SEET'17
Engineering for Self-Reliance

Proceedings of the 2017 Annual Conference of the School of Engineering & Engineering Technology (SEET), The Federal University of Technology, Akure, Nigeria, 11-13 July, 2017.

SYNTHESIS AND CHARACTERISATION OF BIO-LUBRICANT FROM PALM KERNEL OIL (RESPONSE SURFACE METHODOLOGY)

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ABSTRACT

Research has shown that plant oils (edible or non-edible) are potential source of lubricants due to their biodegradability, sustainability, renewability and eco-friendliness. Palm kernel oil was used as feed stock in this study due to its availability and affordability. It was trans-esterified without esterification (as its FFA was 1.92 mg KOH/g) to biodiesel using potassium hydroxide (KOH) as catalyst and methanol as solvent. The polyol ester was synthesised by adopting central composite design of response surface methodology (RSM) as the experimental design. Ethylene glycol was use as polyol for the bio-lubricant production with temperature, time and catalyst concentration as the independent variables. The result showed a maximum yield of 97.13 % at operating parameters of 120 ^{O}C, 60 minutes and 0.60 %wt/wt of temperature, time and catalyst concentration respectively. Some physicochemical properties of the bio-lubricant such as viscosity at 40 ^{O}C and 100 ^{O}C, flash point, pour point and viscosity index were determined as 42.10 cSt, 4.22 cSt, 183 ^{O}C, -6 ^{O}C and 232 respectively. The results were compared with relevant international standards which established its potential usage as gear oil.

Keywords: Palm Kernel Oil, Bio-lubricant, Ethylene glycol, Polyol, Temperature, Time and Catalyst

1.0 INTRODUCTION

The inflation in energy demand, depletion in the oil reserve, and negative environmental impacts of petroleum-based lubricants have stimulated the ongoing research on an alternative that is renewable and eco-friendly. Research has shown that vegetable based lubricant is considered to be a suitable alternative. However the use of vegetable oil in raw form is characterized with poor thermal stability, poor oxidation and low temperature properties. A lubricant is a substance (solid or liquid) initiated between two moving surfaces or contact bodies especially of a machine to minimize the effect of friction such as wear and promote its efficiency

(Salimon *et al.,* 2010). Other uses of lubricants are heat transfer (cooling agent), vibration and noise reduction, corrosion prevention and cleaning agent (Jain and Suhane, 2012). However, lubricants have been categorized into three categories depending on the base stock which can either be mineral, synthetic and biological based lubricants. Mineral base lubricants are majorly gotten from the fractionalization of crude oil at 300 ^{O}C and 370 ^{O}C and having carbon atoms in each molecule between 20 and 40 (Fan, 2010). Synthetic base lubricants are result from chemical modification made to mineral based lubricants. They possess preferable properties to mineral based lubricants. They can be used for very low temperature. Its anti-oxidancy ability is low due to the absence of sulphur and nitrogen content which naturally exist in mineral base lubricants (Bhushan, 2012). The mineral and synthetic base lubricants are toxic to the terrestrial and aquatic environment. Furthermore, they are characterized with non-degradability, non-renewability and poses danger to the growth and development of plant, animal and at long run man. The biological based lubricants can be of vegetable (e.g. palm kernel, ripe-seed, castor etc.) or of animal (e.g. sheep (lanolin), fish and wool oil). They are known as chemically triglycerides of fatty acid with higher inherent qualities such as excellent lubricity and biodegradability, flash point and lower toxicity enhancement, higher viscosity and viscosity index. They are non-toxic, renewable and eco-friendly. This unique features of biologically base lubricants has led to its increase in demand which recently accounts for 85-90 % of the total global lubricant production worldwide (Erhan *et al.,* 2006). Bio-lubricants are biologically base lubricants that are renewable, biodegradable and non-toxic to human, plant, animal and aquatic environment. Bio-lubricant has to undergo a lot of chemical modification in order to enhance the physicochemical properties and serve as a considerable substitute for petroleum or synthetic based lubricants (Jain and Suhane*,* 2012). The possibility of using vegetable oil as a potential feed stock for lubricants is due to the presence of triglycerols (Srivastava and Sahai, 2013; Willing, 2001). However chemical modification such as epoxidation, esterification, trans-esterification and selective hydrogenation can be carried out on crude vegetable oil to overcome the above constrains (Resul *et al.,* 2011). This study was aimed at the production of bio-lubricant from PKO by Response surface methodology (RSM). Major physicochemical properties of the synthesized PKO bio-lubricant were determined and compared with relevant international standards. Response surface methodology (RSM) for central composite design (CCD) was used to develop the experimental design used for this work. Response Surface Methodology (RSM) has gain the attention of many researchers in design of experiments owing to its numerous advantages. This is because Response Surface Methodology aids the improvement of the product from predicted property values as well as predicting the interactions of more than two or more parameters and effects due to combined contributions of the measured responses. It also helps in reducing the number of experiments and gives ideas of the pattern in which the measured response is affected by the corresponding variations in parameters (Alhassan *et al.,* 2014). The number of experiments designed by CCD is $X = 2^k + 2K + N$. Where X is the total number of experiments, K is the number of factors studied and N is the number of replicates. Central composite design in Response Surface Methodology is often laid out using Minitab or Design Expert Software.

2.0 MATERIALS AND METHODS

2.1 Materials

The crude palm kernel oil used for this study was obtained from a local market at Wushishi, Wushishi local Government area of Niger State. The materials used to conduct the experiment were separating funnel, measuring cylinder, thermometer, magnetic heating stirrer, viscometer, density bottle and two necks round bottom flask. Reagents such as Methanol ($CHOH_4$), Sulphuric acid (H_2SO_4), Potassium hydroxide (KOH), Phenolphthalein, and Ethylene glycol were sourced and used in the Department of Agricultural and Bioresources Engineering Laboratory, Federal University of Technology Minna, Niger State, Nigeria.

2.2 Methodology

2.2.1 Determination of acid value and free fatty acid

Three titrations were carried out and an average titre value of 0.7 was obtained. The acid value was then calculated using equation 1 (Bilal *et al.,* 2013).

$$\boldsymbol{Acid\ value} = \frac{(\boldsymbol{Molarity\ of\ KOH})(\boldsymbol{Titre\ value})\times(\mathbf{56.10})}{\boldsymbol{Mass\ of\ the\ sample}}\times\mathbf{100} \qquad 1$$

The result from equation 1 was then divided by two (2) to obtain the percentage of the free fatty acid.

2.2.2 Base trans-esterification

The base trans-esterification was done by measuring 500 ml of the crude PKO via measuring cylinder. It was then poured into a 1000 ml beaker and heated to a temperature of 55-60 ^oC. Methanol was used as the solvent in the ratio 1:5 of methanol to oil. 5.47 g potassium hydroxide (KOH) pellet was dissolved in the methanol to form potassium methoxide. The mixture was poured gently into the pre-heated crude PKO while maintaining the temperature at 55-60 ^oC on a magnetic heating stirrer and continuously stirred for 60 minutes. The product of the mixture was poured into a separating funnel and allowed to settle for hours until glycerol and impurities settled below the impure palm kernel oil methyl ester (PKOME). The impure PKOME was decanted and washed gently with warm water to discard KOH content until the warm water after washing appears clean. The pure PKOME was then air dried (Ojolo *et al.,* 2011).

2.2.3 Experimental design

The experimental design used for the synthesis of palm kernel oil bio lubricant was response surface methodology (RSM) using central composite design (CCD). This method was used to examine the relationship between the response variable and a set of experimental factors. The experimental factors for this study were temperature, time and catalyst concentration as shown in Table 1. The three (3) experimental factors were used to determine the number of experimental runs ($2^k + 2k + N$) which gave a total of 20 experiments as shown in Table 2. The produced palm kernel oil lubricant was then characterised according to ASTM standard.

Table 1: Independent variables and levels used for CCD for bio-lubricant

S/n	Independent variables	Code	Levels				
			-α	-1	0	+1	+α
1	Temperature (^oC)	X_1	93.18	100	110	120	126.82
2	Reaction time (min)	X_2	39.55	60	90	120	140.45
3	Catalyst concentration (%wt.)	X_3	0.33	0.40	0.50	0.60	0.67

Table 2: Palm kernel oil bio-lubricant yield using central composite design

RUNS	CODED FACTOR			ACTUAL FACTOR		
	X_1	X_2	X_3	Temp	Time	Catalyst
1	-1	-1	-1	100	60	0.40
2	+1	-1	-1	120	60	0.40
3	-1	+1	-1	100	120	0.40
4	+1	+1	-1	120	120	0.40
5	-1	-1	+1	100	60	0.60
6	+1	-1	+1	120	60	0.60
7	-1	+1	+1	100	120	0.60
8	+1	+1	+1	120	120	0.60
9	-1.68	0	0	93.18	90	0.50
10	+1.68	0	0	126.82	90	0.50
11	0	-1.68	0	110	39.55	0.50
12	0	+1.68	0	110	140.45	0.50
13	0	0	-1.68	110	90	0.33
14	0	0	+1.68	110	90	0.67
15	0	0	0	110	90	0.50
16	0	0	0	110	90	0.50
17	0	0	0	110	90	0.50
18	0	0	0	110	90	0.50
19	0	0	0	110	90	0.50
20	0	0	0	110	90	0.50

2.2.4 Bio-lubricant production

Thirty grams (30 g) of palm kernel oil methyl ester (PKOME) was weighed and poured into a two round bottom flasks attached to a Liebig condenser. After which a specific amount of ethylene glycol and KOH as catalyst were added. The mixture was then maintained at a temperature while stirring at a duration predetermined from the experimental design (CCD Matrix) and same was done for all the twenty (20) experimental runs as shown in Table 2. The product of the mixture was gently poured in a separating funnel and left to separate. This separation left the palm kernel oil bio-lubricant on top which was separated and washed with warm water to remove the catalyst added until clarity was obtained. It was then air dried (Bilal *et al.,* 2013).

3.0 RESULTS AND DISCUSSION

3.1 Acid value and free fatty acid (FFA)

The acid value or acidity of the crude palm kernel oil (CPKO) was determined as 3.93 % which was divided by two (2) and gave 1.91 % as the FFA. This value (1.91 %) was within the limit recommended for direct trans-esterification without necessarily esterifying the oil for effective base catalysed reaction (Nie, 2012).

3.2 Interaction effect of the process variables

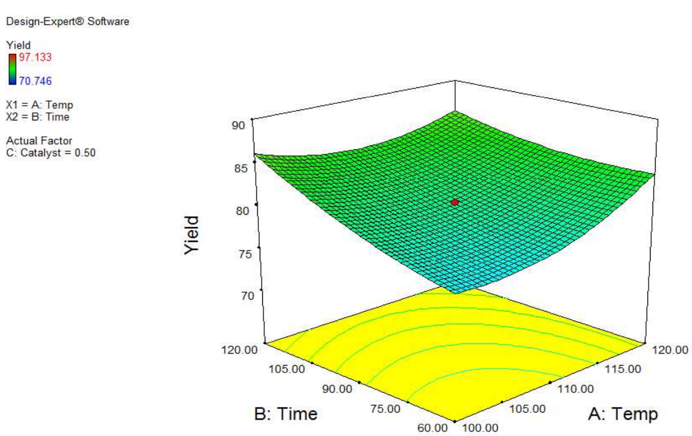

Figure 1: Effect of temperature and reaction time on the PKO bio-lubricant yield

Figure 1 shows the effect of temperature and time on the bio-lubricant yield as the catalyst concentration was kept constant at 0.50 %. Temperature was varied at low and high value of 100 ^{o}C and 120 ^{o}C respectively, while reaction time was varied from 60 to 120 minutes. The reaction time had more effect on the bio-lubricant yield as shown in Figure 1. Simultaneous increase in the temperature and time also increased the yield.

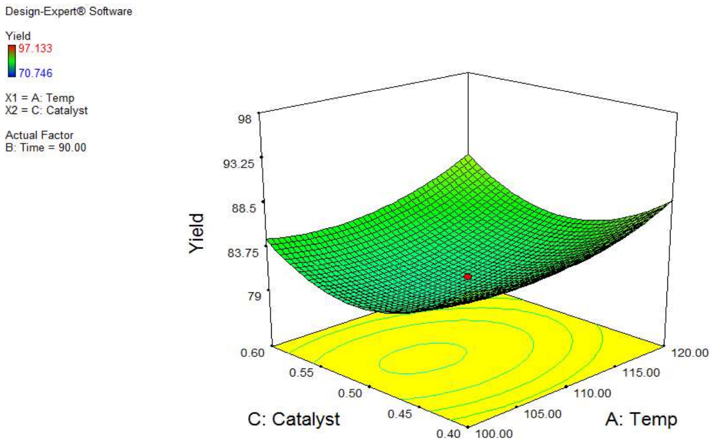

Figure 2: Effect of temperature and catalyst concentration on the PKO bio-lubricant yield

Figure 2 shows the effect of temperature and catalyst concentration on yield. The Figure shows that the temperature had more significant effect on the bio-lubricant yield while an increase in temperature and catalyst concentration also increases the yield.

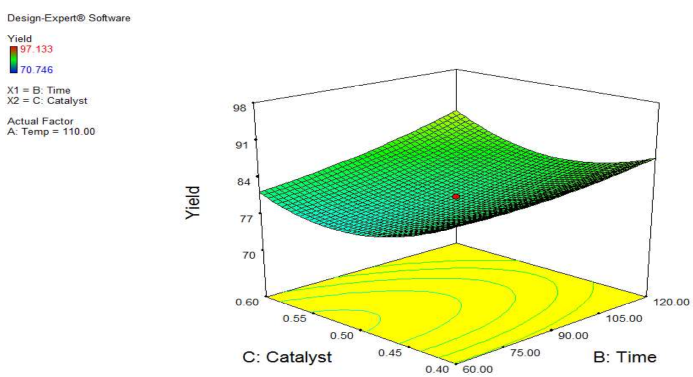

Figure 3: Effect of time and catalyst concentration on the PKO bio-lubricant yield

Figure 3 shows the interaction of time and catalyst concentration as the factors were varied from low level to high level at 60 to 120 ^{O}C and 0.40 to 0.60 % respectively . It shows that the reaction time had more significant effect on the bio-lubricant yield than the catalyst concentration while the interaction of the two factors also increases the bio-lubricant yield.

3.3 Palm kernel oil bio-lubricant yield and its physicochemical properties

Table 3: Palm kernel oil bio-lubricant yield

INDEPENDENT VARIABLES				YIELDS	
RUNS	**X_1**	**X_2**	**X_3**	**PREDICTED YIELD %**	**ACTUAL YIELD %**
1	100	60	0.40	84.096	86.793
2	120	60	0.40	80.318	80.470
3	100	120	0.40	80.318	84.283
4	120	120	0.40	91.929	93.083
5	100	60	0.60	92.641	84.283
6	120	60	0.60	94.222	97.133
7	100	120	0.60	78.391	70.746
8	120	120	0.60	80.318	80.476
9	93.18	90	0.50	90.232	87.917
10	126.82	90	0.50	80.318	80.480
11	110	39.55	0.50	89.978	90.533
12	110	140.45	0.50	91.344	94.640
13	110	90	0.33	89.012	87.797
14	110	90	0.67	86.986	93.153
15	110	90	0.50	80.318	80.470
16	110	90	0.50	89.703	86.993
17	110	90	0.50	80.318	80.473
18	110	90	0.50	79.991	86.553
19	110	90	0.50	87.707	89.906
20	110	90	0.50	83.575	79.343

X_1 = Temperature, X_2 = Time and X_3 = Mole Ratio

Table 4: Physicochemical properties of palm kernel oil bio-lubricant

S/N	Property	This study	ISO VG-46	ISO VG-220
1	Pour point (^{0}C)	-6	<-10	-6
2	Flash point (^{0}C)	183	220	265
3	Viscosity @ 40 ^{0}C (cSt)	42.10	>41.40	>12
4	Viscosity @ 100 ^{0}C (cSt)	4.22	>4.10	>4.10
5	Viscosity index	232	>90	>50

The results of the yield and characterisation of the PKO bio-lubricant are shown in Tables 3 and 4 below. The result showed a maximum yield of 97.13 % at operating parameters of 120 ^{O}C, 60 minutes and 0.60 %wt/wt of temperature, time and catalyst concentration respectively as shown in Table 3.

3.3.1 Pour point

Pour point is the property of bio-lubricant that determines its low temperature usability. The PKO lubricant has a pour point of -6 ^{O}C as shown in Table 4. This value is in agreement with the value specified by International standard organisation for viscosity grade (ISO VG-220). The value from this work (-6 ^{O}C) is slightly higher than the value (-7 ^{O}C) reported by Bilal *et al.* (2013) for jatropha curcas bio-lubricant but slightly lower than -5 ^{O}C obtained by Biniyam *et al.* (2015) for castor seed oil bio-lubricant. This value is also much lower than the value (19) reported by Musa *et al*. (2016) for PKO lubricant. Arbain and Salimon (2010) reported that higher degree of branching of esters leads to higher pour points which are desirable properties of a lubricant. Also, from the result shown in Table 3, the pour point value recorded in this study agrees with ISO VG-220 but higher than ISO VG-46 viscosity requirements. The reported value of pour point for the synthesized PKO lubricant shows that it can be used at low temperature regions.

3.3.2 Viscosity

The measure of the ability of oil to flow is known as viscosity (Dave *et al.,* 2014). The viscosities of PKO bio-lubricant were determined to be 42.10 cSt at 40 ^{O}C and 4.22 cSt at 100 ^{O}C respectively. The values are in line with ISO VG-46 and ISO VG-220 requirements. This is an indication that the oils will have low deposit upon injection into the combustion chamber (Abdulkareem *et al.,* 2014). These values obtained for this research are lower than the values (55.22 cSt and 10.96 cSt at 40 ^{O}C and 100 ^{O}C respectively) reported by Bilal *et al.* (2013) for *jatropha curcas* bio-lubricant. The differences observed may be due to the fatty acid profile of the base oil or the process conditions/catalytic modification techniques used. The finding depict that PKO polyol ester (bio-lubricant) has potential application as a gear oil in automobile as its properties conform to ISO VG 46 and ISO VG 220 requirement for this type of lubricant (Musa *et al*., 2015).

3.3.3 Viscosity index

The variation in the behaviour of the lubricant when subjected to different temperatures is referred to as viscosity index (VI). For this study, the viscosity index of PKO bio-lubricant recorded was 232 as shown in table 3. This value obtained (232) is in agreement with the standard specified by ISO VG-46 and ISO VG-220 standard specification for light gear oil and higher than 195.22 reported by Bilal *et al.* (2013), 191 reported by Musa *et al*. (2015) and 201 reported by Musa *et al*. (2016). High VI permits lesser wear and lubricant consumption during application. Lubricants with higher VI (>130) find a wide variety of applications and the higher the VI, the less significant the viscosity variation of the synthesized PKO base oil lubricant with temperature from the ambient temperature when engine components are at rest to high operating temperatures (Musa *et al*., 2015).

3.3.4 Flash point

Flash point is the lowest temperature at which a lubricant gives off enough vapour to form an ignitable mixture with air. In evaluating the un-safe nature of PKOME and its bio-lubricant during usage and storage, its flash point has to be determined. For this study, 183 ^{O}C was obtained for the PKO bio-lubricant as given in table 3. However, this value is lower than the values (215 ^{O}C and 249 ^{O}C) reported by Musa *et al*. (2015) for castor oil bio-lubricant and Musa *et al*. (2016) for palm kernel oil lubricant.

4.0 CONCLUSION

This study showed that PKO has the potential for the production of biodegradable lubricant using reactive extraction. Some physicochemical properties of the bio-lubricant such as viscosity at 40 ^{O}C and 100 ^{O}C, flash point, pour point and viscosity index were determined as 42.10 cSt, 4.22 cSt, 183 ^{O}C, -6 ^{O}C and 232 respectively which show a quantitative agreement with ISO viscosity grade requirements and established its potential usage as light gear oil.

REFERENCES

Alhassan, Y., Kumar, N., Bugaje, I. M. & Mishra, C. (2014). Optimization of Gossypium arboreum seed oil biodiesel production by central composite rotatable model of response surface methodology and evaluation of its fuel properties. *Journal of Petroleum Technology and Alternative Fuels*, *5*(1), 1-12.

Arbain, N. H. & Salimon, J. (2010). Synthesis and characterization of ester trimethylolpropane based Jatropha curcas oil as bio-lubricant base stocks. *Journal of Science and Technology*, *2*(2).

Bhushan, B. (Ed.). (2012). *Fundamentals of tribology and bridging the gap between the macro- and micro/nanoscales* (Vol. 10). Springer Science & Business Media.

Bilal, S., Nuhu, M., & Kasim, S. A. (2013). Production of bio-lubricant from Jatropha curcas seed oil. *Journal of Chemical Engineering and Materials Science*, *4*(6), 72-79.

Erhan, S. Z., Sharma, B. K. & Perez, J. M. (2006). Oxidation and low temperature stability of vegetable oil-based lubricants. *Industrial Crops and Products*, *24*(3), 292-299.

Fan, W. T. C. (2010). Regeneration of used petroleum-based lubricants and bio-lubricants by a novel green and sustainable technology. University of Southern California.

Jain, A. K. & Suhane, A. (2012). Research Approach & Prospects of Non edible vegetable oil as a potential resource for bio-lubricant-A review. Advanced Engineering and Applied Sciences: *An International Journal*, 1(1), 23-32.

Mohammed-Dabo, I. A., Ahmad, M. S., Hamza, A., Muazu, K. & Aliyu, A. (2012). Cosolvent transesterification of Jatropha curcas seed oil. *Journal of Petroleum Technology and Alternative Fuels*, *3*(4), 42-51.

Musa, U., Mohammed, I. A., Auta, M., Gana, E. M., Ahmed, A. N. & Ibitoye, J. O. (2016). Parametric Studies of Bio-lubricant Production from Palm Kernel Oil. *Proceedings of the Fourth International Conference on Engineering and Technology Research February 23 - 25, 2016, 4, 376-381.*

Musa, U., Mohammed, I. A., Sadiq, M. M., Aberuagba, F., Olurinde, A. O. & Obamina, R. (2015). Synthesis and Characterization of Trimethylolpropane-Based Bio-lubricants from Castor Oil. *Proceedings of the 45th Annual Conference of NSChE, 5th-7th November, Warri, Nigeria. 248-253.*

Nie, J. (2012). *Synthesis and evaluation of polyol based bio-lubricants from vegetable oils* (Doctoral dissertation, University of Saskatchewan Saskatoon).

Ojolo, S. J., Adelaja, A. O., Ogbonnaya, M. & Ogunsina, B. S. (2011). Study of an effective technique for the production of biodiesel from Jatropha oil. *Journal of emerging trends in Engineering and Applied Sciences*, *2*(1), 79-86.

Resul, M. F. M. G., Ghazi, T. I. M. & Idris, A. (2011). Temperature dependence on the synthesis of jatropha bio-lubricant. In *IOP Conference Series: Materials Science and Engineering* (Vol. 17, No. 1, p. 012032). IOP Publishing.

Salimon, J., Noor, D. A. M., Nazrizawati, A. T., Firdaus, M. M. & Noraishah, A. (2010). Fatty acid composition and physicochemical properties of Malaysian castor bean Ricinus communis L. seed oil. *Sains Malaysiana*, *39*(5), 761-764.

Srivastava, A. & Sahai, P. (2013). Vegetable oils as lube basestocks: A review. *African Journal of Biotechnology*, *12*(9).

Willing, A. (2001). Lubricants based on renewable resources–an environmentally compatible alternative to mineral oil products. *Chemosphere*, *43*(1), 89-98.