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Bio based grease A value added product from renewable resources

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ABSTRACT

Finite resources of crude petroleum oil and growing concern over climate change are driving investment and innovation in the sector of biofuels. Vegetable oils in comparison with mineral oils are renewable, easily available, environmentally friendly, economically cheaper than mineral oil and hence sustainable indeed. This paper presents a series of structural modifications of vegetable oil–Karanja oil using various alcohols to form fatty acid esters. This fatty acid esters were then used as base oil in the formulation of grease. Formulated bio-based grease was then evaluated for its tribological properties against mineral oil based grease.

1. Introduction

Global grease consumption is estimated at 1296 KT of which industrial applications accounts for 691 KT. Mineral oil based greases account for close to 90% of the global demand, while 9% of synthetic esters is used and only 1% of bio degradable base oils are used for manufacturing of greases. It is assumed that global consumption of grease in industrial application will be up to 758 KT till 2017 (Sharma and Phadke, 2014). The question of sustainability as related to industrial lubricants is an interesting dichotomy. By the very nature of being based on crude oil as a raw material for both mineral oil based and synthetic ester based lubricants, lubricants appear to be the antithesis of sustainability. Crude oil is a finite resource that is fully consumed in the conversion process to a usable lubricant. All over the globe usage and disposal of lubricants has to fulfill the need to protect the environment. Manufacturing and application of eco-destructive lubricants should be decreased as much as possible (Waara et al., 2001). Since 1970s environmental impact of lubricants, both in their manufacture and application, has attracted increasing attention toward environment protection policies (Bartz, 1998). Recently, due to the urge to protect the environment, the sulfur element of the automotive fuels is restricted within 10 ppm (Xu et al., 2014). Along with the finiteness of crude petroleum its detrimental effects over environment makes everyone look toward renewable resources as they are easily available, environmentally friendly and hence sustainable indeed (Zulkifli et al., 2013; Asadauskas and Erhan, 1999; Beran, 2008).

Bio-lubes play an integral part in the overall scheme of sustainable lubrication. Sourced from plants or organisms that can replenish themselves, this class of lubricant seems poised to become the focus of sustainable lubrication. Vegetable oils, as renewable resources, are gradually used as green raw materials in various areas of research in bio based lubricants (Salimon and Salih, 2009). Vegetable oils as compared to mineral oils have differed in physicochemical as well as tribological properties due to the presence of triglyceride in its chemical structure. High flash point over 300 °C classifies vegetable oils to non-flammable liquids. Also, they have good lubricity, viscosity indices, superior film strength and affinity to metal surfaces (Fox and Stachowiak, 2007; Doll et al., 2007). In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules (Dinda et al., 2008). On the other side vegetable oils lags behind in thermo-oxidative and hydrolytic stability which makes them incapable to be used directly as lubricant as compared to petroleum based oils. These drawbacks of vegetable oil can be overcome by chemically modifying vegetable oils.

Researchers have developed various routes to chemically modify vegetable oil and use it as bio-lubricant. These modification involves transesterification (Masood et al., 2012; Bokade and Yadav, 2007; Gryglewicz et al., 2003), epoxidation (Salimon and Salih, 2010; Adhvaryu and Erhan, 2002), enzyme catalyzed esterification (Uosukainen et al., 1998; Dossata et al., 2002; Stergiou et al., 2013) and estolide formation (Cermak et al., 2013; García-Zapateiro et al., 2013). Various methods for formulating grease using

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thickeners is also reported by a number of authors in which mineral oils are replaced by vegetable oils and fats (García-Zapateiro et al., 2014; Núñez et al., 2013). Modifications of vegetable oils enhance the properties related to viscosity, adherence to the metal surfaces, stability, etc. which impacts its tribological properties.

Present work is based on chemical modification of Karanja oil, and these modified Karanja oil was then used as base oil for formulating grease, using lithium-12-hydroxy stearate as thickener. Karanja is a medium sized tree and is found throughout India. Biologically, it is named as *Pongamia pinnata.* It is easy-growing tree for tropical and sub-tropical regions and can be easily grown-up from its seeds. Oil content in its seeds varies from 27% to 39% (Sangwan et al., 2010). Karanja oil was converted into its methyl ester which were then further modified by trans-esterification with different alcohols viz. hexanol, octanol and neo-pentyl glycol. Trans-esterified products were characterized by GC–MS. These esters of Karanja oil were then thermo mechanically dispersed with lithium-12-hydorxystearate to obtain grease. All-purpose grease of mineral oil, SN-500, based used as a standard to compare various properties of bio-lubricants.

2. Materials and methods

All the chemicals were procured from SD Fine chemicals Ltd. (Baroda, Gujarat) were of laboratory reagent grade and were used without any further purification. Karanja oil was procured from Anand Agriculture University (Anand, Gujarat). Lithium-12-hydroxy stearate was procured from Petrochem Industries (Palghar, Mumbai). Karanja oil was evaluated for Iodine value, Saponification value and Peroxide value as per ASTM D5554, ASTM D5558 and ISO 3960, respectively. Fatty acid profile of Karanja oil was evaluated by Gas Chromatography. Tribological properties of the formulated grease such as roll stability, cone penetration, drop point, wear preventative and weld load were evaluated by ASTM D1831, ASTM D1403, ASTM D566, ASTM D2266 and ASTM D2596, respectively. All the test samples were taken as raw, no additives were added in any of the samples.

2.1. Gas chromatography analysis

Gas chromatography of Karanja oil was carried out using Perkin Elmer Auto System XL. The column used was BP-225, having 25 meters length and 250 mm diameter. Nitrogen as carrier gas at head pressure of 6 psi. Temperature programming was initiated at 60 °C at the rate of 10 °C per min to reach a temperature of 220 °C. The inlet temperature was 250 °C and detector temperature was 280 °C.

2.2. Synthesis of Karanja oil methyl esters

Karanja oil was esterified with methanol to form Karanja oil methyl ester. Catalyst used for esterification was sodium hydroxide, 1% (w/v), oil to alcohol ratio was kept as 1:6. The temperature of the reaction mass was maintained at 60–65 °C for 60 min (Naik and Katpatal, 2013). After the completion of the reaction the mixture of methyl esters and glycerol was separated in a separating funnel overnight. The methyl ester thus synthesized was used for the production of lubricating grease base stock.

2.3. Transesterification of Karanja oil methyl esters

Fatty acid esters of Karanja oil were synthesized by trans-esterifying Karanja oil methyl esters with hexanol, octanol and neopentyl glycol. Methyl esters were further transesterified with various alcohols such as hexanol, octanol, neo-pentyl glycol to form various high molecular weight esters – lubricating grease base stock. 100 g of methyl ester, 71 g of hexanol and 5.13 g of sodium methoxide, catalyst, were charged in a three-necked round bottom flask. The reaction was carried out at a desired boiling temperature under vacuum condition using 3% sodium methoxide as catalyst. Entire reaction was conducted under vacuum which simultaneously removed the byproduct. The product obtained was washed repeatedly with hot water to remove catalyst. Similarly octyl as well as neo pentyl esters of Karanja oil were prepared keeping the mole ratio of methyl ester:alcohol, 1:1 for octyl esters and 1:0.5 for neo pentyl esters, respectively. The product was characterized by GC–MS and was further used as base oil in the formulation of grease.

2.4. Gas chromatography–mass spectroscopy analysis

GC–MS analysis of all Karanja oil esters was carried out on Perkin Elmer Auto system XL with turbo mass. The column used was PE-5MS, 30 meters in length. A split injection system 70:1 was used with nitrogen carrier gas at a head pressure of 6 psi. The column temperature was held at 80 °C throughout the entire 10 min. Temperature programming was initiated at 80 °C at the rate of 10 °C per min to reach a temperature of 290 °C. The transfer line temperature was 250 °C and the detector temperature was 280 °C.

2.5. Formulation of bio based grease

Transesterified esters of Karanja oil formed using Hexanol, Octanol and Neo-pentyl glycol were further used as a base oil in formulating grease using lithium-12-hydroxy stearate as preformed soap. Lithium soap concentration was fixed at 10% (w/w) in the bio-based grease. Preformed soap was thermo mechanically dispersed using high speed stirrer. The process was performed in a stirred batch reactor, equipped with a Teflon stirrer at rotating speed of 70 rpm. In the first step, 60% of the ester was charged in a vessel which was heated up to 100 °C and 5% of the soap was added. Then, part of the base oil, 20%, and the remaining soap was added and the temperature was raised to 200 °C. The mixture was maintained at this temperature for 40 min, afterward the remaining 20% base oil was added during cooling and the rotating speed was increased to 5000 rpm and the mixture was cooled to room temperature. The formulated grease was then tested for its tribological properties.

2.6. Drop point

The dropping point of grease is the temperature at which the thickener loses its ability to maintain the base oil within the thickener matrix. This may be due to the thickener melting or the oil becoming so thin that the surface tension and capillary action become insufficient to hold the oil within the thickener matrix. Drop point of all the test samples was determined using ASTM D566 method.

2.7. Cone penetration

Lubricating greases consistency is measured by ASTM D 1403 method, and is reported in terms of various NLGI grades ranging from 000 for semi fluid to 6 for solid block greases.

2.7.1. Unworked penetration test

All the three samples of Karanja oil ester based grease were subjected to penetration test. Grease cup, cylindrical in shape with 50 ml capacity at 25 °C, was filled completely with grease and its surface was smoothened and placed on the penetrometer. Then penetrometer cone was released and allowed to sink in the grease cup under its own weight for 5 s. The depth the cone has penetrated is then measured, in tenths of a millimeter. Deeper the cone