

Comparative Tribological Investigation of Mahua Oil and its Chemically Modified Derivatives

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ABSTRACT

For the last decade, the lubricant industry has been trying to formulate biodegradable lubricants with technical characteristics superior to those based on petroleum. A renewable resource, mahua oil, is good alternative to mineral oil because of its environmentally friendly, non toxic and readily biodegradable nature. The triacylglycerol structure of mahua oil is amphiphilic in character that makes it an excellent candidate as lubricant and functional fluid. It is also very attractive for industrial applications that have potential for environmental contact through accidental leakage, dripping or generates large quantities of after-use waste materials requiring costly disposal. Vegetable oil in its natural form has limited use as industrial fluids due to poor thermo-oxidation stability, low temperature behavior and other tribochemical degrading processes. Therefore, in the present paper epoxidation and trans-esterification were employed to overcome the mentioned drawbacks of vegetable oil and explore the possibility of modified mahua oil as lubricant because double bonds present in triacylglycerol structure offer sites for additional functionalization This paper compares the lubricating property and mechanical stability of four samples of epoxidized mahua oil, trans-esterified mahua oil, refined mahua oil and a mineral oil based lubricant. The epoxidation of mahua oil followed by oxirane ring opening, by acidic catalyzed reaction with glacial acetic acid and hydrogen peroxide, provides interesting polyfunctional compounds useful as biolubricant with improved low temperature pour properties. The double bonds were epoxidized to improve low temperature and oxidative stability properties of mahua oil. Moreover, another sample of fatty acid methyl ester mahua oil was prepared by two step transesterification process. The four samples-mahua oil, transesterified mahua oil, epoxidized mahua oil and mineral oil based lubricant were tested for their viscosity index, density variation, coefficient of friction and wear tests using four-ball tester. Comparative tests concluded that epoxidized mahua oil and transesterified mahua oil have superior lubricant characteristics with respect to oil and conventional lubricant.

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INTRODUCTION

Anti-wear/Antifricition lubricants are made up of a base oil which is blended with a number of additives so that it can withstand the mechanical stresses under lubricant conditions easily.[1] Currently, the Indian lubricant industry, which is 7th largest lubricant market in the world, is projected to cross 2 million metric ton (MMT) by 2014-15 as against the global lubricant market of about 45 MMT.[2,3] Various types of lubricants are available in the market these days such as mineral oil, synthetic oil, refined oil, and vegetable oil.[4]. Increasing attention to the environmental issues drives the lubricant industry to increase the ecological friendliness of its products. [5] Most of the lubricants that are made these days are derived from petroleum products that are toxic to environment and are non-biodegradable.[1,6] Leakage or spills of such type of lubricants in applications such as chain saw-bar oils, two-stroke engine oils, marine oils and outboard engine lubricants can further affect the environment adversely. [7,8]. Nowadays, governmental directives are in place regarding the

preservation of the environment and product eco labeling, has been introduced. These are having a significant impact on lubricant formulations.[9,10] In this regard, vegetable oils (VO) constitute a suitable alternative for replacing 'mineral oils', as they are wholly biodegradable, non-toxic, and 'Generally Regarded as Safe' (GRAS) products[11,12,13]. Vegetable oils are tri-esters of straight-chained, mostly unsaturated fatty acids with glycerol and have higher levels of biodegradability and lower toxicity than conventional mineral or synthetic oils [14]. The vegetable oils have various desirable characteristics for use in lubricant applications. Some of the properties are low volatility, high flash point, high viscosity index(VI), excellent lubricity, superior anticorrosion properties, good solvent capacity for contaminants and additives, better affinity to metal surfaces, eco compatibility, renewable and non-toxic[2]. Most important of all of them is that they are bio-degradable and do not have a serious impact on the environment. Therefore, vegetable oils can be used in applications such as rolling, cutting, drawing and quenching. It makes them very attractive

for industrial applications that have potential for environmental contact through accidental leakage, dripping or generates large quantities of after-use waste materials requiring costly disposal. [15,16,1]. Unfortunately, vegetable oils have low thermal and oxidative stabilities, narrow viscosity range and higher pour points than both mineral or synthetic oil-based lubricants due to the presence of saturated fatty acids and inferior oxidation stability on account of presence of polyunsaturated fatty acids. This confines their use as lubricants to a modest range of temperature. So their use in industry is not yet extensive [7, 17]. However due to the presence of double bonds in triacyl glycerol structure, they offer sites for additional functionalization, for further improving such technical defects. Epoxidation and esterification of vegetable oils can produce such poly functional compounds that can improve the properties of the vegetable oils to some extent. [18]

In this research, we have used non-edible mahua oil (*Madhumicalndica*) as our vegetable oil and it has been epoxidized and transesterified for the improvement of its properties. The samples were checked for various parameters such as coefficient of friction, wear scar diameter and density and their results were displayed.

LUBRICANT PREPARATION

The following samples were prepared-Epoxidized Mahua Oil (EMO) and Transesterified mahua oil. Raw mahua oil and Mineral oil based lubricant were used without further refining.

Preparation of Epoxidized Mahua Oil

Materials used- mahua oil, concentrated sulphuric acid, Glacial acetic acid (100 %) and hydrogen peroxide (40 wt %).

The epoxidation reaction was carried out by means of a magnetic stirrer in a flask made up of glass. The temperature was maintained by the means of the heating plate and a 6.5 cm long stirrer was used to stir the mixture.

The method reported by Swern was used. 425 gm of mahua oil was placed in the flask and 43 ml of glacial acetic acid (100%) and 5 ml of concentrated sulphuric acid were added to the initial mixture. The mixture was stirred for about 30 min. The temperature during this stirring was maintained in between 50-55 °C and the stirring speed of about 1600-1700 rpm was maintained. After this, 165 ml hydrogen peroxide was added drop-wise such that it got completed in about 1 hour. The temperature of the mixture was increased to about 60-65°C. The reaction was continued at the same temperature for about 6-6.5 hours at the same stirring speed. After the completion of the reaction, the epoxidized mahua oil sample was cleaned by addition of diethyl ether to it and then keeping the mixture in gravimetric flask. The separated sample was then collected in another beaker and was washed with water and taken for testing of its lubrication properties.

Preparation of Transesterified Mahua Oil

The FFA of mahua oil was found to be 27%, which is way higher than the stipulated limit for base catalyzed transesterification, hence first we employ acid catalyzed esterification till the FFA drops between 1-2%. The first step will yield mono-esters. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono esters and glycerol. The upper layer is separated and washed with distilled water to remove catalyst present in the ester. Then, it is allowed to settle under the action of gravity for 3 days in gravity separator. The water separates out from ester forming a distinct layer. Thereafter, the ester is heated in an oven for an hour for removing the traces of water. Finally, the product obtained is mahua oil methyl ester which is called as biodiesel.

Accelerated Ageing of Vegetable Oils

Accelerated ageing of vegetable oil samples was simulated by storing oil samples in a dark oven at 60°C and was based on the version of American Oil Chemists Society (AOCS) recommended practice [19]. Dark oven conditions were used to eliminate the possibilities of photo-oxidation. About 900 ml of epoxidized, trans-esterified and raw mahua oil samples were taken in one litre beakers and stored in an oven at the specified temperature. The oil samples were removed at an regular intervals of 25 days for further analysis and were compared with a fresh oil sample which was used as reference in the present study. Further the ageing process was also carried out at 100°C in order to see the influence of temperature on the process. [20]

ANALYTICAL TESTS

The following enlisted tests were conducted on raw mahua oil, trans-esterified mahua oil, epoxidizedmahua oil and a mineral oil lubricant. The samples were also aged to study the effect of oxidation on the various samples.

Pour Point Temperature Measurement

The pour point of a fuel or oil is the lowest temperature at which it will pour when cooled under defined conditions. Pour point of Epoxidized Mahua Oil was determined by following ASTM method D 97 at an accuracy of $\pm 3^\circ\text{C}$. Test jars, thermometers, corks, and rubber rings fully met ASTM D 97 specifications. All runs were carried out at least in duplicate. Sample temperature was measured in 5°C increments at the top of the sample until it stopped pouring. [21]. It was found to be 4°C . For mahua oil it was 15°C .

Four Ball Test

A four-ball wear tester was used according to the standard test of ASTM D4172. Tests were conducted with 40, 60, 80, 100 and 120 kg normal loads. The experimental temperature and rotational speeds were held constant at 90°C and 1200 rpm respectively. The test duration was 60 minutes in all cases. For