SYNTHESIS AND CHARACTERIZATION OF ESTOLIDE ESTERS FOR TRIBOLOGICAL PROPERTIES

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Abstract- The development of vegetable oil based resources with eco-friendly and sustainable alternatives have encouraged replacing petroleum based resources. Our study envisages on synthesis of estolide from ricinoleic acid and different saturated fatty acids through improvement in its lubrication properties. These reactions were conducted under vacuum at 60°C for 24 h without solvent and different acid catalyst such as NH₂SO₄, and CH₃SO₃H. The hydroxy site on the ricinoleic acid makes it a suitable site for esterification with saturated fatty acids yield estolide, which shows superior low temperature properties i.e. pour point from -25 to -15°C and viscosity index ranged from 150 to 198. As the synthesized estolide products are vegetable oil based lubricants they are biodegradable and show superior low temperature properties, viscosity index as well as comparable cost to petroleum oils which will widely acceptable in the marketplace. Solvent free and use of sulphamic acid, which is green and noncorrosive material supports the prospects of commercialization of estolide-ricinoleic based biolubricants.

Keywords- Biolubricant, Estolide, Pour point, Ricinoleic acid

I. INTRODUCTION

Biolubricants, the biodegradable, ecofriendly products derived from vegetable oils such as high oleic canola, castor, palm, sunflower, soyabean and mustard, are a very small part of the overall lubricant market, predominantly used in the US and Europe, as their high costs limits their appeal elsewhere. On the other hand, although expensive, the vegetable oils and oleochemicals are known to possess several desirable characteristics for use in industrial lubricant applications such as rolling, cutting, drawing, quenching operations, and greases either alone or in combination with mineral oils: low volatility, high flash point, high viscosity index (VI), excellent lubricity, superior anticorrosion properties, good solubilizing capacity for contaminants and additives, better affinity to metal surfaces, eco-compatibility, renewable and non-toxic. The long fatty acid chain and presence of polar groups in the vegetable oil structure makes it amphiphilic in nature, therefore allowing them to be used as both boundary and hydrodynamic lubricants. In the future, the emphasis on shift from non-biodegradable lubricants to the environmentally safe and green products will drive high-powered growth in biolubricants.

Castor bean oil contains ricinoleic acid, a hydroxy monounsaturated fatty acid as main constituent of its fatty acid profile. Ricinoleic acid, has an unusual polarity due to position of hydroxyl group. Castor oil is the only commercially available vegetable oil containing hydroxy functionality of a fatty acid present abundantly (70–90%). Ricinoleic acid can undergo a wide range of reactions enabling formation of several derivatives are used in pigment, printing ink, and textile finishing. However, its main use is as chemical intermediate to produce various oleochemicals. Estolides and estolide esters from castor oil, or any source of hydroxy fatty acids, have been explored and show promise as cosmetics, coatings, and biodegradable lubricants. Estolides are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters.

Complex estolides have been synthesized by where oleic acid and various saturated fatty acids, butyric through stearic, were treated with 0.4 equivalents of perchloric acid at either 45 or 55°C to produce a new class of saturated estolides with superior low-temperature properties. The current work involves the synthesis of a new series of estolide ester from ricinoleic acid and various fatty acids. The effect of fatty acid carbon chain length on physical characterization of these estolide esters was determined.

II. PROCEDURE FOR PAPER SUBMISSION

A. Materials
Ricinoleic acid [AV = 175, IV = 82, SV = 180, HV = 155, ρ = 0.940] was obtained from Ruchi Soya Ltd., Gujarat. Reagents used in the synthesis and characterization of estolide and esterification were obtained from S D Fine Chem, Mumbai: formic acid ≥95%, hydrogen peroxide 50%, sulphuric acid 97%, methane sulphonic acid 98%, sulphanic acid 98%.
2-EH. The fine fumed alumina (AEROXIDE® Alu C, source- Evonik, Al2O3 and silica used as catalyst, has 13 nm average particle size and BET surface area- 100 m²/g. Methanol (95%), potassium hydroxide (KOH) and hydrated sodium sulphate (99%) were purchased from Merck India.

B. Methods

Physical properties. Physical properties of the estolide ester were determined. These analyses were ¹H-NMR, FTIR, acid value, viscosity, flash point and pour point.

(a) ¹H-NMR spectroscopy. The ¹H-NMR spectra were recorded on Bruker Avance II 400 spectrometer (Bruker, Rheinstetten, Germany) operated at 400 MHz using CDCl₃ as solvent.

(b) FTIR spectroscopy. The FTIR spectra were recorded on a Shimadzu FTIR – 8400 equipped with KBr beam splitter. Diffuse reflectance system (DRS) was used for powder samples and NaCl plate for liquid samples by thin film deposition technique. A regular scanning range of 400–4000 cm⁻¹ was used for 45 repeated scans at a spectral resolution of 4 cm⁻¹.

(c) Acid value (AV). To determine the acid value, 1 g of the solid resin is dissolved in 25 ml MeOH and titrated with 0.5 N KOH (in MeOH) using phenolphthalein as indicator, until the faint pink colour stays for 30 seconds. The consumption of the KOH in MeOH for neutral end point is taken as a blank value. The AV is defined as the number of milligrams of KOH required to neutralize 1 g of reaction mixture (DIN EN ISO 3682) and is calculated using Eq. 1.

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\text{AV} = \frac{56.1 \times N_{KOH} \times [\text{Sample - Blank}]}{\text{Weight of sample in gm}} \quad \text{(Eq. 1)}
\]

(d) Pour point (PP) analysis. PP of mustard oil, EMO and 2-EH esters were determined by following ASTM method D 97 at an accuracy of ±3°C. The low temperature flow and high temperature stability characteristics of vegetable oils are extremely poor which restrict their use as automotive and industrial fluids. Present investigation analyses the effect of estolide formation on tribochemistry of ricinoleic acid for use in industrial applications as evidenced by pour point a viscosity index.

vacuum. As the reaction completed, it was neutralized with KOH (10 mL, 2 mol) in 90% ethanol. The material was filtered through a Buckner funnel using whatman 42 filter paper. The organic layer was transferred to a separation funnel and was washed with distilled water to remove any excess ethanol used to neutralize. The organic layer was then distilled using the simple distillation method at 80–140°C to remove any lactone, byproducts, excess ethanol and water.

III. RESULTS AND DISCUSSIONS

The low temperature flow and high temperature stability characteristics of vegetable oils are extremely poor which restrict their use as automotive and industrial fluids. Present investigation analyses the effect of estolide formation on tribochemistry of ricinoleic acid for use in industrial applications as evidenced by pour point a viscosity index.
measures due to the presence of unsaturation and -OH group its use as lubricants at low temperature gets restricted. Presence of unsaturation and hydroxy group is responsible for its poor thermal which rule out its use at higher temperature. The estolide ester improves the low temperature and thermal properties of ricinoleic acid using nano based catalyst.

The FTIR and 1H NMR spectroscopic analysis were conducted to investigate the effect of on structural variation in Estolide ester. Disappearance of OH stretching vibration around 3400-3550 cm⁻¹ corresponding to –OH group, indicates utilization of OH group and disappearance of 1650-1710 cm⁻¹ corresponding to –COOH group and presence of 1735 cm⁻¹ confirms formation of esters in the FT-IR spectra Fig. 2.

The 1H-NMR spectrum (Fig. 3) of Estolide esters showed that the peak at 4.8 and 3.6 ppm corresponding to the α-acid methylene hydrogen and α-ester methine hydrogen corresponding. The peak at 5.3 ppm where observed showing -HC=CH- and -CH₂-COO- and -CH-COO- shows peak at 2.3ppm and 2.0ppm respectively.

a) Effect of acid catalysed for formation estolide ester

The effectiveness of following materials, as catalysts for estolide formation of ricinoleic acid, was examined: sulphamic acid, methane sulphonic acid and combination with nano silica and alumina and the corresponding changes in lubricant characteristics of estolide esters of ricinoleic acid and lauric acid were studied. The results of estolide ester investigations have been reported in Table 1. In general, estolide ester formation resulted with acid value (AV) in the range from 1.4- 2.2.

Incorporation of nano- SiO₂ and Al₂O₃ combination with sulphamic acid and methane sulphonic acid shows effective conversion to estolide. It was more effective at higher loading batch i.e. RL:03 and RL:04 , in its role as catalyst, as evidenced by AV and viscosity index measurements. Use of nano- SiO₂, Al₂O₃ and sulphamic acid as estolide formation catalyst has not been reported in literature. Sulphamic acid is a green non corrosive catalyst. On the other hand Methane Sulphonic acid is corrosive. Thus present study establishes use of sulphamic acid alone or in combination with nano- SiO₂, Al₂O₃ as estolide formation catalyst.

b) FTIR and NMR analysis

c) Evaluation of Estolide ester as biolubricant

A high viscosity index (VI) indicates that the product retains viscosity at high temperature and thus possesses favourable high temperature characteristics. The Estolide esters facilitates partial restoration of VI characteristics. The VI results are presented in Fig. 4.
CONCLUSION

Use of nano SiO$_2$ and Al$_2$O$_3$ in combination with sulphamic acid and methane sulphonic acid reported in this study have shown considerable potential for use in lubrication applications because of their low melting temperatures in range of -24 to -40°C and viscosities. Thus these products are acceptable as biolubricants in applications involving the use of high temperatures and exposure to extremes of temperature variations with excellent cold flow characteristics. The results thus established the feasibility of utilisation of estolide ester as biolubricant for diverse operating conditions.

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REFERENCES


