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Influence of structural modification on lubricant properties of sal fat-based lubricant base stocks

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ABSTRACT

Effect of structural modification of sal fatty acid-based branched mono- and polyol esters on lubricant properties was explored. In an attempt to improve the pour point of the sal fatty acid- based lubricant base stocks, enrichment of unsaturation in sal fat was carried out using urea adduct complexation method. Oleic acid rich (73.2% by GC) sal fatty acids were reacted with 2-ethylhexanol and polyols, namely, neopentyl glycol (NPG) and trimethylolpropane (TMP) to obtain the corresponding branched mono- and polyol esters. These were further epoxidized to their epoxy esters. All the base stocks were evaluated for lubricant properties and compared with different lubricant specifications. The oleic acid rich branched mono- and polyol esters exhibited low pour points (−9 °C to −3 °C) and high viscosity indices (178–201). While, the epoxy esters exhibited higher viscosities, high flash points, and good thermal and oxidation stabilities compared to sal fatty acid-based lubricant base stocks and their oleic acid rich polyol esters. Overall, all the base stocks have potential to be developed into hydraulic and metalworking fluids, and other industrial applications with appropriate formulations.

1. Introduction

The growth of the industry has been accompanied by the development of new materials for different industrial applications. Lubricants are one such material being used extensively in machines and materials by all sectors of industry. Approximately 85% of all lubricants presently being used in the world are petroleum based oils (Shashidhara and Jayaram, 2010). It is estimated that 50% of all lubricants used worldwide are disposed of into the environment through accidental spillage, urban runoff, refinery process and total loss applications like chainsaw oils, two stroke engine oils, concrete mold release oils, exhaust fumes in engines, and metal cutting and forming processes (Horner, 2002; Gawrilow, 2004). These oils contaminate the soil, water and air, causing severe damage to the various forms of life. The growing human interference with the environment has resulted in unsustainable effects on the ecological systems. In this context, the use of renewable resources like vegetable oils in various industrial applications including lubrication has gained considerable interest. The vegetable oil-based products are sustainable and biodegradable, which could contribute to reducing global warming effects. Recently markets for vegetable oil-based materials have recorded tremendous growth due to the economic, environmental and availability advantages.

Apart from ecological advantages, vegetable oils also have ideal lubricant properties like high flash point, lower volatility, higher solvency for contaminants and additives, and higher viscosity indices due to molecular linearity and high molecular weight of the triacylglycerol molecule. However, they have some disadvantages like poor oxidative and thermal stability and hydrolytic instability, which are due to the high degree of multiple C–C unsaturation in fatty acid chains, and the presence of the allylic protons and β-hydrogen atom in the triglyceride (Gapinski et al., 1994; Bünemann et al., 2000). The compound due to which is more prone to oxidation resulting in degradation and polymerization leading to increased viscosity and reduced lubrication functionality. The shortcomings related to unsaturation can be overcome by chemical modifications like epoxidation, hydroxylation and acylation. The properties of lubricants namely the oxidation stability, pour point, and viscosity index (VI) are known to be highly influential by the structural modification of the molecules (Yunus et al., 2004).

Presence of β-hydrogen atom in the triglyceride leads to partial fragmentation of the molecule, resulting in unsaturated compounds which undergo polymerization and formation of precipitate particles (Bunemann et al., 2000). Esterification of the vegetable oils with polyols and branched chain alcohols overcomes this disadvantage. Esterification of fatty acids or transesterification of fatty acid methyl esters with polyols like trimethylolpropane

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(TMP) or neopentyl glycol (NPG) has been developed for preparing a variety of lubricating oils (Eychenne and Mouloungui, 1998; Uosukainen et al., 1998; Gryglewicz et al., 2003; Yunus et al., 2004; Hafizah and Salimon, 2010; Chang et al., 2012; Padmaja et al., 2012; Kamalakar et al., 2013a,b, 2015). It was observed that the polyol esters exhibited good viscosity indices, lower pour points and better thermal and oxidation stabilities. Asadauskas and Erhan (1999) used 2-ethylhexyl esters of oleic acid as additives to improve the pour point properties of the biolubricant.

Another important modification of olefinic group which is more vulnerable to oxidation is the epoxidation. Epoxidation of oleochemicals has been performed for more than 5 decades (Findley et al., 1945; Schmits and Wallace, 1954). Epoxides are reactive intermediates that readily generate new functional groups. Ring-opening of epoxides via nucleophilic addition leads to a large number of products, such as diol, alkoxy alcohol, hydroxy ester, amino alcohol, and others. Epoxidized products are being used for a number of potential applications such as fuel, lubricant additives and in the preparation of number of polymers (Muir, 2005; Kurth et al., 2007). Unsaturated fatty acid rich soybean (Hwang and Erhan, 2001; Adhvaryu and Erhan, 2002) and rapeseed oils (Wu et al., 2000), when epoxidized were found to show base stocks with improved oxidation stability and friction reducing ability compared to original oils. Naidir et al. (2012) observed that epoxidation of palm-based TMP esters has improved the oxidation stabilities of the base stocks significantly.

Most of the reported literature was carried out either on the removal of β-hydrogen atom of the glycerol backbone or modification of unsaturation in the fatty acid chain. In the present work we have prepared base stocks by the modification at both the reactive centers. Similar type of work was carried out by Naidir et al. (2012) on epoxidation of palm based-TMP esters.

India has more than 100 types of diverse varieties of tree borne oils which are underexploited. In this context, the present study was designed to prepare lubricant base stocks from sal seed fat by modifying the reactive sites like unsaturation and removal of β-hydrogen. Sal tree (*Shorea robusta*) is one of the non-traditional oil yielding trees, which can adapt to a wide range of climatic conditions. Globally, the sal forests lie between 20 and 32°N lat. and 75–95°E long., and are native to South Asia, ranging from Myanmar in the east to Bangladesh, Nepal and India in the west. In India, it covers nearly 25.4% of the forested landscape, and is dominantly distributed on the plains and lower foothills of the Himalayas and also along the valleys (Chitale and Behera, 2012). The tree is moderate to slow growing and can attain heights of 30–50 m with a diameter of 3–3.5 m. Sal forests form a major source of timber and can also yield non-timber forest products including fodder (Edwards, 1996), seed for oil, bark for tannin and gum (Narayanmurti and Das, 1951) and leaves for plate making. The sal seed is collected as a source of income by tribals during the months of May and June, before the commencement of the agricultural season. Sal seed fat is semi solid at room temperature and contains 20–25% oil, with fatty acid composition palmitic (5.5%), stearic (43.2%), oleic (41%), linoleic (1.7%), arachidic (7.3%), and epoxy (0.3%) and dihydroxy stearic (0.5%) acids.

Earlier our group has reported sal fatty acid-based polyol esters (Kamalakar et al., 2013a). These esters exhibited high pour points due to the presence of high percentage of saturation (56.5%). Hence, an attempt was made to improve the pour points of the sal fat based lubricant base stocks by increasing the unsaturation employing urea adduct method (Christie, 1989). The unsaturated rich sal fatty acids were esterified to branched mono- and polyol esters. Similar type of modification was carried out on rubber and thumba fatty acids (Kamalakar et al., 2013b, 2015), rich in unsaturated fatty acids to obtain polyol esters with low pour points. The branched mono- and polyol esters of oleic rich sal fatty acids were then epoxidized using Prilezhaev peracid process (Schmits and Wallace, 1954) to obtain the corresponding epoxy esters. All the branched mono- and polyol esters and their epoxy esters were evaluated for basic lubricant properties and were compared with different lubricant specifications. These epoxy branched mono- and polyol esters are reported for the first time. In addition, the study also helps to understand the influence of structural modification i.e enriching unsaturation and epoxidation of the unsaturated rich branched mono- and polyol esters on the lubricant properties.

2. Materials and methods

2.1. Materials

Sal fat was procured from M/s. Paras Vanaspathi, Raipur. Hydrogen peroxide (30%), formic acid (85%), sulphuric acid, acetic acid, 4 N hydrobromic acid, iodine monochloride, potassium hydroxide, hydrochloric acid, *n*-butanol, pyridine, chloroform, acetic anhydride, 2-ethylhexanol (2-EtH), neopentyl glycol (NPG), trimethylolpropane (TMP), para toluenesulfonic acid (*p*-TSA), xylene, aluminium oxide active basic, sodium hydroxide, methanol, urea and sodium sulphate were procured from M/s S.D. Fine chemicals Pvt. Ltd., (Mumbai, India). All the reagents and solvents were of analytical grade and used directly without purification.

2.2. Methods

2.2.1. Analytical methods

The fatty acid composition was analyzed using an Agilent 6890 N series gas chromatograph equipped with a flame ionization detector (FID) on a split injector. A fused silica capillary column (DB-225, 30 × 0.32 mm i.d., J & W Scientific, USA) was used with the injector and detector temperatures maintained at 230 and 250 °C, respectively. The oven temperature was programmed at 160 °C for 2 min and then raised at a rate of 4 °C /min to 230 °C, and held for 20 min at 230 °C. Nitrogen gas was used as carrier gas with a flow rate of 1.5 mL/min.

Infrared (IR) spectra were recorded on a 1600 FT-IR PerkinElmer spectrometer (Norwalk, CT) with a liquid film between NaCl cells. The spectrum was recorded in transmittance mode. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained using a Avance 300 MHz spectrometer in $CDCl_3$. Chemical shift values relative to TMS as internal standards are given as δ values in ppm. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in $CDCl_3$ using a Varian (75 MHz) spectrometer. Mass spectra were recorded by electrospray ionization (ESI–MS) on Shimadzu LC/MS instrument.

Thermo gravimetric analysis was carried out in non-isothermal mode in a Mettler Toledo TGA instrument to get the decomposition pattern of the base stocks. About 5 mg of the sample was taken in an aluminum crucible and was heated under nitrogen atmosphere at the rate of 10 °C/min up to 600 °C to obtain the curve of the TGA onset temperature.

2.2.2. Physico-chemical analysis

The physico-chemical analyses of the lubricant base stocks was determined using standard AOCS methods namely total acid number, AOCS, 2009; iodine value, AOCS, 2003; oxirane value, AOCS, 1997a, and hydroxyl value, AOCS, 1997b. All the analyses were carried out in duplicates and the results are an average of the two independent analysis.

The lubricant base stocks were evaluated for lubricant properties using standard ASTM methods, namely density, ASTM, 2011; kinematic viscosity, ASTM, 1998; viscosity index, ASTM, 2002a; pour point, ASTM, 2005; flash point, ASTM, 2002a; copper strip corrosion, ASTM, 2004; oxidative stability, ASTM, 2002b; weld load,