



Rubber seed oil-based biolubricant base stocks: A potential source for hydraulic oils



K. Kamalakar, Amit Kumar Rajak, R.B.N. Prasad, M.S.L. Karuna*

Centre for Lipid Research, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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ABSTRACT

Rubber seed oil (*Hevea Brasiliensis*) a non-edible oil, widely grown in India with fatty acid composition, palmitic, 9.3%; stearic, 8.4%; oleic, 25.4%; linoleic, 41.1% and linolenic, 15.3% acids, was exploited for the preparation of lubricant base stocks. The oil was hydrolyzed to obtain fatty acids and these fatty acids were reacted with branched chain alcohol, 2-ethyl-1-hexanol (2-EtH) and polyols namely neopentyl glycol (NPG), trimethylolpropane (TMP), pentaerythritol (PE) at 135–140 °C in the presence of para toluene sulfonic acid (p-TSA) as catalyst in xylene medium. The branched and polyol esters were obtained in the range of 91–96.5% yields. These esters were characterized using IR, ¹H NMR, ¹³C NMR and mass spectral techniques. The esters were evaluated for lubricant properties namely kinematic viscosity, viscosity index, copper corrosion, oxidative stability (RBOT), weld load, wear, pour and flash points using standard ASTM methods. Among the base stocks prepared, polyol esters were found to possess good viscosity indices (205–222) compared to branched esters (187). Good weld load behavior was observed in the case of PE (170 kg) and TMP (160 kg) esters compared to NPG (130 kg) and 2-ethyl-1-hexanol (120 kg) esters. All the esters exhibited good copper corrosion values of 1a. The study revealed that all the esters can be well exploited for a number of hydraulic fluid formulations.

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1. Introduction

The demand for environmental concern, and depletion of mineral reserves, increased the attention towards biolubricants from natural triglycerides, fatty acids derived from them and their potential applications. Vegetable oil based lubricants have much superior viscosity index, lubricity characteristics like antiwear, antifricition, load carrying capacity, low temperature properties and high flash points. However, they are in more demand in critical areas requiring “Total Loss” or “Once Through Materials” into applications such as chainsaw bar lubricants drilling oils, metal working fluids, marine oils, oils for water and underground pumps, agricultural equipments with two stroke engine lubricants etc. But these lubricants suffer from properties namely oxidative and thermal stabilities.

These disadvantages can be overcome by the esterification of vegetable oils with polyols and branched chain alcohols (Uosukainen et al., 1998). Presence of β -hydrogen atom in the triglyceride leads to partial fragmentation of the molecule resulting in unsaturated compound which undergoes polymerization and formation of precipitate particles (Bünemann et al., 2000). The reaction with polyol eliminates the presence of hydrogen atom in

β -position of the triglyceride thereby increasing the stability of the biolubricant base-stock. The polyol esters involving esterification of fatty acids or transesterification of fatty acid esters with polyols like TMP, NPG have been developed for preparing a variety of lubricating oils (Linko et al., 1997; Uosukainen et al., 1998; Gryglewicz et al., 2003; Yunus et al., 2003a,b, 2004; Hafizah and Salimon, 2010; Chang et al., 2012; Padmaja et al., 2012). The researchers observed that the polyol esters prepared exhibited good viscosity indices and lower pour points. The properties of the esters depend on the nature of the constituent fatty acids, their chain lengths, number of unsaturated bonds and their positions. The polyols with saturated fatty acids exhibited better oxidative stabilities at higher temperatures and those with unsaturated fatty acids exhibited lower pour points (Gryglewicz et al., 2003). For example vegetable oils with high oleic content were found to be potential candidates, as substitutes to mineral oil-based lubricating oils and synthetic esters (Randles and Wright, 1992; Asadauskas et al., 1996).

Therefore the fatty acid composition of the vegetable oils plays an important role in governing the properties of lubricant base stocks. Most of the studies reported involved preparation of polyol esters from edible oils and animal fat, while on the other hand India is importing 10.3 million tons (2012) of vegetable oil for edible purpose. Hence, cannot afford to use edible oil for non-edible applications, also India has more than 100 types of trees yielding oil bearing materials which are left unexploited. In this context,

* Corresponding author. Tel.: +91 40 27193179; fax: +91 40 27193370.

E-mail addresses: karuna@iict.res.in, mslkaruna@gmail.com (M.S.L. Karuna).

rubber seed which is a non-edible oil seed, available in plenty, about 75,000 tons, annually in India (2010) and being cultivated on a commercial scale from past several years, has been exploited in the present study. Rubber trees are found abundantly grown in Amazon valley, Venezuela, Peru, Ecuador and Columbia. In India they are widely grown in Kerala, Tamilnadu, Karnataka and Andaman Islands. It grows in deep, well drained soils, with pH tolerance of the plant from 3.8 to 8.0. It is a small genus plant growing to a height of 60–100 ft. Though rubber seed is a rich source of essential fatty acids, cannot be used for edible purpose due to the presence of glycoside which releases hydrogen cyanide and this makes it a reserve for the use of oil for non-edible applications (Salimon et al., 2012). The fatty acid composition enables its use in cosmetic formulation, metal soaps, alkyd resins and the production of biodiesel (Okieimen, 2002; Aigbodion et al., 2003; Joseph et al., 2003; Gonen et al., 2005). The seed produces more oil and exploring the existing plantations can provide a large percentage of world energy consumption. However, due to the presence of high free fatty acid (FFA), the oil remains unsuitable for many applications. On the other hand presence of high FFA is not a limiting factor in case of biolubricants prepared from fatty acids. Taking this as an advantage, the present study was focussed on the use of unsaturated fatty acid rich rubber seed oil (82% unsaturation) for lubricant base stock preparation. Though there are reports on the utilization of rubber seed oil for lubricant base stock preparation (Salimon and Ishak, 2012), no systematic study was carried out on the preparation and evaluation of rubber fatty acid based lubricant base stock.

2. Materials and methods

2.1. Materials

Rubber seeds were procured from M/s. Sanjeevani Herbal Health Society, Hyderabad. 2-Eth, NPG, TMP, PE, p-TSA, xylene, aluminium oxide active basic, sodium hydroxide (NaOH), sodium sulfate, hydrochloric acid (HCl) were procured from M/s S.D. Fine chemicals Pvt. Ltd., Mumbai, India. All the solvents and reagents were analytical grade and were used directly without purification.

2.2. Methods

2.2.1. Gas chromatography analysis

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

2.2.2. Spectral analysis

Infrared (IR) spectra were obtained on a 1600 FT-IR Perkin-Elmer Spectrometer (Norwalk, CT) with a liquid film between NaCl cells. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on Avance 300 MHz in CDCl₃. Chemical shifts relative to TMS as internal standards were given as δ values in ppm. Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded in CDCl₃ on a Varian (75 MHz) spectrometer. Mass spectrometry was recorded by electrospray ionization (ESI) on Shimadzu LC/MS instrument.

The physico-chemical properties namely FFA, iodine number, peroxide value, saponification value, unsaponifiable matter, density and viscosity of the rubber seed oil were determined

Table 1
Physico-chemical properties of rubber seed oil.

Property	Method	Value
FFA (wt%)	AOCS Cd 3d-63	39.7
Iodine number (g/100 g)	AOCS Cd 1-25	133.0
Peroxide value	AOCS Cd 8-53	0.12
Saponification value	AOCS Cd 3-25	172.2
Unsaponifiable matter (wt%)	ASTM Cd 6a-40	2.75
Density (g/cm ³) at 40 °C	ASTM D-4052	0.8709
Viscosity (cSt) at 40 °C	ASTM D 445	31.4

using standard AOCS and ASTM methods. The lubricant properties namely total acid number, hydroxyl value, kinematic viscosity, viscosity index, pour point, flash point, copper corrosion, oxidative stability, weld load and wear of the 2-ethylhexyl and polyol esters were determined using standard AOCS and ASTM methods. All the analysis were carried out in duplicates and the results are an average of two values.

2.2.3. A typical procedure for the extraction of rubber seed oil

The dried kernels were finely powdered and the powder (1000 g) was soxhlet extracted using hexane (3000 ml) as solvent for 12 h. After 12 h, solvent was removed using rotary evaporator and dried under reduced pressure to obtain rubber seed oil 400 g (40% yield).

2.2.4. Fatty acid composition of the rubber seed oil

Fatty acid methyl esters of the oil were prepared by refluxing the oil at 70 °C for 4 h in 2% sulfuric acid in methanol (Christie, 1982). The esters were extracted into ethyl acetate, washed until acid free and passed over anhydrous sodium sulfate. The ethyl acetate extracts were further concentrated using rotary evaporator to obtain fatty acid methyl esters. The converted fatty acid methyl esters were analyzed for its fatty acid composition by gas chromatography. The fatty acid composition of the rubber fatty acid methyl esters is as shown in Table 2.

2.2.5. A typical procedure for the preparation of rubber fatty acids

Rubber oil (300 g, 0.33 mol) and sodium hydroxide solution (54 g in 675 ml water) were stirred mechanically for 4 h at 80–90 °C. After 4 h, the reaction mixture was cooled to 50 °C, neutralized with dilute hydrochloric acid and the contents were extracted with ethyl acetate followed by drying over anhydrous sodium sulphate. The sample was concentrated using rotary evaporator and dried under reduced pressure (3–5 mm Hg) to obtain rubber fatty acids 280 g (98% yield).

2.2.6. A typical procedure for the preparation of 2-ethylhexyl esters of rubber fatty acids (R2-EtHE)

2-Ethyl hexanol (210 g, 1.61 mol), rubber fatty acids (300 g, 1.078 mol) and xylene (100 ml) were taken in a three necked reaction flask equipped with a thermometer, condenser and a dean stark. The reaction mixture was stirred at 135–140 °C in presence of p-TSA (3.0 g) as catalyst until theoretical amount of water was collected. The product was distilled at 110–115 °C under reduced pressure of 2–3 mm Hg to remove xylene. The reaction mixture was passed through basic alumina column chromatography to remove unreacted fatty acids. The product obtained was 397.5 g (96.5% yield) and the ester was analyzed for acid value and hydroxyl value. The structure of R2-EtHE was characterized by IR, ¹H NMR, ¹³C NMR and ESI-MS spectral studies.

IR(neat, cm⁻¹) : 3010.26(–C=C–H); 1736.92(–C=O);
1181.26(C–O)

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