ISSN No:-2456-2165

Synthesis of Biolubricant from Virescens Specie of the Elaeis-Guineensis (Palm Fruit) Kernel Oil

Ebuka Emmanuel Ezennajiego; Julius Nnamdi Ndive
Department Chemical Engineering,
Chukwuemeka Odumegwu Ojukwu University,
Uli Campus Anambra State Nigeriia

Abstract:- The objective of this study is to synthesize bio lubricant using kernel oil fromvirescens specie of the palm fruit (Elaeisguineensis)via atwo-stage transesterification process in the presence of potassium hydroxide and trimethylolpropane (TMP) catalyst. The kernel oil was first extracted then characterized using standardlaboratory techniques before being synthesized to produce bio lubricant. The synthesized bio lubricant properties were studied to determine its unique physical and chemical properties. The viscosity at 40 and 100^{0}C were 42 and 10.34cSt respectively, the viscosity index was quite high with a value of 132, the FFA value was found to be 0.34 which was very appropriate while the flash and pour point value were 310^{0}C and -6^{0}C respectively. The property values were comparable with that of petro lubricant and within the range of recognized testing standards such as viscositygrade 46 (VG-46). The Fourier Transform Infrared (FTIR) analysis was used to identify if the reaction did take place and its level of completion. From the values obtained, it can be deduced that the NigerianElaeisguineensis kernel oil-based biolubricantpossesses quality lubricating properties and it's a suitable alternative to petro lubricant.

Keywords:- *Biolubricant, palm kernel oil, palm fruit,Virescens, Transesterification.*

I. INTRODUCTION

In any production facility, proper lubrication of mechanical parts is necessary to achieve optimum results from every operation. Lubricants, which is a substance (often a liquid) mostly applied between interacting mechanical components to reduce the frictional resistance between them, thereby making the process more efficient and reduces wear, is an essential partof any mechanizedindustry (Jumat *et al.*,2010). They reduce mechanical wear and tear of machine components thereby increasing their durability and efficiency and also accelerates heat transfer, contaminant suspension, and corrosion protection. (Bilal *et al* 2013; Jumat *et al.*,2010). Lubricants utilized in various industrial applications are usually manufactured from petroleum sources, the quantity of available petroleum reserves are constantly depleting at a very rapid rate owing to increase in industrialization and population growth. Lubricant from petroleum sources comes with other limitations such as contamination of the soil and its level of toxicity to the atmosphere. Emphasis on the development of biodegradable, renewable, and environmentally friendly industrial fluids have raised the need to search for alternative renewable fuels. (Refaat, 2010; Yang *et al*, 2012). This has driven the interest of researchers to seek out renewable sources of producing lubricants with better properties such as bio lubricants etc. Bio-lubricant is synthesized from natural sources, this comes with better properties when compared to petroleum sourced lubricants, and bio-lubricant is more preferable due to its rapid biodegradability and low environmental toxicity. Plant-based oils are exhibiting great potentials and are a highly feasible alternative to replace the conventional mineral oils for the use in lubricant production because they are similar in structure to the longchain hydrocarbons in mineral oils with better characteristics of being non-toxic, renewable, biodegradable, eco-nomic and environmentally friendly. (Chandu et al, 2013, Nagendramma*et al* 2012) Although vegetable oils possess many favourable properties, currently they are not widely used as base oils for lubricant. This is largely due to unfavourable characteristics of most vegetable oils, which include both a high melting point and insufficient thermal oxidative stability etc.(Nagendramma et al 2012). Vegetable oils are mainly triglycerides which contain three hydroxyl groups and long chain unsaturated free fatty acids attached at the hydroxyl group. (Fox and Stachowiak 2007), (Waleska et al 2005) Chemical modifications may improve the thermal, oxidative and hydrolytic stabilities of the vegetable oils. Hence, there is need to investigate the possibility of obtaining an environmentally friendly and economically viable lubricant from one of such sources such as the virescens specie of the Nigerian palm fruit (elaisguineensis) kernel seed oil.

ISSN No:-2456-2165

The (elaeisguineensisjacq.) is a crop native to the tropical rain forest region of africa, (naher et al., 2013). the nigerian oil palm (elaeisguineensisjacquin) produces two different kinds of oil namely, palm oil and palm kernel oil (Ekwenye and Ijeomah, 2005) the pericarp consists of three distinct layers: the exocarp (skin), the mesocarp (pulpy part which contains palm oil), and the endocarp which is the shell enclosing the kernel, this on a dry basis contains about 50 % oil known as kernel oil (Naher et al., 2013). There are mainly two species of the fruit palm, nigrescens (ordinary oil) which is the specie commonly utilized and the virescens popularly known as Ojukwu palm in eastern part of Nigeria. the different types of oil palm fruits all have distinct features. nigrescens specie has blackish-purple colouration on most parts of the body when immature, then turns yellow at the base of the fruit once the fruit has matured. meanwhile, the virescens specie has a pale-yellow colour as well as its green pigmentation at the base and tip of the immature fruit. the colour changes to full orange when the bunch has matured, reflecting chlorophyll degradation. (Corley and Tinker 2016). Most of the local oil palm growers ignored the virescens specie as it did not appear to give any real economic value when compared to the nigrescens specie (Heri *et al* 2020). This study aims to syntheizebiolubricant using oil obtained from the virescens specieof the palm oil fruit.

II. MATERIALS AND METHODS

A. Materials

The Palm kernels used were sourced locally from a palm oil processing plant. The reagents used in the study include Methanol (98%),sulphuric acid (H_2SO_4), orto-phosphoric acid (H_3PO_4), trimethylolpropane (TMP) 98%., sodium methoxide, 96 %, n hexane (98%), and they were all of analytical grade.

B. Oil extraction process

The oil content of the kernel seed was extracted using soxhlet extraction technique. The solvent choice selection was based on a study by (Ibiama and Anosikem 2014), which identified n hexane as a better solvent for the extraction of oil from palm kernel seeds. In the process, the palm fruits were sun dried for 6 days, and then it was cracked open to obtain the kernels. The kernels were then ground into fine particles to open up enough surface area for optimum extraction. 50gram of the sample was placed inside the thimble of the soxhlet extractor. 150 ml of the n-hexane solvent was poured into round bottom flask of the extraction set up which was placed on a heating mantle. The extraction wasperformed for one hour at 60^0C. After the extraction time had elapsed, the solvent oil mixture was separated using a distillation apparatus. The extracted oil was then placed in an oven at 50^0C for 5 hours so as to obtain a solvent free oil sample. The weight of the oil sample was recorded so as to obtain the percent oil yield of the seed sample. The process was repeated for three different runs.

C. Characterization of oil sample

- *Viscosity*

The viscosity of the oil sample was performed using a cannon viscometer at 40^0C and 100^0C respectively. The various temperatures of the oil samples were achieved using a heating mantle with uniform stirring. The viscometer spindle was immersed into the oil sample. The equipment was then turned and left to run until uniform values is obtained.

- *Acid value*

The acid value of the oil sample was determined using 2 grams of the sample. The measured mass of the extracted palm kernel oil sample was placed in cornical flask. 25ml of diethyl was mixed with 25ml of ethanol. 1ml of phenolphthalein (1%) indicator solution was then introduced. The solution was then neutralized using one gram of sodium hydroxide solution. The sample was then dissolved using these solutions and titrated gradually with constant agitation until a faint pink end point appears for about thirty seconds. The acid value is then determined using equation (1) below.

$$\text{Acid value} = \frac{\text{titre value} \times 5.61}{\text{weight of sample}} \quad (1)$$

- *Pour point*

The oil sample was poured into a test-tube this was then placed into a refrigerator. It was then left long enough to solidify. The sample was removed and a thermometer capable of measuring very low temperatures was used. The lowest temperature at which the solidified sample will begin to melt and flow is then recorded.

- *Moisture content determination*

The following method was used to determine its moisture content. 5ml of the extracted oil was weighed into a very dried and clean crucible with a known weight. The sample is then placed in an oven at 105^0C for an hour. The heated sample was removed from the oven and allowed to cool before reweighing it. The same process was repeated at intervals until a constant weight has been attained.

$$\%\ \text{moisture content} = \frac{\text{initial weight of sample} - \text{weight of oven dried sample}}{\text{initial weight of sample}} \quad (2)$$

- *Peroxide value determination*

The peroxide value was determined by heating one gram of the oil sample with one gram of iodide and 20ml of a solvent mixture between glacial acetic acid and chloroform in the ratio 2:1 for about one minute. This was

poured into 20ml of 5% potassium iodide. The solution was then titrated with 0.002 M $Na_2S_2O_3$. Using a starch indicator, a blank was similarly titrated. (Eddy *et al.*, 2011).

$$\text{Peroxide value} = \frac{1000(v2-v1)T}{M} \quad (3)$$

➢ *Determination of density*

To determine the density of the oil, a clean and dry measuring cylinder will be weighed, then it will be filled with 10ml of the oil sample and the new weight will be measured and recorded. The following relation will then be used to derive the value for density.

$$\text{Density} = \frac{\text{weight of cylinder and cylinder} - \text{weight of empty cylinder}}{\text{volume of sample}} \quad (4)$$

➢ *Determination of iodine value*

To determine the iodine value, 25ml of iodine monochloride was added to 1ml of the oil sample, stoppered and left to stand in the dark alongside a blank containing 10ml of chloroform, for 30 minutes. The flask was rinsed with 50ml distilled water and 10ml of 10% potassium iodide solution was added. The liberated iodine was immediately titrated with 0.1M $Na_2S_2O_3$until the iodine solution turned brownish yellow. Iml of starch indicator was then added. The titration continued until the blue colouration disappeared(Onwuka, 2005)The iodine value is now given as

$$\text{Iodine value} = \frac{Blank\ titre\ value \times molarities\ of\ Na_2S_2O_3 \times 12.69}{\text{weight of sample}} \quad (5)$$

➢ *Determination of saponification value*

To determine the saponification value, two grams of the oil was refluxed with 25ml of 0.5Mpotassium hydroxide solution for one hour with continuous agitation. The excess alkali was titrated with 0.5M hydrochloric acid and 1ml of phenolphthalein indicator. This was performed alongside a blank titration. The saponification value was then calculated using the following relation.

$$\text{Saponification value} = \frac{\text{blank titre value} \times 28.05}{\text{weight of oil sample}} \quad (6)$$

D. Synthesis of Bio lubricant

The method used in the production of biolubricant from palm kernel oil was based on a study by (Arbian and Salimon 2010)**.** This usually involves a two-step transesterification process which was preceded by an esterification process normally used to reduce the FFA value of the oil sample to a value below 2%. In the first step transesterification process, 150ml of the extracted oil was transesterified using methanol in the presence of a 0.5 % wt/wt potassium hydroxide catalyst. The ratio of oil to methanol used was 1:3. The reaction was carried out for one hour, at a temperature of 60^0C to yield the intermediate product methyl ester. The next step was performed using a two necked bottom flask equipped with a thermometer sited on a magnetic stirrer hot plate.

100ml of the trans esterified oil was poured into the round bottom flask and heated up to a temperature of 60^0C after which 2.3g of Trimethylolpropane (TMP) and 0.016g of potassium hydroxide catalyst were added at a temperature of 130^0C. The molar ratio of the palm kerneloil methyl esters to TMP was kept at 4:1 using a catalyst concentration of 0.8% w/w.After the reaction was completed, the solution was transferred into a separation funnel and washed with water containing 0.6 gram of orthophosphoric acid which is equivalent to 10% wt/wt of the oil. The resulting TMP ester was then dried in an oven.

III. RESULTS AND DISCUSSION

Table1: Table of physicochemical properties of the crude oil sample

Property	Oil sample
Moisture Content (%)	1.80
Density (Kg/M3)	912.00
Viscosity @ 40°C	23.00
Viscosity @ 100°C	5.07
Acid (mgKOH/g)	14.025
Perioxide (mol/kg)	8.00
Iodine value	121
Saponification value	191.80
Fire point	329
Flash point	294
Pour point	24.00

ISSN No:-2456-2165

A. Physicochemical Characterization of oil

The physicochemical properties of the oil were studied and the values are listed in Table 1. The quality of bio lubricants is a function of the properties of the base oil used in its production. The viscosities of the oil at 40^0C and 100^0C were found to be 23 and 5.07 respectively.This shows the effect of temperature increase on its viscosity. These values are lower than 66.74 cSt and 14.28 cSt obtained by (Bilal et al 2013) for jatropha oil. The pour point, flash point and fire point which are important properties of the oil are 24^0C, 294^0C and 329^0C respectively. The free fatty acid value of 7.01% is quite higher than the maximum value required for efficient production of bio lubricant from the base oil. Usingbase oil with FFA value greater than 2% will lead to soap formation during the transesterification reaction, which will hinder the optimum yield of the desired product from the process. Esterification process was used to reduce the FFA value to below 2%. The peroxide value of 8 is close to the value of 10 obtained by (Ihiam and Anosike, 2014).Saponification value tells us the amount of alkali needed to saponify a known mass of oil. Every oil sample has its own unique value because their free fatty acids are molecules of various sizes(Ihiam and Anosike, 2014). The saponification value of 191.8 was obtainedfor the oil.

➢ *GC- Analysis*

The Gas Chromatography Mass Spectroscopy of the oil sample was performed. The GC-MS plot is shown in Figure 1. From the analysis the major components present in the oil was identified to include butanoic acid (35.8 %) which was the most abundant component. Others include Butanoic acid, 3-methyl (12.30%), Hydrocinnamic acid also called phenyl propanoic acid (4.43%), 9-Hexadecenoic acid commonly known as palmitoleic acid (2.93), 9,12-Octadecadienoic acid (Z, Z) known as linoleic acid (7.05%), n-Hexadecanoic acid commonly called palmitic acid (4.0%), etc

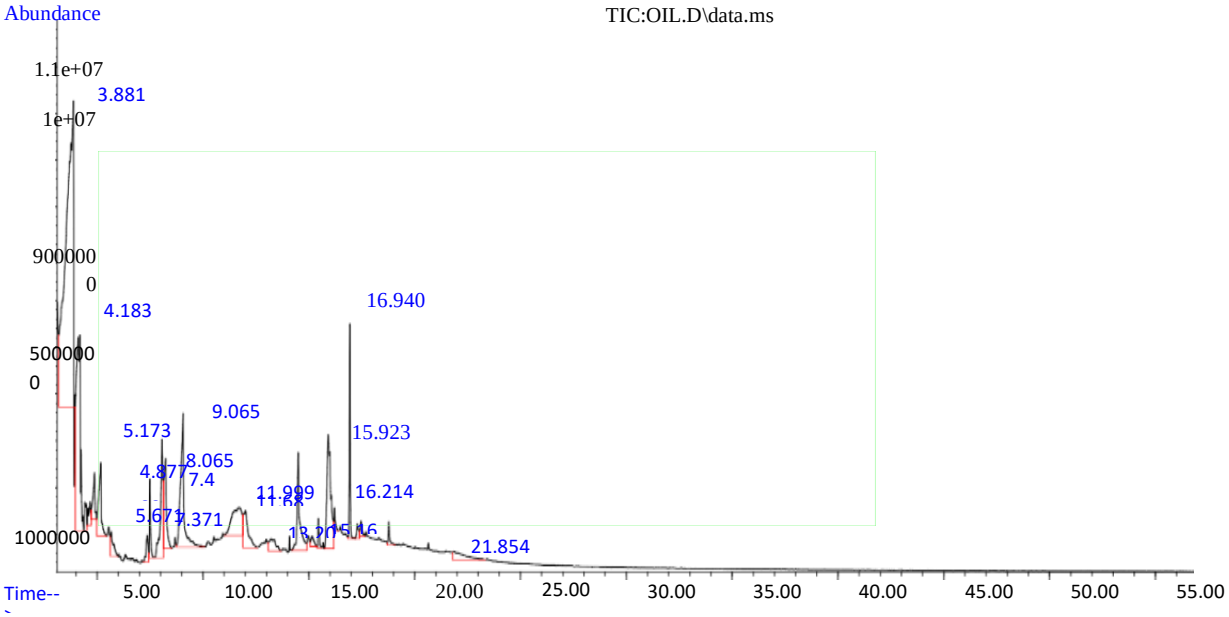

Fig. 1: GCMS plot of oil sample

B. Bio lubricantProperties

The use of vegetable oils as lubricants comes with unfavourable results and performance which requires it undergoes some basic modifications to improve its lubricity. The production of bio lubricants from vegetable oil takes place in two distinct steps. The first transesterification step separates the glycerol molecule while the second step introduces a potent molecule Trimethyl propane in place of glycerol(Alang*et al* 2018)**.** The produced bio lubricant was subjected to physicochemical tests to determine some of its fundamental properties; these properties are pertinent in determining the quality of the bio lubricant and its expected performance as a suitable substitute to Petro lubricants. The values of these properties were listed in Table 2and they also were compared to that of Petro lubricant and ISO VG 46 standard range. The viscosity of the bio lubricantat 40^0C and 100^0C was found to be 42^0C and 10.34^0C respectively. The viscosity at these temperatures helps us to understand the flow potentials and stability of the bio lubricant at higher temperatures.The ideal oil for many processesis one that maintains a unique viscosity value throughout different temperature changes.The viscosity index of the bio lubricant was132. This value is lower than the value of 173 obtained for palm kernel oil by(Appiah*et al*2021).

ISSN No:-2456-2165

Table 2: Characterization of Palm Kernel Oil TMP Esters

Parameters	Biolubricant	Petrolubricant	ISO VG 46
Viscosity @ 40°C	42.00	47.00	13-60
Viscosity @ 100°C	10.34	6.90	1.9-6.0
Viscosity Index	132	105	> 90
Free fatty acid (mg/g)	0.38	0.50	< 0.80
Flash point °C	310	220	> 130
Pour point °C	-6.00	-20	-10

Viscosity indexis theproperty of a liquid which tells us its ability to resist changes in viscosity when temperature increases or decreases (Alang*et al* 2018)**.**High viscosity index of any bio lubricantsuggests that viscosity changes at higher temperatures are minimal(Bilal*et al* 2013). Higher values for viscosity index are usually preferable.The flash point was found to be 310 ^{O}C. The high flash point value is necessary for safe handling of the product. The pour point value is -6^{O}C, which is the lowest temperature at which the bio lubricant would flow. It helps us to understand the flow characteristics and performance of the bio lubricant under very cold conditions. The value obtained is quite comparable to pour point of other bio-basedbio lubricant such as palm oil -5%, jatropha -6%, rape seed oil -12% (Appiah et al 2021).

➢ *IR Spectrum of oil and bio lubricant*

The FTIR spectrum of PKO oil is shown in figure2.The different assignments of the FTIR spectra are show the presence of various compounds with their functional group.

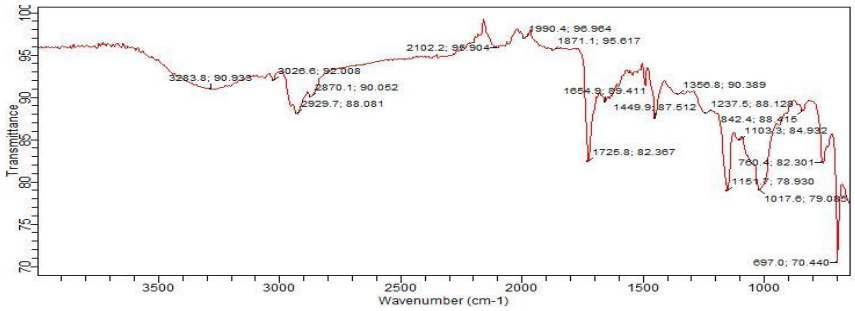

Fig. 2: FTIR Plot for Palm Kernel Oil

The presence of aromatic compounds was detected at 1990.4 cm^{-1} and 1871.1 with C-H bending. The strong absorbance at 697 cm^{-1} indicates the presence of alkanes**.**The presence of amines was detected at 1103.3, 1151.7, 1237.5 cm^{-1} with C-Nstretch. The OH stretch at 2870.1 cm^{-1} depicts the presence of hydroxyl group. Alkanes were detected at 1449.9 and 2929.7.

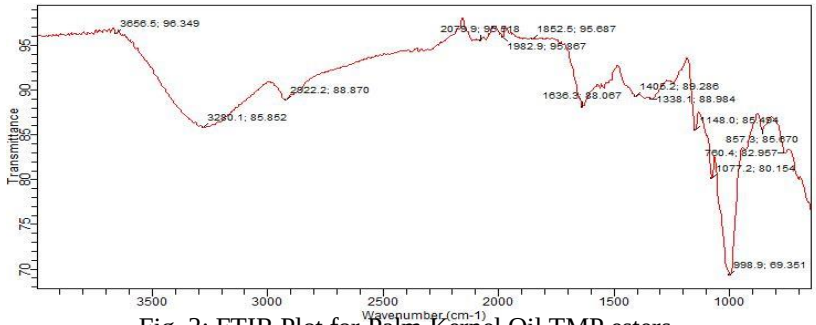

Fig. 3: FTIR Plot for Palm Kernel Oil TMP esters

The synthesized palm kernel oil-basedbio lubricant was analyzed by Fourier Transform infrared to ascertain that the transesterification reaction between methyl esters and trimethylolpropane (TMP) did effectively take place (Alang et al 2018)**.**FT-IR spectra were recorded using the IR Tracer-100 equipped with an Attenuated Total Reflectance (ATR) accessory. The spectrum diagram is shown in figure 3. The medium peak at 1077.2 cm^{-1}

represents amine group with C-N Stretching, the presence of aromatic group was detected at 1852.5 and 1982.9 with C-H bending. The weak absorption peak at 2822 depicts the presence of O-H group which is probably from the trimethyl-propane alcohol impurities used in the synthesis of bio lubricants.

IV. CONCLUSION

A bio lubricant was produced using Nigerian palm fruit (Elaeisguineensis) kernel oil as the base oil, this new bio lubricant development is essential so as to mitigate the environmental challenges associated with petro lubricants. The bio lubricant was synthesized using the two-stage transesterification reaction process. This bio lubricant was analyzed and the determined properties conformed to the approved ranges of the various biodiesel standards such as ISO VG 46. The quality of the produced bio lubricant can be improved by blending with different additives depending on the properties needing improvements.

ACKNOWLEDGEMENT

The authors of this paper will like to thank the Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University for providing an enabling environment to perform this work.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

[1]. Alang, M.B., Ndi-kontar, M.K., Sani, Y.M. and Ndifon, P.T. 2018. Synthesis and Characterisation of a Biolubricant from Cameroon Palm Kernel Seed Oil Using a Locally Produced Base Catalyst from Plantain Peelings. Green and Sustainable Chemistry, 8, 275-287. https://doi.org/10.4236/gsc.2018.83018

[2]. Appiah G. Tulashie S. K., Akpari E. E. A., Rene E. R., Daniel D. 2021. International Journal of Energy Research.;1–31.

[3]. Arbain, N.H and Salimon, J 2010. Synthesis of Jatropha curcas Fatty Acid Based Trimethylolpropane Ester.Empowering Science, Technology and Innovation Towards a Better Tomorrow, 9-15.

[4]. Bilal, S1, Mohammed-Dabo, I., Nuhu, M., Kasim, S., Almustapha, I. and Yamusa, Y. A 2013 Production of Biolubricant from Jatropha curcas Seed Oil Journal of Chemical Engineering and Material Science, 4,72-79.

[5]. Chandu S. Madankara B, Ajay K. Dalaia, S.N. Naik, Ind. 2013 CropsProd. 44139–144.

[6]. Corley,R.H.V.,Tinker, P. B. 2016. The oil palm. West Sussex, UK: Wiley-Blackwell. https://doi.org/10.1002/9781118953297

[7]. Eddy NO, Ukpong JA, Ebenso EE 2011. Lipids characterization and industrial potentials of pumpkin seeds (Telfairiaoccidentalis) and cashew nuts (Anacardiumoccidentale). E- Journal Chem. 8(4):1986-1992

[8]. Ekwenye UN, Ijeomah CA. 2005. Antimicrobial effects of palm kernel oil and palm oil. KMITL Sci J.;5;502-505.

[9]. Fox N, Stachowiak G. 2007. Vegetable oil-based lubricants — a review of oxidation. Tribology international; 40:1035-1046.

[10]. Heri A S, Yurna Y, Retno D S, Nanang S, Edy S and Abdul R P .2020. Cameroon Virescens Oil Palm (ElaeisGuineensis) From IOPRI's Germplasm AGRIVITA Journal of Agricultural Science. 42(2): 1–2

[11]. Ibiam J. A., and Anosike P. O., .2014. Extraction and Characterization of Palm Kernel Oil from The Kernel of Palm Tree (ElaeisGuineensis). International Journal of Current Research.vol 6. (11). 6696 – 6698

[12]. Jumat, S., Nadia, S. and Emad, Y. .2010.Biolubricants: Raw Materials, Chemical Modifications and Environmental Benefits. European Journal of Lipid Science and Technology, 112, 519-530

[13]. Nagendramma P, Kaul S. 2012. Development of Ecofriendly/Biodegradable Lubricants: an overview. Renew Sustain Energy; 16:764 –74

[14]. Naher L, Yusuf UK, Ismail A, Tan SG,2013..Ecological Status OfGanoderma and Basal Stem Rot Disease of Oil Palms (Elaeisguineensis Jacq.) AJCS. 2013; 7:1723-1727

[15]. Onwuka, G.I 2005. Food Analysis and Instrumentation: Theory and Practice. Naphthali Print, Lagos, 133-137.

[16]. Refaat AA 2010. Different Techniques For The Production of Biodiesel From Waste Vegetable Oil. Int. J. Environ. Sci. Technol. 7(1):183-213

[17]. Waleska C, David EW, Kraipat C, Joseph MP. 2005. The effect of chemical structure of base fluids on antiwear effectiveness of additives. Tribol. Int.; 38:321–6

[18]. Yang CY, Li ZFB, Long YF 2012. Review and prospects of Jatropha biodiesel industry in China.Renew. Sustain. Energy Rev.16:2178-2190.