric Acid

Molar ratios defined as the ratio of number of moles of alcohol to number of moles of vegetable oil. Theoretically, transesterification reaction requires 3 moles of alcohol for each mole of oil. However, practically a higher molar ratio is required to shift reaction equilibrium towards the products for more methyl esters yield. As can be seen in Figure 1, the highest conversion efficiency is achieved when methanol-to-oil molar ratioproportions increased from 3.5:1 to 4.5:1 (catalyst amount 0.5 wt.%, reaction temperature 60°C and reaction time 40 min), the last two of the series being, 5.0:1 and 5.5:1 produced only a slight decline. In economic sense 4.5:1M is chosen as the optimum reaction condition. Beyond this ratio, the additional methanol did not contribute positively to the production yield.

Effect of acidcatalystamount variation affects the conversion efficiency. Maximum conversion efficiency is observed when the catalyst amount increased from 0.25 to 0.5 %v/vH₂SO₄.The product turns black beyond 0.5 % v/vH₂SO₄. Catalyst variation is shown in Figure 2.

Maintainingmethanol to oil molar ratio at 4.5:1, catalyst amount at 0.5 %v/vH₂SO₄ and reaction time at 40 min, the increase in temperature from 40 °C to 60°C resulted in an increase in conversion efficiency. Optimum temperature is achieved at 60°C.At higher reaction temperature methanol is lost because melting point of methanolis 65°C. Above 60°C product colour became black. Effect of temperature variation is shown in figure 3.

The reaction time was varied from 30 to 70 min. As can be observed in Figure 4, the reaction was slow in the initial stages possibly due to inadequate stirring time to enhance proper mixing and dispersion of methanol and catalyst onto the oil. The maximum conversion efficiency (90.1%) was however, achieved in 50min. The excess reaction time (after 50min) resulted in a slight reduction in the conversion efficiency due to reversibility of the reaction.

The observation in this study compares favourably with that of Sathya and Manivannan.(2013) who reported a catalyst amount of 0.5 % v/v H₂SO₄, methanol : oil molar ratio (0.45:1 v/v) at 50°C temperature and 45 min reaction time as optimum reaction conditions for the esterification of neem seed oil. In this experiment, 0.45:1 methanol to oil molar ratio,

50min reaction time, 60°C reaction temperature and 0.5wt.% catalyst amount were finally selected as the finally attained optimum reaction conditions.

The oil's acid value reduced to less than 2mgKOH/g and its color became lighter after acid treatment. This made it much more convenient for alkali transesterification (Ghadge & Raheman, 2006; Veljkovic et al., 2006; Wang et al., 2011). The viscosity of the oil reduced after transesterification from 43.75 to 5.53cSt likewise the density from 0.9182 to 0.8762 g/ml, which is acceptable as per ASTM D664-01 recommendation for biodiesel.

4.2. Alkali transesterification Using NaOH

Theoretically one mole of triglyceride requires three moles of methanol, but in practice higher amount is required to shift the reaction equilibrium forward and maximize the yield. Effect of methanol on the FAME yield was studied at constant temperature, time and catalyst to oil weight ratio i.e. 60°C, 70min and 1%, respectively. As can be observed in Figure 5, the increase in methanol to oil molar ratio from 1:4 to 1:6, increased FAME yield from 87.43% to 90.33%. However, further increase did not have a significant impact on the yield. Methanol to oil molar ratio of 1:10 results in 90.83% FAME yield which is almost similar to methanol to oil molar ratio of 1:6. This is because, as the amount of methanol increases, it shifts the reaction equilibrium forward (i.e. since transesterification reaction is reversible) which consequently results in increase in rate of reaction. However, further increase in methanol leads to dilution of the catalyst. In addition, most probably at higher amount of methanol, reverse reaction which is a combination of glycerol and ester may have started to take place, these phenomena often leads to the formation of di and monoglyceride, which results in incomplete conversion.

The amount of catalyst is an important process variable in the production of biodiesel. In this experiment, catalyst to oil weight ratio was varied from 0.5% to 2.0%. The reaction condition of 60°C temperature, 60min reaction time and 6:1 methanol to oil molar ratio was maintained as reported previously (Aransiola et al., 2010; Muthu et al., 2010). Figure 6 shows that increasing the catalyst amount has a significant positive effect on FAME yield. It was observed that when the catalyst dose was low, incomplete transesterification occurred. However, as the amount increased, more triglycerides changed to ester. This is because, increasing the catalyst amount provides more active sites for the reaction of available triglyceride and methanol. In addition, a further increase in catalyst amount (beyond 1wt.%), slightly lowered the yield from 1wt.% (92.3%) to 2wt.% (91.0%), a development attributable to soap formation.

Effect of temperature was studied by holding methanol to oil molar ratio, catalyst and time constant at 1:6, 1% and 70min respectively. Figure 7 has shown that, increasing the temperature at higher catalyst loading (beyond 1.0%) has a negative effect on the yield, however this effect was negligible at lower catalyst to oil weight ratio. This is because maximum yield was observed at a higher catalyst, methanol amount; any action disrupting this combination has negative effect on the FAME yield. The yield is increased with increase in reaction temperature.

The effect of temperature variation on yield is shown in figure 7 where, temperature was varied in four different levels i.e. 50, 60, 70 and 80°C. Amongst these variations, 60°C reaction temperature gave the maximum methyl ester yield (92.6%). The slight decline observed beyond 60°C is possibly as a result of loss/escape of methanol. The conversion rate increased with increase in reaction time. In this experiment, reaction time varied from 50-80min.

The effect of reaction time variation on the conversion efficiency is shown in Figure 8. Increase in reaction time from 50min to 70min increased FAME yield from 87.0% to 92.5%. A further increase in reaction time caused a slight decline in yield possibly due to reversible reaction. 1:6 methanol to oil molar ratio, 70min reaction time, 60°C reaction temperature and 1wt.% catalyst amount were finally selected as the attained optimum reaction conditions.

The observation in this study compares favorably with Aransiola et al. (2010) who reported a catalyst amount of 1.25wt.% NaOH, methanol : oil molar ratio (6:1), at 60°C temperature and 90min reaction time as optimum reaction conditions for the transesterification of neem seed oil. In this experiment, 6:1 methanol to oil molar ratio, 70min reaction time, 60°C reaction temperature and 1wt.% catalyst amount were finally selected as the optimum reaction conditions.

As can be seen in the FAME chromatogram presented in Figure 9, the biodiesel eluted at a retention time of 2.310 minutes which was lower than that of the standard (2.460 minutes). The slight difference is possibly as a result of instrumental and/or experimental error.

As can also be seen in Table 1, the high initial neem oil figures of kinetic viscosity, saponification and acid value (43.74cSt, 199.86Kg/m³ and 31.13Kg/m³ respectively) reduced to kinetic viscosity 4.68cSt, saponification 189.4Kg/m³ and acid value 0.31Kg/m³ after alkali transesterification using NaOH. The values obtained were within the American Standard Test Method (ASTM D6751), European Standard and Ghana Standard Authority acceptable limits. The other parameters were also within the standard limits thus, making the biodiesel suitable for usage.

5. Conclusion

The following conclusions were made on the basis of the results obtained from this present study:

- The optimum reaction conditions for the acid – base transesterification reaction used in producing biodiesel from the neem oil are 1:6 methanol to oil ratio, 1wt.% (NaOH) catalyst amount, 60°C reaction temperature and 70min reaction time.
- The FAME yield obtained at optimum reaction conditions is 92% for two step acid base transesterification reaction of neem oil.

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