

Synthesis and Characterization of Custard Apple seed oil Bio-Lubricant

Leelamani Pillai¹, Gajendra Kumar^{2*}

¹ Department of chemical Engineering Bhagwant University Ajmer-305004 (R.J.)

²Department of Chemistry, Krishna College, Bijnor-246701 (U.P.)

Abstract:

World crude oil reserves are limited; its prices are going up and out of control. Their environmental issues created a big problem for emerging generations. Therefore, it is necessary to explore the possibility of using automotive lubricants with vegetable base oil. Vegetable oils have many of the desirable properties of lubricants such as good contact lubrication, high viscosity index, renewal capacity, degradability and high flash point. The direct application of vegetable oil as a vehicle lubricant is less favourable due to its poor thermo oxidative stability; cold flow behaviour and poor anti wear characteristics. The present research detailed in this document refers to chemical modification of custard apple seed oil through the process of epoxidation, hydroxylation and esterification to improve its thermo oxidative stability, the behaviour of cold flow and antiwear characteristics. The formation of epoxide and hydroxyl group was confirmed by infrared spectral analysis by Fourier transform infrared radiation. The present work also focussed on the problem of friction and wear characteristics of chemically modified custard apple seed oil bio lubricant and commercial synthetic lubricant (SAE20W40) both contaminated by diesel using a four ball tribometer under same operating conditions. The chemically modified custard apple seed oil shows good oxidative stability, better cold flow behaviour and improved performance in terms of frictional force and coefficient of friction.

Keywords: Custard apple seed oil, bio-lubricant, epoxidation, hydroxylation, Four ball tribometer, Fourier transform infrared radiation.

I. Introduction

The greater attention to environmental resources, limited oil resources, the scarcity, the high cost of synthetic products and the high carcinogenic content in petroleum products make it necessary to study the possibilities of producing fuels and lubricants for alternative feeding. Interest in the use of automotive fuel and lubricants from plants has increased considerably in many countries and in India. Although India is agriculture-oriented, there is little information and development of automotive lubricants from agricultural feed stock. (Horner, 2002) reported that over half of the lubricants sold worldwide pollute the environment due to the complete spill of lubrication and evaporation[1]. The most desirable components for lubricants are oils with a high percentage of monounsaturated fatty acids, a moderate amount of poly saturated fatty acids and a low amount of saturated fatty acids. Vegetable oil and in particular custard apple seed oil is an alternative raw material for the production of automotive lubricant, as well as alternative fuel for the next generation. (Erhan and Sharma, 2006) reported that a high content of unsaturated bonds indicated by the high iodine value of rapeseed oil-based bio-lubricant allows higher performance, a key factor for the economic production of rapeseed oil base bio lubricant [2]. When using vegetable oil as a base for lubricants, they have good lubrication, higher viscosity, a low pour point, a high flash point and a high degree of biodegradability. On the other hand,

vegetable oils have poor oxidative stability at high temperatures and suffer from opacity, precipitation, poor flow and solidification after long-term exposure to cold winter temperatures. Wang and Erhan (2001) reported that the poor oxidative stability of vegetable oil is typically attributed to the rapid reaction occurring at C=C double functional group in molecule[3] .

In previous years, Sharma and et al. (2007) attempted to improve oxidative stability by adding commercially available antioxidants to the oil, preparing new antioxidants or genetically modifying the plants from which the vegetable oils are derived[4]. Ajithkumar and Jayadas (2009) have made efforts to improve low temperature properties by mixing vegetable oil with diluents such as poly- α -olefin and diisodecyladipate[5]. Uosukainen E, Linko and Lamasa (1998) conducted research to improve the oxidative stability of rapeseed oil by transesterifying trimethylolpropane (TMP) and methyl ester from rapeseed oil[6]. (Fang et al, 2011) prepared modified rapeseed oil (SRO) by chemical modification with Sulphur compounds[7].

The unsaturation present in the fatty acid molecule of the vegetable oil can be used to introduce various functional groups by carrying out chemical modifications. Among these, epoxidation, hydroxylation and esterification are the most used chemical modifications. In the epoxidation phase, the unsaturated double bond in the vegetable oil is converted to produce an epoxy group indicated by the percentage of oxirane content. (Holser, 2008) predicted that a high percentage of oxygen content in epoxidized oil has a greater number of epoxy groups[8]. Adhvarayu and Erhan (2002) explored the effectiveness of the use of epoxidized soybean oil in some high temperature applications[9]. Salimon and Slih (2009) have extensively documented a three-step synthesis of oleochemical diesters, including epoxidation, opening the epoxidized oleic acid ring to produce monoesters for the production of diesters[10]. Such types of vegetable oils can overcome these shortcomings. The piston ring cylinder liner is the most complex tribological component in an internal combustion engine which contributes significantly to the engine's total friction loss. Arumugam and Sriram (2009) reported the effect of rapeseed oil esterified with a package of biodegradable additives, i.e. 10% castor oil and 5% palm oil methyl ester used as a bio-lubricant to influence tribological characteristics[11]. The formulation has been found to have poor thermo-oxidative stability. Abdullah and Salimon (2010) have extensively documented epoxidation with organic and inorganic oxidants such as potassium peroxomonosulfate and metachloroperoxybenzoic acid[12]. Kim and Sharma (2012) also discussed the possibilities of using epoxidized vegetable oil based products in PVC and bi-hardening plastic formulations[13]. (Quincha et al 2009) have developed new ecological lubricants using sunflower oil with a high oleic content mixed with polymeric additives to improve the kinematic viscosity values and the thermal sensitivity of the viscosity[14]. Furthermore, the researchers reported the tribological behavior of chemically modified rapeseed oil and synthetic lubricant SAE20W40 .Various publications have revealed that the tribological improvement of vegetable oil based lubricants was due to the chemical modification of vegetable oil. There is evidently no research on the literature on wear and the friction effect of the typical engine material contact when lubricated by chemically modified custard apple seed oil bio degradable automotive lubricant . In this content the present research investigates the tribological characteristics of the chemically modified custard apple seed oil using a four ball tribometer . Also made comparison with tribological behaviour of commercial synthetic lubricant of equivalent viscosity grade SAE20W40.

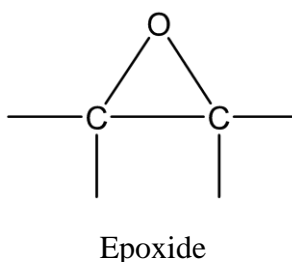
II. Experimental

2.1 Material.

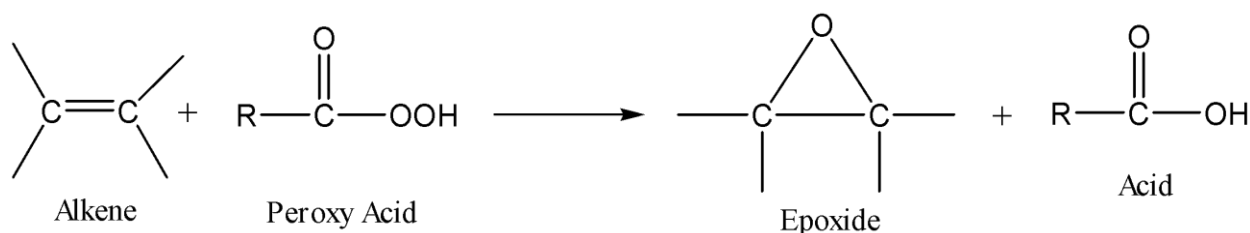
The raw materials used for this study of epoxidation reaction were high grade custard apple seed oil, which was procured from a local oil dealer from Pune. 0.1N thiosolution, AR Grade 30% hydrogen peroxide, 90 wt.% formic acid, 98wt% conc. Sulphuric acid and Methanol. Para-toluene Sulphonic acid used for hydroxidation reaction were produced from Loba Chemie, Mumbai, India.

2.2 Epoxidation reaction.

The utilization of epoxidised oil has become more common over the past few years, such epoxidised oil derived from vegetable oils is environmentally friendly. Epoxidised oil contains epoxide group or oxirane ring. The chemical structure of epoxide can be illustrated as follows



The general process for synthesis of epoxide group is known as an epoxidation reaction where in an alkene is reacted with an organic peroxy acid. The simplified epoxidation reaction is summarised as follows



The custard apple seed oil was epoxidized in a batch type reactor consisting of four-necked 1000 mL round bottom flask. A motorized speed regulator agitator was inserted in the reactor through the central neck while the other neck was used for inserting thermometer. A reflux condenser was mounted on the reactor through the third neck & fourth neck was used for feeding the raw materials into the reactor via dropping funnel. The reactor was heated by an electric heating jacket having provision for precise temperature control within $\pm 10^{\circ}\text{C}$ of the desired temperature. A photographic view of the experimental setup for the epoxidation reaction is illustrated in figure1.

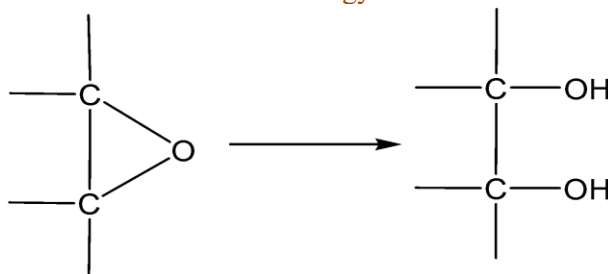


Fig (1): Epoxidation Process

- i. Prior to epoxidation reaction, custard apple seed oil was analysed to determine its iodine value. Custard apple seed oil (500mL) was placed in a round bottom flask of 1000 mL capacity with four neck..
- ii. Formic acid (45mL) at an acid molar ratio 0.75:1 was added to the oil, 1wt.% (10gm) of H_2SO_4 catalyst are added to the contents and mixed by a means of a stirrer, maintained at 0-10°C with the help of an Ice bath.
- iii. 30 wt.% Hydrogen peroxide (295.5mL) (of which 88mL H_2O_2 and 207.2mL Water) is added drop wise to the reaction mixture at a rate such that the addition is completed in 15min. Feeding strategy is very important since epoxidation is very exothermic process.
- iv. The stirring speed should be 300 rpm. The temperature is slowly increased to the required temperature (40-60°C) by keeping the four necked flasks in hot water bath of required temperature and stir the content by using magnetic stirrer.
- v. The reaction product is cooled and decanted to separate the oil from water phase.
- vi. The epoxidized oil is then washed with warm water in small aliquots to remove residual contaminants.

2.3 Hydroxylation process or Ring opening

The term ring opening reaction is used to refer to the process of introducing hydroxyl groups into unsaturated bonds of the oil. There are different sources of hydroxyl groups that can be used in the hydroxylation reaction such as alcohol and water. Before the hydroxylation reaction occurs, the oxirane ring must be opened. In the present work ring opening using acid catalyst is performed. The mechanism of this process can be described as



- i. Epoxidation Oil (300mL) is treated with Methanol and Water in molar ratio 1:4:2 in an Earlenmeyer flask equipped with magnetic stirrer.
- ii. P-toluene Sulphonic acid is used as a catalyst and gradually added to flask drop by drop.
- iii. The course of reaction was followed by withdrawing samples at regular intervals to measure its oxirane percent and iodine value. After 4.5 hrs the Product is extracted in a separating funnel with Ethyl acetate, washed with warm distilled water and Neutralized using saturated Sodium bicarbonate solution.
- iv. Residual solvent and water from the product is removed by Rotatory evaporator connected to a Vacuum pump.

2.4 *Transesterification*

- i. The Hydroxylated Custard apple seed oil is added 44.67 gm of Acetic anhydride in 1:2ratio and then 21.5 gm of Pyridine in equi-molar ratio is added to the reaction mixture.
- ii. The mixture is stirred in 500mLround bottom flask with Mechanical stirrer for 48 hrs.at room temperature.
- iii. The reaction mixture is cooled by pouring it onto ice cubes in a beaker and again stirred for 12 hrs. The reaction mixture was extracted 3 times by dichloromethane.
- iv. The organic phase with 75mL 3% Hydrochloric acid, 5% NaHCO₃ and water. Finally dried over 100gm MgSO₄ for 24hrs (Solvent is removed by rotary evaporator).
- v.

III. Results and discussion

3.1 *Fourier transforms infrared spectroscopic analysis*

Bruker Alpha T- FTIR spectroscopic (Germany), was used for monitoring the disappearance of double bonds and formation of epoxy groups during the reaction by qualitative identification of main signal.

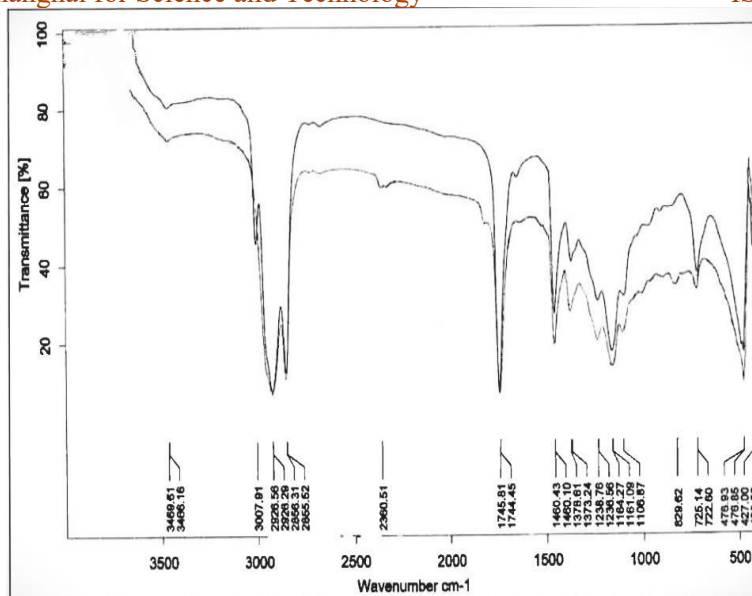


Figure (3): Overlaid FTIR Spectra of raw and formulated custard apple seed oil.

Table (1): IR peaks and its functional groups

Frequency Range (cm ⁻¹)	Functional Group
720-730	C-C bending of saturated carbon atom
115-1170	C-O stretching of ester
1460-1465	C-H bending of unsaturated alkanes
1745-1760	C=O stretching representing aldehyde, ester, keton or carboxylic acid
2853-2922	C-H stretching of alkanes, sp ³ hybridised carbon atoms
3000-3015	C-H stretching of non-conjugated unsaturation

Overlaid FTIR Spectra of raw and formulated custard apple seed oil shown in figure 3. Main IR peaks and their corresponding functional groups are listed in table (1). Upper graph of figure 3, shows raw custard apple seed oil and lower represents the modified custard apple seed oil. According to the graph the disappearance of band at 3014cm^{-1} shows C=C has been used up. The appearance of band at 825cm^{-1} which is not seen in raw custard apple seed oil is characteristic of the epoxide and also results in the appearance of epoxy group. The epoxy ring opening reaction could occur by acid catalysis in the presence of water associated with H_2O_2 used. The hydrolysis of ester group during epoxidation reaction in oil is the main side reaction. The band corresponding to carboxylic acid group is located at 1743cm^{-1} at wavelength 2853- 2992cm^{-1} represents the C-H stretching. (fig. 3).

3.2 Epoxidation Test.

This analysis was used to evaluate the performance from the epoxidation reaction in terms of two key variables, namely iodine value and oxygen content of oxirane. Iodine value was determined by applying Wijs method, i.e. 0.1 to 0.5g of sample was placed in a flask and then 10ml of chloroform was added to the sample. Subsequently, 15ml of Wijs iodine solution was added. Using the same procedure, blank solution was also prepared. Then the mixture was stored in a dark place for at least 30min at temperature of $25 \pm 5^\circ$ and subsequently, 10ml, 15wt% of potassium iodide (KI) solution and 50ml of water were added into the mixture. The iodine content of the mixture was titrated using 0.1N sodium thiosulphate solution until the yellow colour of the solution almost disappeared. Then a few drops of starch indicator solution were added and titration was continued until the blue colour completely disappeared. The iodine value and percent conversion was calculated using the following equation

$$\text{Iodine value (IV)} = [(B-A) \times N \times 12.69] / C$$

Where A is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for titration of the sample (mL), B, the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for titration of the blank solution (mL), C, the weight of sample (g), N, the normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution

$$\% \text{ conversion} = \{(IV_0 - IV) / IV_0\} \times 100$$

where IV_0 is the initial iodine value and IV the iodine value at certain condition

The oxirane content of the epoxidised oil must be quantified to determine the conversion of unsaturated bonds in custard apple seed oil to oxirane group. A definite amount of epoxidized oil was added into a flask. 5mL of ethyl ether was used to wash the flask side and then 10mL of the hydrochlorination reagent (0.2 N HCL in ethyl ether) was added into the flask. Simultaneously, a blank solution was prepared using an identical procedure. Then the mixture was allowed to stand for 3hr at room temperature, then it is titrated with standard 0.1N sodium hydroxide solution. Prior to this, a few drops of phenolphthalein indicator solution and 50ml of ethanol was added. The percentage of oxirane content was calculated using the following equation

$$\% \text{ oxirane content} = \frac{[(V_b - V_s) \times N \times 16 \times 100]}{[W \times 100]}$$

Where V_b is the volume of NaOH used for blank (mL), V_s the volume of NaOH used for sample (mL), N the normality of NaOH and W, the weight of the sample (gm).

3.3 Oxirane percentage and pour point analysis.

The oxirane oxygen content of formulated oil and raw rapeseed oil were determined according to American Oil Chemists' Society Method Cd 9-57. After the process of epoxidation oxirane content was improved up to 7.04%. Further the epoxidation by in situ per formic acid generation is almost complete as indicated from the iodine value, which was controlled under

60mg I₂/g. The pour point of the ring-opened products was measured as per ASTM D97. The relatively excellent pour point (-15°C) of the ring-opened reaction products may be attributed to hydrogen bonding of the hydroxyl group present in the final product.

3.4 Oxidation stability

The oxidative stability of oils was determined using rotary oxygen bomb test method. The rotary oxygen bomb test was carried out at 150°C with O₂ as per ASTM D2272 using copper spirals as catalyst. The life time of oil sample was evaluated by the time of pressure reduced to standard pressure of 172.3 KPa from 826.8 KPa. As a result of formation of epoxide group, the oxidative stability of chemically modified rapeseed oil bio-lubricant was dramatically promoted two times higher than that of raw rapeseed oil as shown in table 2.

Table 2: Tested properties of Raw and Formulated Custard Apple Seed Oil

PROPERTIES	RAW OIL	FORMULATED OIL
Oxirane content (%)	-	7.04%
Saponification value	197.795mgKOH/gm of oil	146.4mgKOH/gm of oil
Acid value	2.28mgNaOH/g	12.457mgNaOH/gm of oil
Iodine value	60.213	60.09
Wear scar diameter(mm)	-	878mu
Viscosity index	220	160
Colour	Pale yellow	Brownish yellow
Density(kg/m ³)	922	966.5
Flash point (°C)	320	240
Pour point (°C)	-11	-15
Viscosity at 40 °C (mm ² /s)	35	90.1
Viscosity at 100 °C (mm ² /s)	8	31

3.5 Frictional Characteristics

The purpose of this testing is to determine the load carrying capabilities of a lubricating grease under high load application.

3.5.1 Four ball tribometer

Wear scar properties and coefficient of friction of a lubricating grease can be determined using a four ball tribometer. The purpose of this testing is to determine the wear preventive characteristics of a lubricant. In the four-ball wear test, a steel ball is rotated against three lubricative stationaries against three lubricated stationary steel balls under specified load, speed, temperature and time as per ASTM D-2266(grease), or ASTM D-4172 (oils) the better the lubricant is at preventing the wear, the smaller the wear scar will be on the three stationary balls. At the conclusion of the test the three wear scar are measured and the average is reported. The coefficient of friction is also measure throughout the sixty minute test with the average being reported at the end of the test. Four ball data is useful to differentiate between lubricating greases having different levels of load bearing capabilities, wear protection and friction reduction. To investigate the tribological behaviour of chemically modified custard apple seed oil based bio-lubricant, two different lubrication samples were prepared. The details are as follows

- Chemically modified custard apple seed oil bio lubricant was contaminated with 7% vol. Of diesel

ii. Synthetic lubricant (SAE20W40) was contaminated with 7 vol.% of diesels

Mixing was affected using a stirrer. The 7 vol.% of diesel contamination is based on the fact that the permissible maximum value of diesel fuel contamination in the lube oil is on the order of 7% due to the possibility of crank case dilution. In the current study the test were conducted on a four ball tribometer as per ASTM D4172 2018. Three 12.7 mm (0.5 in) diameter steel balls are clamped together and covered with the lubricant to be evaluated. A fourth 12.7 mm diameter steel ball, referred to as the top ball, is pressed with a force of 40kgf (392N) into the cavity formed by the three clamped balls for three point contact. The temperature of the test lubricant is regulated at 75° C (167°F) and then the top ball is rotated at 1200 rpm/min for 60 min. Lubricants are compared by using the average size of the scar diameters worn on the three lower clamped balls (table 3).

Sr. No.	Sample Name	Average wear Scar, μ	Average COF
1	CSO + 7% Diesel	878	0.06375
2	SAE20W40 + 7% Diesel	521	0.10723

CSO-Chemically modified custard apple seed oil.

COF: Coefficient of Friction

The present study is a bench test for simulating the wear and frictional behaviour of synthetic and bio-lubricant using four ball tribometer. However, good results for the lubricity in terms of friction coefficient, frictional force and wear for the different lubricants were achieved. Variation in the friction coefficient, frictional force with respect to time for experiment with different lubricating oil are shown in the table. The coefficient of friction for diesel contaminated chemically modified custard apple seed oil based lubricant was considerably different from that of diesel contaminated synthetic lubricant (SAE20W40). The coefficient of friction for diesel contaminated chemically modified custard apple seed oil bio lubricant was almost 40.5% lesser than that of diesel contaminated synthetic lubricant. Similarly the frictional force was 2.55 N for the diesel contaminated custard apple seed oil bio-lubricant. The value was relatively higher of about 4.2N for diesel contaminated synthetic lubricant. This clearly shows that chemically modified custard apple seed bio-lubricant reduces the friction more effectively than synthetic lubricant for the same load and temperature conditions. This can be attributed to the fact that the presence of ester group in custard apple seed oil bio-lubricant decreases the friction. The esters have high affinity towards metal surfaces due to their polar functional group and thus form a protective film on the surface. In addition the presence of long chain fatty acid in custard apple seed oil bio-lubricant produces hydrocarbon layer that protects frictional surfaces thereby bio-lubricant reduces the friction effectively. Also the presence of oxygenated moieties in the bio-lubricant leads to an additional improvement in overall lubricity. The same may not be available in the synthetic lubricants.

3.5.2 Wear Characteristics

From the table it can be observed that the wear was higher for diesel contaminated chemically modified custard apple seed oil bio lubricant. It was approximately 40% higher than that of commercial synthetic lubricant (SAE20W40) under similar operating conditions. This can be attributed to the fact that the presence of anti-wear additives in synthetic lubricant reduces the wear effectively.

4 Conclusion

- i. The above synthesis process is an efficient method without any side reactions and provides a greener alternative to the production of petroleum-based lubricant. Further the basic structure of is retained even after chemical modification of custard apple seed oil, thus maintaining excellent bio degradability.
- ii. The chemically modified custard apple seed oil bio lubricant formulated using above approach will have better cold flow behaviour of -15°C of oxirane content of 7.04 % and improved oxidation stability.
- iii. The coefficient of friction for diesel contaminated chemically modifies custard apple seed oil bio-lubricant was 40% lesser than that of diesel contaminated synthetic lubricant due to the formation of stable polymeric film on the metal surface during boundary lubrication.
- iv. Forty percent higher wear was observed with chemically modified custard apple seed oil bio-lubricant than that of commercial synthetic lubricant (SAE20W40).The synthetic lubricant exhibited better performance in terms of wear due to the presence of anti-wear additives

References

1. Horner, D., 2002. *Recent trends in environmental friendly lubricants. J Syn Lubr.* 18, 327-347
2. Erhan, SZ., Sharma, BK., Liu, Z., et al. 2008. *Lubricant base stock potential of chemically modified vegetables oils. J Agric Food Chem.* 56, 8919-8925.
3. H wang, H., Erhan, SZ., 2001. *Modification of epoxidized soybean for lubricants with improved oxidative stability. J Am. Oil Chem. Soc.* 78, 1179-1184.
4. Sharma, BK., Perez, JM., Erhan, SZ., 2007. *Soybean oil based lubricants; A search for synergistic antioxidants. Eng Guels.* 21, 2408-2414.
5. Ajith, KG., Jaydas, NH., Bhasi, M., 2009, *Analysis of the pour point of coconut oil as a lubricant base stock using differential scanning calorimetry. Lubr Sci.* 21, 13-26.
6. Uosukainen, E., Linko, YY., Lamasa, M., 1998. *Transesterification and rapeseed oil methyl ester to environmentally acceptable lubricants. J Am. Oil Chem. Soc.* 75, 1557-1563.
7. Fang, JH., Pans. FS., Chen, BS., et al. 2011. *Friction and wear performance of magnesium alloy against steel under lubrication of rapeseed oil with S-containing additive. Trans Nonferr Met Soc China.* 21, 2649-2653.
8. Holser, RA., 2008. *Transesterification of epoxidized soybean oil to prepare epoxy methyl ester. Ind. Crops and Prod.* 27,130-132.
9. Adhvaryu, A., Erhan, SZ., 2002, *Epoxidized soybean oil as a potential source of high temperature lubricants. Ind. Crops and Prod.* 15, 247-254.
10. Salimon, J., Salih, N., 2009. *Oleic acid diesters; Synthesis 6, characteristics and low temperature properties. Eur J Sci Res.* 32, 216-222.
11. Arumugan, S., Sriram, G., 2012. *Effect of bio-lubricant and biodiesel-contaminated lubricant on tribological behaviour of cylinder liner-poston ring combination. Triblo Trans.* 55, 438-445.
12. Abdullah, BM., Salimon, S., 2010. *Epoxidation of vegetable oils and fatty acid: catalysts , methods and advantages. J Applied Science.* 1545-1553.
13. Kim, JR., Sharma. S., 2012. *The development and comparision of bio thermoset plastics from epoxide plant oils. Ind Crops and Prod.* 36, 485-499.
14. Quincha, LA., Degado, MA., 2009. *Visocity and modification of high oleic sunflower oil with polymeric additives for the design of new biolubricant formulations. J Environ Sci. Technol.* 43, 2060-2065.