P 024

SYNTHESIS AND CHARACTERIZATION OF TRIMETHYLOLPROPANE-BASED BIOLUBRICANTS FROM CASTOR OIL

Musa, U., Mohammed I.A., Sadiq M.M., Aberuagba F., Olurinde A.O.and Obamina R

Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, P.M.B. 65, Minna, Niger State.

Corresponding Author E-mail Address: umar.musa@futminna.edu.ng Mobile no.: +234(0)8032318723

Abstract:

This paper presents the synthesis and characterization of Trimethylolpropane (TMP) based biolubricant from castor oil seed. Castor Oil Methyl Ester (COME) was synthesized at a temperature of 60 ^{o} C, reaction time of 1 hour, molar ratio of oil to methanol of 1:250 and 1 % wt/wt catalyst via (in situ transesterification) reactive extraction. The TMP ester (Biolubricant) from castor oil was further subsequently synthesized at a temperature of 120 ^{o} C, reaction time of 1 hour, molar ratio of COME to trimethylolpropane (TMP) of 4:1 and catalyst concentration of 0.8 wt%. The TMP ester of castor oil was characterized for its flash point, pour point, viscosity at 40 ^{o} C and at 100 ^{0} C and viscosity index. Fourier Transform Infra-Red (FT-IR) and Gas Chromatography-Mass Spectrophotometer (GC-MS) analysis were carried out on the Biolubricant to confirm the presence of ester group and the composition of the synthesized lubricant. The COME yield was 98.42wt% based on the weight of the oil seed. The transesterification of in situ derived COME with TMP yielded 96.56 wt% of the TMP ester (Biolubricant). The characterization of biolubricant shows favourable lubricating characteristics. The presence of ester group in the resulting biolubricant was confirmed by FT-IR analysis and the percentage of the composition of biolubricant determined by GC-MS analysis revealed a fatty acid composition of 2.88 %, monoester of 0.63 %, diester of 1.70 % and triester (desired end product) of 94.79 %. These FT-IR and GC-MS analysis result shows the effectiveness of the chemical modification of castor oil to biolubricant. The result of characterization of the biolubricant compares favourably with the ISO VG thereby establishing the potential of the biolubricant as gear oil.

Keywords: *Biolubricant; in situ transesterification; Trimethylolpropane; Characterization; Methyl ester; Castor oil*

1.0 Introduction

Lubricating oils have found wide varieties of application in automobile, refrigeration and compressor (Kamil and Yusup, 2010). A number of lubricant base oils such as petroleum or mineral oil, synthetic oil, re-refined and vegetable oil are used for the manufacturing of lubricating oil (Salimon and Salih, 2009). Synthetic lubricating oils characteristically have great lubricity when compared with petroleum based lubricants (Resul *et al.*, 2001). However, they are four to eight times more expensive than mineral oil based lubricants. Mineral oil based lubricants derived from petroleum are the ones in common use and they have a global market share of 95 % (Resul *et al.,* 2001; Amit and Amit, 2012).

Petroleum reserves are finite (Amit and Amit, 2012). Petroleum products are also very toxic and non biodegradable. Vegetable oil is another example of base oil that can be used for lubricant production. Its advantage over the latter base oil because it can be locally produced, cheap, renewable and very biodegradable when compared to mineral oil. It has excellent lubricity, low volatility, non-toxic and high viscosity index (Kamil and Yusup, 2010; Salimon and Salih, 2009). The use of vegetable oil as a lubricant base oil has is limited because of low thermo-oxidative stability (Resul *et al.,* 2001), poor corrosion protection and hydrolytic stability (Kamil and Yusup, 2010). The presence of β hydrogen atom in the hydroxyl group of the glycerol is the major cause of low thermal and oxidation stability associated with pure vegetable oil (Resul *et al.,* 2001).

Research has shown that a number of chemical modification techniques such as epoxidation, selective hydrogenation and transesterification of vegetable oil can be used to overcome these limitations. Transesterification of vegetable oil have a more probable possibility for the production of lubricant with better temperature performance and appreciable fluidity (Resul *et al.,* 2001). This techniques help to effectively replace the hydrogen atom on the β-carbon structure of the oil. This improvement brought about by change in the structure of the oil by conversion into a new ester called the polyol ester (PE). Common polyhydric alcohols used in the transesterification of fatty acids methyl ester are neopentyl glycol (NPG), pentaerythritol (PT) and trimethylolpropane (TMP). TMP is however the most popular alcohol for polyol ester synthesis because the resulting ester are characterized with superior lubricating properties. TMP is known for it high melting point and branched structure which are vital features for biolubricant synthesis (Kamil and Yusup, 2010). Numerous research have been documented on the synthesis of biolubricant from vegetable oil using TMP as a polyol (Kamil and Yusup, 2010; Resul *et al*., 2001; Uosukainem *et al.,* 1998; Jose, 2011; Arbain and Salimon, 2011; Phani *et al.,* 2013; Mohammed *et al.,* 2011; Ghazi *et al.,* 2010). Nearly in all these studies reported conventional methods of transesterification were used for biodiesel synthesis. This involves various stages: oil extraction, purification and subsequent esterification /transesterification. These multiple biodiesel processing stages constitute greater than 70 % of the total biodiesel production cost if refined oil is used as feedstock (Ponsak *et al.,* 2012) Reactive extraction (*in situ* transesterification) permits the synthesis of biodiesel from oil bearing seed directly without prior extraction. This technique is characterized with the simplification of the biodiesel production technology (Zakaria and Harvey, 2012). The process allows essentially both extraction of oil from its seed and subsequent conversion to take place in a just one single step with the alcohol acting as a solvent for extraction and as a reagent for transesterification (Shuit *et al.,* 2010). Madankar *et al.* (2013) reported the *in situ* transesterification of castor oil seed and stated the methyl ester produced has appreciable potential for biolubricant production.

Castor plant also known as *Ricinus communis* L. belongs to the family *Eurphorbiaceae* and grows mostly in tropical and subtropical areas. Castor plants seed contain castor oil. The seed contains up to 55 % of the oil and can be up to 69 % when released from a peel. Castor seed contains highly poisonous protein (ricin) (ICOA, 2013). Castor oil is soluble in alcohol (Nurbakhit, 2012). Castor oil possesses greater density, viscosity, ethanol solubility and lubricity when compared with other vegetable oils. Castor oil has been used on the manufacturing of more than 800 products, ranging from bullet-proof glasses, contact lenses, lipsticks, metal soaps, special engine and high rotation reactors lubricants, high resistance plastics, and polyurethanes (ICOA, 2013; Nurbakhit, 2012). According to Bugaje and Mohammed (2008) castor plant is known to grow very well across the entire northern states of Nigeria as weed. The authors are of the opinion that using edible oil for bio energy generation may lead to food crises and uneconomical.

The objective of work is to study the synthesis and characterization of trimethylolpropane ester (TMP ester) of castor oil. To the best of our knowledge this study is one of the very attempts to develop a biolubricant from a typical Nigerian Castor oil seed using an *in situ* transesterification (reactive extraction) for castor methyl ester production.

1. Methodology

1.1. Materials

The castor seed was obtained from a local farm in Minna, Nigeria. The moisture content of the seed was determined to be 4.67 %. The seed was ground to a small particle of 0.5 mm using mortar and pestle. Oil was
Extracted from the seed using sohxlet extractor and the oil content of the seed were determined. n- hexane and potassium hydroxide, methanol obtained from Sigma-Aldrich (St. Louis) and were of analytical grade

1.2. Transesterification of COME and analysis

The COME was initially synthesized according to methods reported by Madankar *et al.,* (2013) and Zakaria and Harvey (2012). The production of Castor oil Biolubricant (COB) was carried out according to the work of Arbian and Salimon (2011). The experimental was conducted in a two-necked round bottom flask equipped with a thermometer and mounted on a magnetic stirrer hot plate. The flask was fitted with Liebig condenser and 1 horse power vacuum pump. A known quantity (20 g) of COME was poured into the round bottom flask and preheated to 60^{o}C, after which 2.3g of TMP and 0.016g of KOH catalyst were added then the temperature increased to 130^{o}C. The molar ratio of methyl ester to TMP was kept at 4: 1; reaction time at 1 hour and catalyst concentration of 0.8 % wt/wt. After the reaction time was completed, the solution was transferred into a separating funnel and washed with warm water containing 0.6 g of ortho-phosphoric acid which corresponds to 10%wt/wt oil. The resulting TMP ester then was dried over a hot plate

Result and Discussion

The sample was analyzed using FT-IR and GC-MS and results tabulated as shown in Table 2 and Table 3. The physio-chemical properties were also determined and compared with other reported work as shown in Table 1

Table 1: Characterization of Biolubricant

Properties	Viscosity at 40°C	Viscosity at 100°C	Viscosity Index	Pour Point (°C)	Flash Point (°C)	Reference
This study	45.3	9.21	191	-8	215	
ISO VG 46	>41.4	>4.1	>90	-10		Bilal *et al*. (2013)
ISO VG 220	>12	>4.1	>50	-6	265	(Nandor *et al.*, 2012)
Mineral Oil based Lube	568	27.8	62	-4		Nandor *et al.*(2012)
Synthetic Lube	9.03	2.70	148	-	204	Nandor *et al.*(2012)
Fusel oil based Lube	6.30	2.28	207	-27	211	Nandor *et al.* (2012)
Canola oil based Lube	40.5	7.8	204	-66		Phani *et al.* (2013)
Jatropha oil based Lube	42.37	9.37	183	-3		Mohammed *et al.* (2011)

The yield of the oil extracted was obtained to be 55.2% based on weight of oil seed used while the optimum methyl ester yield was 98.42 % with a corresponding purity of 90.05 %.The percentage yield of COB was 96.56% at the optimum conditions; COME to TMP ratio of 4:1, temperature 120 °C, catalyst concentration 0.8 % w/w and reaction time of 60 minutes.

The viscosity of the castor oil based biolubricant was determined to be 45.3 and 9.21 Cst at 40 and 100 °C respectively as shown in Table 1. This result shows that there was a remarkable improvement in the viscosity of the castor oil methyl ester (11 cst) upon transesterification with TMP. The value obtained shows the biolubricant synthesized met the ISO viscosity grade requirement and consistent with some reported literatures (Nandor *et al.*, 2012; Bilal *et al*., 2013). The variations observed may be attributed to differences in the fatty acid profile of the base oil or the process conditions /catalytic modification techniques used. The finding depict that castor polyol ester (biolubricant) 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. There are three standard specification for lubricants of which ISO Viscosity Grade (VG) 46 is one of them and it represents over 80 % of all lubricant consumed (Bilal *et al*., 2013).

Viscosity index (VI) shows the behaviour of the lubricant at different temperature. Castor base oil synthesized lubricant was observed to have a high VI of 191 as shown in Table 1. This exceptionally good VI value obtained was higher than reported values (Mohammed *et al.*, 2011) but lower than the value of Phani (2012). High VI permits lesser wear and lubricant consumption during application. Lubricants with higher VI (>130) find a wide variety of applications (Mohammed *et al.*, 2011). The value observed in this study fulfils the ISO VG 46 and ISO VG220 standard specification for light gear oil. The result indicate that the higher the VI, the less significant the viscosity variation of the synthesized castor base oil lubricant with temperature from ambient temperature when engine components are at rest to high operating temperatures. The quality of the biolubricant synthesized were of comparable standards with commercial lubricants.

Pour point is the property of biolubricant that determines its low temperature usability. The castor derived biolubricant has a pour point of -8 °C which is an appreciable improvement from - 4 °C for the COME reacted with the TMP. This improvement is one of the properties imparted on the COME upon reacting it with a branched polyol (TMP). Arbain and Salimon (2011) stated that higher degree of branching of esters leads to higher pour points which are desirable properties of a lubricant. From the result shown in Table 1, the pour point value recorded in this study shows close proximity to the ISO viscosity requirement. The reported value of pour point for the synthesized TMP ester shows its excellent low temperature usability/performance.

Flash point is the lowest temperature at which a lubricant gives off enough vapour to form an ignitable mixture with air. It is used as an assessment for the hazardous potential of a lubricant. The result of the analysis in Table 1 shows that the flash point of ester TMP produced was 215 °C. The high flash point indicates the safety of the resulting ester of TMP. The value also shows appreciable consistency with the reported literature (Nandor *et al.*, 2012)

3.1 FT-IR Analysis

FTIR was used to determine the presence of ester group of TMP ester in the biolubricant produced

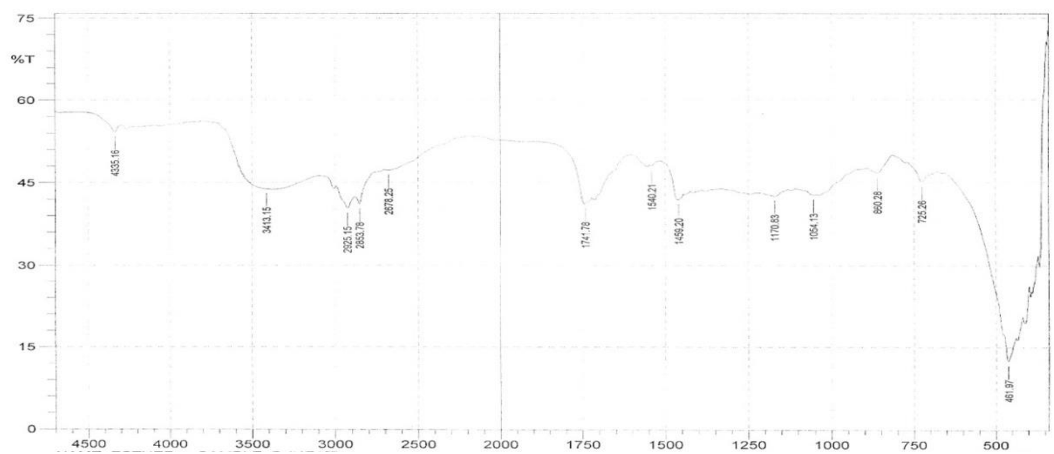

Figure 1.1: FT-IR Result for Castor Oil Biolubricant

Table 2: FT-IR composition of biolubricant

No. of Peaks	Peaks Position	Wave length (cm^{-1})	Identification
1	461.97	477.40	Polysulfides (S-S Stretch)
2	725.26	770.59	Aromatic C-H
3	860.28	892.11	Vinylidene C-H
4	1054.13	1107.18	Aliphatic fluoro compounds (C-F Stretch)
5	1170.83	1219.05	Aromatic C-H
6	1459.20	1461.13	Carbonate ion
7	1540.21	1543.10	Carboxylate (carboxylic acid salt)
8	1741.78	1742.74	Ester
9	2678.25	2680.18	Aldehyde
10	2853.78	2881.75	Methyl C-H
12	3413.15	3430.51	Hydroxyl group

According to Coates (Coates, 2000) wavelength between 3300 cm^{-1} - 3100 cm^{-1} shows the presence of alcohol, the non-appearance of this wavelength in this result as shown in Table 2depicts the absence of alcohol. This is because the OH bond in TMP has effectively reacted with the fatty acid methyl ester to produce TMP ester. There was also an observed shift in the wavelength of 1543.1 cm^{-1} for the spectrum of carboxylic acid functional group to 1742.74 cm^{-1} for the spectrum of TMP ester. This is quite related to the work of Arbain and Salimon (2011).

3. 2 Result of GC analysis

The summary of the fatty acid composition of castor oil biolubricant is shown in Table 3.

Table 3: Composition of castor oil biolubricant

Products	Percentage (%)	Composition
Fatty acid	2.88	
Monoester	0.63	
Diester	1.70	
Triester	94.79	

The composition of fatty acid in the biolubricant produced was 2.88 % which is higher than that reported by Arbain and Salimon (2011). This may be due to difference in feed stock and variation in experimental conditions. However, the fatty acid consists mainly of ricinoleic acid which has good lubricating properties and can however improve the properties of the biolubricant. The percentage of monoester (ME) is quite low (0.63) due to rapid reaction that takes place in the conversion of ME to diester (DE). However, the rate of conversion of DE to TE is lower compared to that of ME to DE, thus, the percentage of DE is higher (1.70) than that of ME. As the reaction proceeds DE is converted to Triester (TE) which is the desired product composition in biolubricant. Composition of TE was 94.79 % which is higher than that reported by Ghazi *et al.*, (2010) at 90 % composition of TE and lower than 98.1 % reported by Arbian and Salimon (2011).

Conclusion

This study showed that Castor oil has the potential for the production biodegradable lubricant using reactive extraction. The experimental result of biolubricant produced show that TMP ester exhibit favourable characteristic. FTIR analysis result shows the absence of OH group of TMP and presence of TMP ester. Complimentary GC-MS analysis result shows that high value of triester (94.79 %) was obtained after chemical modification depicting the effectiveness of the conversion process. The TMP esters of castor oil produced shows quantitative agreement with ISO viscosity grade requirement and establish its potential usage as light gear oil. The innovation in this manuscript is that it is one of the very first attempts to study the synthesis of TMP ester of castor oil employing in-situ transesterification for production of COME before subsequent conversion to biolubricant.

Acknowledgements

The authors acknowledge the Tertiary Education Fund (TETFUND) of Nigeria for providing the grant that financed this research and Federal University of Technology for the support provided to facilitate the attendance of the conference. We also wish to acknowledge the support of Jikkah Ester Bello during the course of Laboratory synthesis of biodiesel via reactive extraction.

References

Amit K. J.and Amit S. (2012). Research Approach & Prospects of Non Edible Vegetable Oil as a Potential Resource for Biolubricant - A Review, *Advanced Engineering and Applied Sciences*: An International Journal, pp.23-32, available online at http://www.urpjournals.com

Arbain, N. H. and Salimon J. (2011);Synthesis and characterization of ester trimethylolpropane based *Jatropha curcas* oil as biolubricant base stocks, *Journal of Science and Technology*, 47-58.

Bilal S, Mohammed-Dabo I. A, Nuhu M, Kasim, S. A, Al-mustapha I. H & Yamusa Y. A (2013) Production of biolubricant from *Jatropha curcas* seed oil, *Journal of Chemical Engineering and Materials Science*, 4(6), pp. 72-79,

Bugaje I.M. & Mohammed, I.A (2008) *Biofuel Production Technology*. Science and Technology Forum (STF), 1st Edition, Zaria, Nigeria, pp 1-65.

Coates J. (2000). Interpretation of infrared spectra: A practical approach in encyclopedia of analytical Chemistry, R. A. Meyers (Ed.) John Wiley & Sons, Newtown, USA, 2000, 10815- 10837.

Dormo N., K. Belafi-Bako, L. Bartha, U. Ehrenstein, L. Gubiczaan (2004) Manufacture of an environmental-safe biolubricant from fusel oil by enzymatic esterification in solvent-free system, *Biochemical Engineering Journal*, 22, pp. 229–234

Ghazi, T. I. M., Gunam R. M. F., and Idris A (2010) Production of an improved bio based lubricant from *Jatropha curcas* as renewable source. In: Proceedings of the Third International symposium on Energy from Biomass and waste, Nov. 8-11, Venice, Italy,1-10.

Interntional Castor Oil Association (ICOA) Castor Oil Chemistry It's Derivatives and Their Applications: Technical Bulletin 2013.

José A. C. D (2011). *Biodegradable Lubricants and Their Production Via Chemical Catalysis*, Tribology - Lubricants and Lubrication, Dr. Chang-Hung Kuo (Ed.), InTech. Available from:http://www.intechopen.com/books/tribology-lubricants-and lubrication/biodegradablelubricants-and-their-production-via-chemical-catalysis, pp. 185-200.

Kamil R. N. and Yusup S.(2010). Modeling Kinetics for transesterification of palm- based methyl esters with trimethylolpropane, *Bioresource Technology* 101, pp. 5877-5884.

Madankar, C. S., Subhalaxmi, P., and Naik, S. N. (2013) Parametric study of reactive extraction of castor seed (*Ricinus communis L.*) for Methyl ester production and its potential use as biolubricant, *Industrial crops and Products,* 43, 2283 – 290.

Mohammed F. M. G. R., Ghazi, I. M. T., and Azni, I. (2011); Temperature dependence on the synthesis of *jatropha* biolubricant, In proceedings of IOP conference series: *Materials science and Engineering*, 17, 012032, doi:10.1088/1757-899X/17/1/012032.

Nándor N, Tamás B, Katalin Bélafi-Bakó, László B. and László G. (2012). Biotechnological utilization of fusel oil for biolubricant production, food Industrial Processes - Methods and Equipment, Dr. Benjamin Valdez (Ed.), InTech, Availablefrom:http://www.intechopen.com/books/food-industrial-processes-methods-and equipment/biotechnological-utilisation-of-fusel-oil-for-biolubricant-production.

Nurbakhit I. (2012). Preparation and research on properties of castor oil as a diesel fuel additive, *Applied Technologies & Innovations,* 6(1), Pp.30-37.

Phani S. K. (2013) Comparative tribological property evaluation of trimethylolpropane-based biolubricants derived from methyl oleate and canola biodiesel, *Industrial Crops and Products,* 50, 95– 103.

Ponsak J., Chantaraporn P. and Anurak P. (2012), Single effects of reaction parameters in reactive extraction of palm fruit for biodiesel production, *Chiang Mai J. Sci*.; 40(3), pp 401-407.

Resul G, M. F. M., Mohd. Ghazi, T. I., Muhammad Syam, A., and Idris, A (2001) Synthesis of Biodegradable lubricant from *Jatropha* oil with high content of free fatty acids, Pp 1-6.

Salimon, J. and Salih, N., (2009). Oleic Acid Diesters: synthesis, characterization and low temperature properties, *European Journal of Scientific Research,* 32 (2), pp. 216 – 222.

Shuit, S. H., Lee K. T., Azlina, H. K., and Suzana, Y. (2010); Reactive extraction and *in-situ* esterification of *Jatropha curcas* L. seeds for the production of biodiesel, *Fuel,* 89, 527 – 530.

Uosukainem E., Linko, Y.Y., Lamsa, M., Tervakangas T and Linko P (1998). Trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants, *Journal of the American Oil Chemist Society*, 75 (11), pp 1557-1563.

Zakaria, R and Harvey, A. P. (2012) Direct production of biodiesel from rapeseed by reactive extraction /*in-situ* trans-esterification, *Fuel processing technology*, 102, 53 – 60.