

Investigation of Tribological Properties of Chemically Modified Custard Apple Seed Oil Bio-lubricant Dispersed with Nano Copper Oxide

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Abstract: Finiteness of global crude oil reserve, increasing crude oil prices and problems related to environment seems to be a reality check for the issues of emerging generation. Vegetable oil-based lubricants are an attractive alternate to conventional petrol-based lubricants due to number of its physical properties like renewability, biodegradability, high lubricity and high flashpoint. Direct application of vegetable oil as vehicle lubricants is less favorable due to its poor thermo oxidative stability, cold flow behavior and poor anti-wear characteristic. Present research detailed in this document refers to chemical modification of custard apple seed oil through epoxidation, hydroxylation and trans esterification process to improve its thermo-oxidative stability and cold flow behavior. The CuO nanoparticle of size 30-50nm was dispersed in this chemically modified custard apple seed oil in three different concentration (0.1 wt.%, 0.5 wt.% and 1 wt.%) as an anti-wear additive using ultrasonicator. Then the tribological properties was tested with and without CuO nanoparticle using four ball tribometer. It is found that coefficient of friction and wear characteristics was optimum with 0.5 wt.% CuO nanoparticle dispersed in Chemically Modified Custard Apple Seed Oil (CMCASO).

Keywords: Custard apple seed oil, bio lubricant, nano additives, four ball tribometer

1. 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 Arumugam S, and Sriram G(2013) reported the tribo-logical behaviour of chemically modified rapeseed oil and synthetic lubricant SAE20W40. However the chemically modified rapeseed oil did not show any improvement in reducing the wear under tested conditions[15]. Various publications have revealed that the tribological improvement of vegetable oil based lubricants was due to the addition of nanoparticles as anti-wear additive. Wu et.al (2007) studied the effect of using nano-TiO₂, nano diamond and copper oxide (CuO) nanoparticles as anti-wear additives in API-SF engine oil and base oil [16]. The results showed that CuO nanoparticles were more effective in reducing friction and wear than nano diamond and nano TiO₂. Demas NG et. al (2012) have done research on the tribo-logical behaviour with polyalphaolefinbase oil with BN and MoS₂ nanoparticle additives

using HFRR. The friction and wear were reduced effectively to MoS₂ nanoparticles with base oil when compared with BN nano additives [17]. Thottackkad et. al (2012) employed the various concentration of CuO nanoparticles with coconut oil. Result showed that the optimum concentration of 0.34 wt.% of CuO reduces the coefficient of friction and wear.[18] 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 dispersed with nano additive. In this context the present research investigates the tribological characteristics of the chemically modified custard apple seed oil dispersed with CuO nanoparticle using a four ball tribometer. Also made comparison with tribological behaviour of commercial synthetic lubricant (SAE20W40) of equivalent viscosity grade.

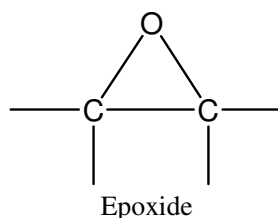
2. Experimental

2.1 Material

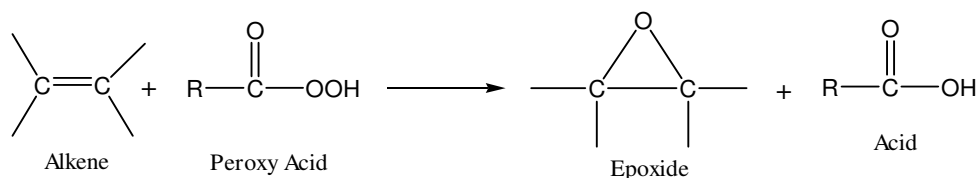
The raw materials used for this study of epoxidation reaction were high grade custard apple seed oil, which was procured from a local oil dealer from Pune. 0.1N thiosolution, AR Grade 30% hydrogen peroxide, 90 wt.% formic acid, 98wt% conc. Sulphuric acid and Methanol. Para-toluene Sulphonic acid used 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 figure 1.



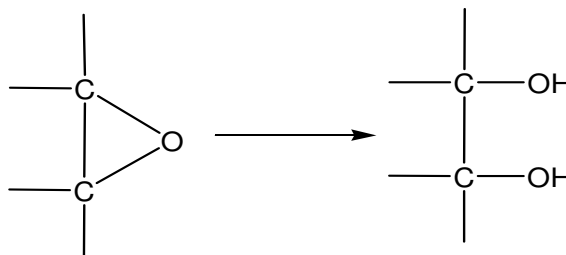
Fig (1): Epoxidation Process

- 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 H₂SO₄ 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 H₂O₂ 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).

2.5 Dispersion of chemically modified custard apple seed oil bio-lubricant with nano CuO

In this study, dispersion of CuO nano particle with chemically modified custard apple seed oil is done in three distinctive concentration,0.1 wt.%,0.5 wt.%, and 1 wt.% as an anti-wear additive. Commercial grade CuO nano particles in the size range of 30-50 nm was supplied by M/S US nano research materials INC. Figure (2) and (3) shows the SEM image and XRD image of CuO nano particles. For dispersion, an ultrasonicator model No: 1.5L501t was used to ensure homogeneous dispersion of CuO nano particle. The chemically modified custard apple seed oil and CuO nano particle (0.1 wt.%, 0.5 wt.% and 1 wt.%) were initially taken separate beakers and kept in an ultrasonic bath sonicator. It is then allowed to vibrate for 2 hours and then the blends were shaken for 5 hours in a rotary shaker to ensure the chemically modified custard apple seed oil and CuO

nanoparticles are in a homogeneous phase without agglomeration.

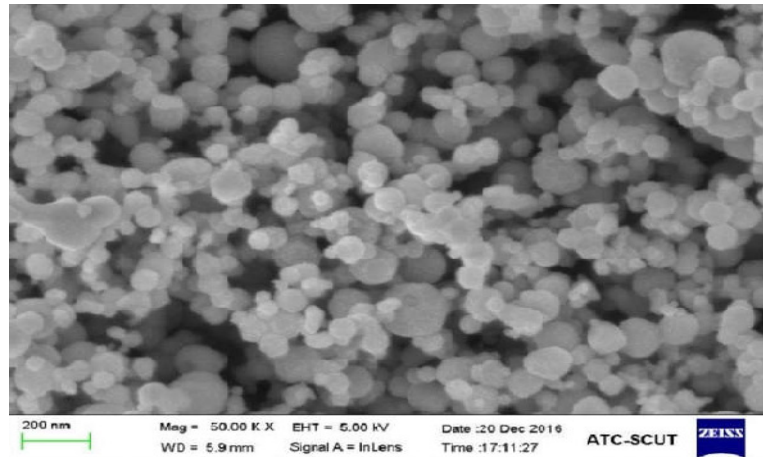


Fig (2): SEM Image of Copper Nano particle

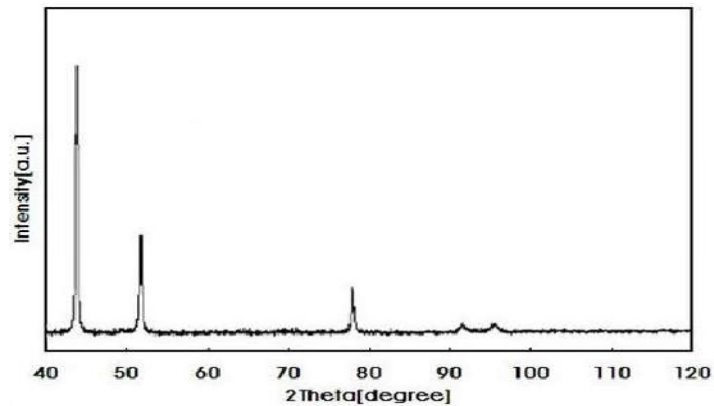


Fig (3): XRD of Copper Nano Powders

2.6 Tribological investigation of chemically modified custard apple seed oil dispersed with CuO nanoparticle.

For this investigation 5 different lubricant samples were prepared as detailed below:

- Sample 1. CMCASO without nano CuO.
- 2. CMCASO + 0.1 wt.% nano CuO.
- 3. CMCASO + 0.5 wt.% nano CuO
- 4. CMCASO + 1 wt. % nano CuO
- 5. SAE20W40

Each sample is contaminated with 7 vol% diesel. The 7 vol% of diesel fuel contamination with CMCASO is based on the fact that the permissible maximum value of fuel dilution in the lube oil is the order of 7% due the possibility of crank case dilution.

The tribological studies under five lubricant samples were performed using a

four-ball tester model TR-30H-KRL PNU DUCON in BPCL in Mumbai. The test was conducted as per ASTM D4172-2018.



Fig (4): Four Ball Tester

The purpose of this testing is to determine the load carrying capabilities of a lubricating grease under high load application. Wear scar properties and coefficient of friction of a lubricating grease can be determined using a four ball tribometer. In the current study the test was 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. At the conclusion of the test the three wear scar diameters worn on the three lower clamped balls are measured and the average is reported. The coefficient of friction is also measured throughout the sixty-minute test with the average being reported at the end of the test.

3. 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.

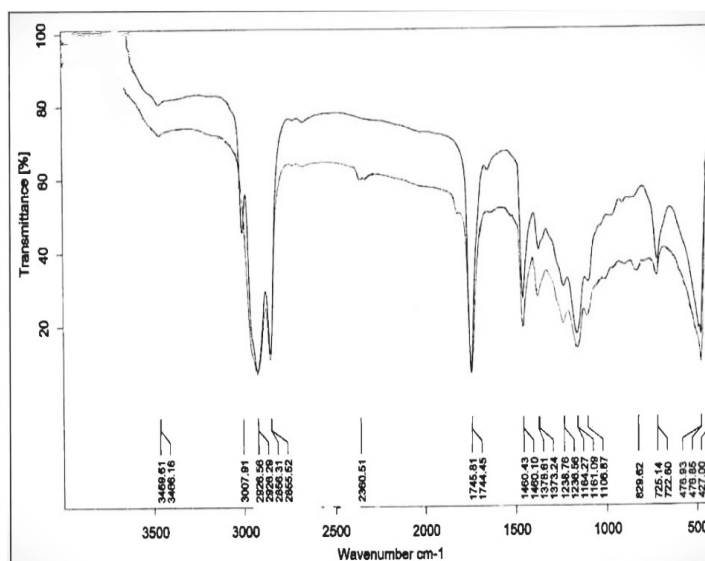


Fig (5): Overlaid FTIR Spectra of raw and formulated custard apple seed oil.

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, ketone 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 H₂O₂ 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 were 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 I_2/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 O_2 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.

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 Tribological characteristics

Table (3): Tribological properties

Sample	Avg. wear scar (micron)	Coefficient of friction
CMCASO + 0.1 wt.% CuO	686	0.062781
CMCASO + 0.5 wt.% CuO	665	0.061742
CMCASO + 0.1 wt.% CuO	675	0.0661842
CMCASO	878	0.06375
SAE20W40	521	0.10723

3.6 Friction characteristics

Table (3) shows the variation of friction coefficient with running time for different lubricant sample. The coefficient is decreased by the addition of CuO nano particle, it also shows that the lowest value of friction coefficient is for a concentration of 0.5 wt.% of CuO nano particle with CMCASO which is also lower than that of CMCASO without the addition CuO nanoparticle, this might be attributed to the fact that the sphere like CuO nano particle which act as a rolling medium between the frictional surfaces when boundary lubrication occurs. It is also 56% lower than that of synthetic commercial lubricant SAE20W40 of same viscosity range of CMCASO. This suggest that the enhanced lubrication of CMCASO is due to the presence of nano CuO. However, the addition of nano CuO to CMCASO beyond 0.5 wt.% does not reduce the friction coefficient. Thottackadetal found that 0.34 wt.% of nano CuO dispersed with coconut oil was effective in reducing frictional characteristics. The nano CuO present in CMCASO fills out the deep cavities, voids and cracks on cylinder liner surfaces and thus provides hydro dynamic effect which is responsible for improving the tribological properties. Further the presence of ester group has high affinity towards metal surface due to their

polar functional group and thus forms a protective film on the surface. In addition, the presence of a long chain fatty acid in CMCASO produces a hydro carbon layer that protects the frictional surface.

3.7 Wear characteristics

The wear characteristics of five different samples are represented in table (3). In the present nano CuO were added to CMCASO to improve the anti-wear characteristics of CMCASO. It was observed that 0.5 wt.% proved efficacious in minimising the wear to the level of 665 micron whereas the addition of 0.1 wt.% of nano CuO to CMCASO resulted a high ware. The result thus begot further accented the fact that the optimum concentration of nano CuO contributed to more prominent interaction between liner and ring inter faces, however at the higher concentration of nano CuO (1 wt.%) causes more solid to solid contact thus increasing the wear high.

4. Conclusion

- 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 It is retained even after chemical modification of custard apple seed oil, thus maintaining excellent bio degradability.
- 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.
- The addition of CuO nanoparticles as an anti-wear additive was effective in enhancing the tribological behaviour of CMCASO
- The optimum concentration of 0.5 wt.% of nano CuO was significantly enhances the anti-wear and anti- friction characteristics. Higher concentration of nano-CuO other than optimum level increases more solid-to-solid contact thus increasing wear, whereas at optimum concentration of nano-CuO, solid –to-liquid contact is more prominent

On the whole, this investigation can promote the establishment of chemically modified custard apple seed oil-based bio-lubricant for automotive applications. With additional, research, genetic modification of custard apple seed and improved oil processing technologies, it has a good potential for commercialization

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