SYNTHESIS OF BIO LUBRICANT FROM NEEM SEED (*AZADIRACHTA indica*) OIL FOR AGRICULTURAL MACHINES

Bosede Adelola Orhevba and Attamah Francis Johnpaul

(Department of Agricultural and Bioresources Engineering Federal University of Technology P. M. B 65 Minna, Niger State, Nigeria).

Abstract

In this study, Neem seed was used as a feedstock for the extraction of oil, production of biodiesel and biolubricant production. The oil was extracted by solvent extraction method using N-hexane as solvent. The oil was analyzed for chemical and physical properties such as density, pour point, acid value, free fatty acid (FFA), smoke point, flash point, specific gravity, saponification value, peroxide value, iodine value as well as viscosities at 35^0C and 40^0C. The method of transesterification was used in the production of the biodiesel from the extracted oil using potassium hydroxide as catalyst. This was characterised using the American standard Test Methods (ASTM) and parameters such as viscosity, specific gravity, cloud point, pour point, smoke point, flash point, fire point, acid value and free faty acid were analysed. The method employed for the production of bio lubricant involved two stages transesterification process, the first stage produced methyl ester of the oil and in the second stage; the methyl ester was transesterified with ethylene glycol to produce the bio lubricant. The result of the analysis of the extracted neem oil reveals that it has a very high FFA (3.7%). Reduction was achieved by esterification with methanol to 0.7%. Major lubricating properties of the product such as pour point, viscosity index and viscosities at 40°C and at 100°C were analyzed and found to have values of -5°C, 185.64, 38.7cSt, and 14.3cSt respectively. It was found that the bio lubricant produced is comparable to the ISO VG-32 standards, hence, the synthesized bio lubricant can satisfactorily serve as substitute for petroleum-based lubricants for industrial and agricultural machines.

Keywords: Neem oil, esterification, transesterification, bio lubricant, chemical and physical properties

1 INTRODUCTION

Neem tree is an evergreen tree relating to mahogany, belonging to meliceae family and grows rapidly in West Africa and Southeast Asia (Muñoz *et al.*, 2007; Liauw *et al.*, 2008). Neem is called '*arista*' in Sanskrit a word that means 'complete, perfect and imperishable', in Sanskrit '*aristhma*' is the name of the neem tree meaning 'reliever of sicknesses' and is regarded as village dispensary in India (Pankaj *et al.*, 2011). It has been observed that the tree could survive in dry and arid conditions and that the tree may become leafless for certain period of time under certain conditions (Liauw *et al.*, 2008). The parts of the neem plants such as bark, roots, leaves, seed, fruits and flower have numerous advantages in industrial products and medical treatment. Its leaves can be used as drugs for eczema, diabetes and fever (Liauw *et al.*, 2008). They also reported that the bark can be used to make toothbrush and its roots has the ability to cure diseases (Liauw *et al.*, 2008).

Neem seed is a part of the neem tree which has high concentration of oil (Liauw *et al.*, 2008). It is bitter, greenish-yellow to brown in colour; it is soluble in ether, chloroform and practically insoluble in alcohol and water and has a strong odour. Neem oil extract which is the fatty acid of the neem seed is the most commonly used product of the neem tree. The seed contain about 25-45% oil and provides the major source of neem chemicals (Okonkwo and Mukhtar, 2013). The average Composition of neem oil is shown in Table 1.

Table 1: Average Composition of Neem Oil

Formula	fatty acid	composition range
Linoleic acid	$C_{18}H_{32}O_2$	6-16%
Oleic acid	$C_{18}H_{34}O_2$	25-54%
Palmittic acid	$C_{16}H_{32}O_2$	16-33%
Stearic acid	$C_{18}H_{36}O_2$	9-24%

(Okonkwo and Mukhtar, 2013)

There are several methods by which neem oil can be extracted from the seeds these include supercritical fluid extraction, solvent extraction and mechanical extraction (Liauw *et al.*, 2008). Mechanical extraction is the most commonly used method to extract neem seed oil from neem seed. However, the oil produced using this method usually has a low price due to its turbidity, amount of metal present and water contents. Production of oil by the use of supercritical fluid has high oil purity. Extraction of the oil using solvent has many advantages. It produces high yield and less turbid oil than mechanical extraction. Neem oil is used for lubricants, insecticides and drugs for curing many diseases such as tuberculosis and diabetes (Liauw *et al.*, 2008).

2 Materials and Methods

Neem seeds were obtained from Gidan Kwano Village, Niger state, Nigeria. The seeds were picked manually by hand and the seeds were washed thoroughly in order to remove dirt. The seeds were dried under the sun for six hours at a temperature of 37^0C and a relative humidity of 55%. The seeds were later dried in the oven for three hours at 105°C to ensure that moisture content is reduced to 8%. The seeds were immediately grounded using mortar and pestle into a paste in order to weaken and rupture the cell. The paste was stored in a labeled airtight container for oil extraction. All chemicals and reagents used were of analytical grade. In all cases, distilled water was used.

Oil extraction

Oil from the grounded neem seeds was extracted with n-hexane solvent for six hours at a temperature of 60^0C using soxhlet extractor. The percentage oil obtained from the sample was calculated using the relationship described by Lawson et al., (2010).

$$\frac{\text{weight of extracted oil}}{\text{Weight of sample}} \times 100 \qquad (1)$$

Physico-Chemical Characterization of crude neem Oil

The physical and chemical properties of the crude neem oil produced were determined in accordance with the methods reported by Bilal *et al.*, (2013), Mohammed-Dabo *et al*., (2012), Aransiola *et al.*, 2012 and American Oil Chemist Society (AOCS) (2010) methods of analysis. The properties determined are as follows: density, viscosity, flash point, specific gravity, smoke point, pour point, saponification value, acid value, FFA, peroxide value and iodine value**.**

Oil esterification

This is required to reduce the FFA content of the oil as it may lead to high saponification. The high FFA content of the oil was reduced by esterification of the oil with methanol using sulphuric acid as catalyst (Bilal *et al.*, 2013). The oil and methanol were initially reacted in molar ratio of 1:4 with sulphuric acid as a catalyst. After 6-8 hours of reaction mixture settlement, two layers were formed; the upper layer is the treated oil which is tested for its acid value. Once the required quantity of acid value has not been obtained, more esterification will be required using sulphuric acid as reported by Ramning *et al.,* (2013).

Trans-esterification of the oil

Trans-esterification is the reaction of triglycerides to fatty acid alkyl esters (FAAE) and low molecular weight alcohols such as methanol and ethanol in the presence of catalyst (Demirbas, 2011; Bilal *et al.*, 2013). Production of bio-lubricant involves a double transesterification; the first one is aimed at producing an intermediate product- methyl ester of the oil, and the second uses the methyl ester as a reactant to produce the desired product, a polyolester (Bilal *et al.,* 2013). The two methods are as follows:

Methyl ester synthesis

This was achieved by trans-esterification of the oil sample with methanol using sodium hydroxide as catalyst as reported by Ghazi *et al.*, (2010) and Bilal *et al.*, (2013).

Bio lubricant synthesis

This is achieved by trans-esterification of the methyl ester with ethylene glycol in 80ml batches using 0.5M Sodium Hydroxide as catalyst (Bilal *et al.*, 2013). The weight ratio of oil-to-methanol used was 3.9:1; the amount of catalyst used was 0.5% of the total reactants and the reaction was conducted at a temperature of 100°C for three hours (Bilal *et al.,* 2013).

Analysis of produced neem bio lubricant

The bio lubricant produced was subjected to analysis as reported by Bilal *et al.,* (2013) and AOCS (2010), in order to define its applicability as lubricating oil. The properties determined include density, specific gravity, kinematic viscosity, flash point, smoke point, cloud point, pour point, viscosity index, acid value test and free fatty acid.

3 Results and Discussion

The percentage of oil yield from the sample was 38%. The result obtained from the characterisation of the neem oil, neem methyl ester and synthesized bio lubricant are presented in Tables 2, 3 and 4.

Table 2: Physicochemical Properties of the Extracted Neem Oil

Property	Unit	Value
Colour	**-**	Brown
Odour	**-**	Strong odour
Density	**(g/ml)**	0.928±0.005
Kinematic Viscosity @ 40^{0}C	**(cSt)**	39.300±0.163
Kinematic Viscosity @100^{0}C	**(cSt)**	16.250±0.204
Viscosity Index	**-**	175.000±4.270
Flash Point	**(^{0}C)**	210.000±4.270
Specific Gravity	**(g/l)**	0.921±0.003
Smoke Point	**(^{0}C)**	182.000±2.449
Pour point	**(^{0}C)**	5.200±0.245
Saponification	**Value**	185.130±1.633
(mgKOH/g)		7.400±0.082
Acid	**Value**	3.700±0.245
(mgNaOH/g)		9.000±0.163
Free Fatty Acid (FFA)	**%**	116.000±3.266
Peroxide Value	**(meq/kg)**	
Iodine Value	**(gI_2/100g oil)**	

Table 3: Physicochemical Properties of the Neem Methyl Esters (biodiesel)

Property	unit	values

Density	**(g/ml**	0.88±0.016
Kinematic Viscosity @ 35^{0}C	**(cSt)**	39.00±0.816
Kinematic Viscosity @40^{0}C	**(cSt)**	35.80±0.082
Flash Point	**(^{0}C)**	153.00±1.633
Specific Gravity	**(g/l)**	0.90±0.003
Smoke Point	**(^{0}C)**	118.00±2.449
Saponification	**Value**	114.00±3.266
(mgKOH/g)		2.00±0.283
Acid	**Value**	1.00±0.141
(mgNaOH/g)		38.00±2.160
Free Fatty Acid (FFA)	**%**	78.00±2.160
Peroxide Value	**(meq/kg)**	
Iodine Value oil)	**(gI_2/100g**	

Table 4: Comparison of the Physicochemical Properties of the Synthesized Bio-Lubricant with Petroleum Based Lubricant and ISO Standard.

Property	unit	values	Petroleum based lubricant	ISO VG 32
Density	**(g/ml)**	0.914	-	-
Kinematic Viscosity @ 35^{0}C	**(cSt)**	77.000	-	-
Kinematic Viscosity @40^{0}C	**(cSt)**	38.700	10.801	> 28.8
Kinematic Viscosity @100^{0}C	**(cSt)**	14.300	3.136	> 4.1
Viscosity Index	**-**	185.640	165.400	>90
Flash Point	**(^{0}C)**	217.000	84.000	-
Specific Gravity	**(g/l)**	0.955	-	-
Smoke Point	**(^{0}C)**	168.000	-	-
Cloud Point	**(^{0}C)**	3.000	-	-
Pour Point	**(^{0}C)**	-5.000	-9.000	< -10
Acid Value	**(mgNaOH/g)**	1.400	1.200	-
Free Fatty Acid (FFA)	**%**	0.700	0.600	-

DISCUSSION OF RESULTS

Characterisation of neem oil

Kinematic viscosity is defined as resistance of a liquid to flow. At 40^{0}C, kinematic viscosity of neem oil was found to be 39.300cSt which is 3.180 higher than the value of 36.120cSt reported by Ramning *et al.*, (2013) for neem oil.

The saponification value of the oil is a measure of the tendency of oil to form soap during the transesterification reaction. The saponification value obtained was 185.130 mg NaOH/g, which is exactly the same value (185.130 mg NaOH/g) obtained by Ramning *et al.*, (2013). Bilal *et al.*, (2013) reported that high saponification value may lead to foam formation and when this oil is used for transesterification to produce methyl ester, the yield will be very low as separation of the methyl ester from its by-product glycerol will be difficult.

The iodine value of oil is the measure of the degree of unsaturation of the oil (Knothe, 2002). This property greatly influences fuel oxidation and the type of aging products and deposits formed in diesel engine injectors (Othmer, 2011). The iodine value of neem oil was determine to be 106.000 gI_2/100g which is higher than the value of 81.28 gI_2/100g reported by Ramning *et al.*, (2013).

Acid value is a very important parameter whether a particular type of oil is edible or non edible. Vegetable oils with high acid value are classified as non edible while those with low acid value are classified as edible oils (Wikipedia, 2016). The acid value obtained for the oil sample was 7.400 mg NaOH/g which is lower than the value of 10.92 mg KOH/g reported by Ramning *et al.*, (2013).

The FFA content of the oil used was found to be 3.7%, this value is lower than 5.41% reported by Ramning *et al.*, (2013). Muazu *et al*., (2013) reported that the oil or fat used in alkaline trans-esterification reactions should contain no more than 1% FFA, which is equal to 2 mg KOH/g triglyceride. Bilal *et al.*, (2013) said that if the FFA level exceeds this limit, saponification delays separation of the ester from glycerine and decreases the yield and formation rate of fatty acid methyl ester.

The density of neem oil was determined to be 0.928g/cm^3; this is 0.045 lower than the 0.973g/cm^3 obtained by Ramning *et al., (*2013).

The pour point is the temperature at which crystal wax is extensive enough to prevent free pouring of fluid. The value of pour point of the neem oil obtained in this study, 5.2^{0}C is close to the value of 7^{0}C reported by Ramning *et al., (*2013).

Analysis of the Neem bio lubricant

According to Bilal *et al.,* (2013) the properties of neem crude oil that are important to lubrication are the pour point, viscosity index and viscosities at 40^{0}C and 100°C. These properties make the neem oil a reliable source for bio lubricant production.

Pour point is the lowest temperature at which oil flows as its container is tilted for a prescribed period. It is important for oils to flow at low temperatures. It is one of the most important properties which determine the performance of lubricants (Bilal *et al.,* 2013). The pour point of the produced neem bio lubricant was -5.0^{0}C which is higher than the value of the petroleum based lubricant and falls above ISO VG 32 specification. The pour point improved from initial 5.2^{0}C to -5°C. This value is also comparable to the pour point value of other plant based oil (Ghazi *et al.,* 2010; Bilal *et al.,* 2013).

The viscosities of the bio lubricant at 40^{0}C and 100°C are very important lubricity properties; they are useful in determining the fluidity of the lubricant at low and high temperatures and they also show the thermal stability of the lubricant (Bilal *et al.,* 2013). The viscosities of the produced neem bio lubricant at 40^{0}C and 100^{0}C were found to be 38.700cSt and 14.3cSt respectively, higher than the values 10.801cSt and 3.136cSt of the petroleum based lubricant. This can meet the specification of ISO VG 32 since the viscosities are within the standard range as presented in Table 4.

Viscosities index (VI) shows the characteristic of the lubricants viscosities when temperature changes are applied. The viscosity index of neem bio lubricant was determined to be 185.640

which is higher than the value of 165.400 of petroleum-based lubricant and falls within the ISO VG 32 specification.

4. Conclusion

The neem bio lubricant which was produced using trans-esterification method was synthesized and the major lubricating properties of the synthesized bio lubricant were analyzed. These properties when compared with standards as specified by ISO conform to those of viscosity grade 32 (VG-32). Hence, the synthesized bio lubricant can satisfactorily serve as substitute for petroleum based lubricants for industrial and agricultural machines.

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