Synthesis and Evaluation of Jatropha Oil Branched Esters as Potential Fire Resistant Hydraulic Fluids

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Jatropha oil (*Jatropha curcas* L.), a non-edible oil with oleic acid (45.7%) and linoleic acid (33%) as major components, was used to prepare basestocks for biolubricants. The hydrolyzed fatty acids underwent reaction with two iso-alcohols, 2-ethyl-1-hexanol (EH) and 3,5,5-trimethyl-1-hexanol (TMH) and 5 different polyols, namely neopentyl glycol (NPG), 2-methyl-2-propyl-1,3-propandiol (MPPD), trimethylolpropane (TMP), trimethylolethane (TME) and pentaerythritol (PE) at around 140 ºC in presence of catalyst *p*-toluenesulfonic acid (*p*-TSA) and xylene as solvent. The yields for the branched mono- and polyol esters ranged from 90% to 97.5%. The physico-chemical, lubricant and tribological properties of these esters as well as their ^{1}H NMR, ^{13}C NMR, IR and ESI-MS techniques were investigated. Among the products, polyol esters were found to possess good viscosity indices, good foam stability, higher thermal stability and higher flash and auto ignition points compared to branched mono esters. TMP and TME esters have matched the specifications of ISO VG 46 and PE esters match ISO VG 68 fire resistant hydraulic fluids, which are in high demand.

Keywords: Jatropha oil, Polyol, Biolubricant, Environmentally friendly, Fire resistant hydraulic fluids.

INTRODUCTION

Biodegradability and environmental compliance are the main drivers leading the search for alternatives to mineral oil as base stocks for lubricants. Preventing lubricant losses to the environment is nearly impractical, therefore, efforts are being done to limit the environmental pollution caused by these lubricants to minimal level possible. Hence, the production and utilization of non-toxic, environmental friendly and biodegradable lubricants is of prime importance. A range of cost effective and commercially available fire resistant hydraulic fluids (FRHFs) that offer unusual fire resistance balance, improved service, shelf-life and mechanical properties, wide pressure range and operating temperature for high risk hydraulic fluids are available [1]. Regarding the commercial availability, at present three different biodegradable base stocks are available for fire-resistant hydraulic fluids namely polyol esters, polyglycols and naturally occurring triglycerides or vegetable oils like soybean, sunflower and rapeseed [2]. Synthetic polyols which are formed by the reaction of a fatty acid with a polyol, diol are proven to be superior in their performance. Among the synthetic polyol esters, trimethylolpropane oleate, neopentylglycol oleate and pentaerythritol oleate are the most common [3]. Polyol esters are becoming increasingly significant because of their good fire resistance characteristics, good thermal stability, relatively high flash, auto ignition points and inherently good oxidation resistance compared to mineral oils [4]. The presence of oxygen in the molecule enables them to burn with less energy compared to mineral oils [5-7]. Like phosphate esters, polyol esters have good lubricity properties [8], but on comparison to phosphate esters they display high biodegradability along with low toxicity on inhalation [9].

Direct esterification of fatty acids with polyhydric alcohols in the presence of an acid catalyst is one way for producing fatty acid-based polyol esters [9] and another a two-stage transesterification technique in which triglycerides are alcoholyzed with methanol to produce fatty acid methyl esters (FAME) before being transesterified with a polyhydric alcohol [10].

Many of the literature reports regarding the polyol esters are based on normal fatty acids from animal fats and typical edible oils [11-18]. *Padmaja et al.* [19] prepared polyol esters with three different polyols by esterification of 10-undecenoic acid (UDA), a derivative of castor oil in 92-96% yields. Thermal degradation initiation temperatures for all three synthesized polyol esters were over 260 ℃, indicating strong thermal stability.

Karanja oil based isoalkyl and polyol esters were synthesized from esterification of iso alkyl and polyols with karanja fatty acids using *p*-TSA as catalyst [20]. All the isoalkyl and polyol esters synthesized from karanja fatty acids showed good potential as base stocks. Rubber seed oil (*Hevea brasiliensis*), which is widely grown in India and thumba seed oil were exploited as lubricant base stocks [21]. The fatty acids were made to react with iso alcohol and polyols and the resulting esters were studied for their lubrication properties. This work significantly revealed that all the esters can be employed as basestocks for hydraulic fluids.

Jatropha curcas L. a flowering plant in the family, Euphorbiaceae, is attracting considerable attention from academics, companies and policy makers throughout the world [17,22]. Jatropha oil is recognized as a logical and viable source for preparation of biodiesel in India. Even though *Jatropha curcas* is a native of American tropical countries like Mexico and Central America. It is also cultivated in other tropical and subtropical regions and naturalized in some areas as it can thrive well in wastelands and an array of terrains like gravelly, sandy and saline oils. Its oil comprises 20% saturated fatty acids and 80% unsaturated fatty acids. Though it contains abundance of essential fatty acids like oleic and linolenic, the presence of toxic constituents like curcasin and cursin make this quite unsuitable for edible purpose. This has become main driver for the use of jatropha oil (JO) as a potential source for biodiesel. Even if some percentage of oil or biodiesel is converted into high performance lubricant base stocks, the economics of biodiesel process can be improved. The present study addresses the synthesis of jatropha oil based branched alcohol and polyol esters as potential lubricant base stocks. No study was reported regarding the synthesis and evaluation of jatropha oil based polyol and other branched esters as fire resistant hydraulic fluids even though little literature is available on the utilization of jatropha oil for polyol ester preparation [22,23]. Jatropha oil fatty acids were esterified using neopentyl glycol (NPG), trimethylolpropane (TMP), trimethylolethane (TME), pentaerythritol (PE), 2-methyl-2-propyl-1,3-propanediol (MPPD), 2-ethyl-1-hexanol (ETH), 3,5,5-trimethyl-1-hexanol (TMH) and their physico-chemical characteristics were analyzed and further evaluated for lubricant properties.

EXPERIMENTAL

Jatropha oil (92 mg of iodine per g) was bought from M/s Sanjivani Herbals (Hyderabad, India). The other chemicals *viz.* neopentyl glycol (NPG), trimethylolpropane (TMP), trimethylolethane (TME), pentaerythritol (PE), 2-methyl-2-propyl-1,3-propanediol (MPPD), 2-ethyl-1-hexanol (ETH), 3,5,5-trimethyl-1-hexanol (TMH), 2-methyl-2-propyl-1,3-propanediol, 2-ethyl

hexanol were procured from Fluka, while 3,5,5-trimethyl-1-hexanol from S.D. Fine Chemicals. Basic alumina, xylene and *p*-TSA from purchased from Alfa Aesar, Mumbai, India. The other reagent-grade chemicals and solvents were used without any filtration.

Characterization: A Bruker AR X 400 spectrometer (500, 300 MHz) was used to record ^{1}H NMR spectra with TMS serving as an internal standard. Using a Varian (75 MHz) spectrometer, ^{13}C NMR spectra were captured in the CDCl$_3$ solvent (400, 500 MHz). IR spectra were captured on a KBr thin film utilizing a Perkin Elmer FT-IR spectrometer, the hydroxyl value was calculated as per AOCS Official method. The viscosity measurements were performed according to ASTM D 445, density by DMA 4500M method and the specific gravity by VP4000 method. The pour points were measured using an Automatic Pour Point Tester by Dott. Gianni Scavini & Co., Italy, in accordance with ASTM D-97 procedure with an accuracy of 3 ℃. All runs were completed in duplicate and pour points were measured in 3 °C increments. Using a Koehler Inc. equipment, the ASTM D-93 technique was used to determine the flashpoint. The rotating pressurized vessel oxidation stability (RPVOT) tests were used to assess the oxidative stability of polyol esters in accordance with ASTM test D-2272. The experiments were conducted with 5 mL of reagent-grade water and a copper catalyst at 150 ℃, with the vessel sealed and filled with oxygen to a pressure of 90 psi.

Preparation of jatropha fatty acids: Sodium hydroxide (19.2 g, 0.48 mol) and jatropha oil (107.20 g, 0.12 mol) were combined in 240 mL of distilled water in a 1:4 mol ratio, then mechanically agitated for 6 h at 80-90 ℃. After the reaction was completed, the mixture was cooled to 50 ℃ and then neutralized with dil. HCl while the reaction's progress was continuously monitored using TLC. The product was then extracted with ethyl acetate, washed with water to remove any remaining acids, concentrated with a rotary evaporator and dried under reduced pressure (3-5 mm Hg) to yield 101.2 g of jatropha fatty acids.

Preparation of neopentyl glycol esters of jatropha fatty acids (JNPG): Refluxing at 135-140 ℃, jatropha fatty acids (JFA, 400 g, 1.43 mol), NPG (59.8 g, 0.57 mol) and 4 g of *p*-TSA based on 1% weight of JFA were heated until the theoretical amount of water was collected in the Dean stark condenser. The reaction was completed in 6 h. Additionally, the reaction's progress was observed utilizing the hexane:ethyl acetate solvent combination (90:10). Distillation of the reaction mixture took place at 110-115 ℃ and 2-3 mmHg of reduced pressure. To eliminate any remaining fatty acids, the end product was forced to pass through an activated basic alumina column, yielding a 334 g product with 96% yield. ^{1}H NMR (CDCl$_3$, δ ppm): 0.9 (m, CH$_2$-C$\underline{H}_3$), 1.0 (s, -C-(C$\underline{H}_3$)$_2$), 1.2-1.4 (m, -C$\underline{H}_2$-), 1.6-1.7 (m, -C-C$\underline{H}_2$-CH$_2$-), 2.0 (m, -CH=CH-C$\underline{H}_2$), 2.3 (t, -C-C$\underline{H}_2$-), 2.7-2.8 (t, =CH-C$\underline{H}_2$-CH=), 3.9-4.0 (s, -C$\underline{H}_2$-O-), 5.3-5.4 (m, -C$\underline{H}$=C$\underline{H}$-); ^{13}C NMR (δ ppm): 14.0 (-$\underline{C}$H$_3$) δ 22.6-29.6 (-$\underline{C}$H$_2$-), 31.5-31.8 (-$\underline{C}$H$_2$-HC=HC-CH$_2$-CH=CH-$\underline{C}$H$_2$-), 34.0 (-CO-$\underline{C}$H$_2$-), 41.8 (-HC=HC-$\underline{C}$H$_2$-CH=CH-), 70.0 (-CO-O-$\underline{C}$H$_2$-CH-), 128.0 (-CH=$\underline{C}$H-CH$_2$-$\underline{C}$H=CH-), 173.1 (-$\underline{C}$O-); IR (neat, cm^{-1}): 3025, 2928, 1730, 757; LC-MS: [*m/z* of (M + Na$^+$)] ions: 603 (16:0

+ 16:0); 627 (16:0 + 18:2); 629 (16:0 + 18:1); 655 (18:1 + 18:1); 685 (20:0 + 18:1); 687 (20:0 + 18:0).

Preparation of 2-methyl, 2-propyl 1,3-propane diol-esters of jatropha fatty acids (JMPPD): Jatropha fatty acid (400 g, 1.43 mol), 2-methyl-1,2-propyl-1,3-dihydroxy propane (61.2 g, 0.46 mol) and yield obtained 95.5%. ^{1}H NMR (CDCl$_3$, δ ppm): 0.9 (m, -C$\underline{H}_3$), 1.2-1.4 (m, -CH$_2$-), 1.6-1.7 (m-C-CH$_2$-C$\underline{H}_2$-), 2.0 (m, -CH=CH-C$\underline{H}_2$), 2.3 (t, -C-CH$_2$-), 2.72.8 (t, =CH-C$\underline{H}_2$-CH=), 3.9-4.0 (t, -CH$_2$-O-), 5.3-5.4 (m, -CH=CH-); ^{13}C NMR (CDCl$_3$, δ ppm): 14.0 (C$\underline{H}_3$), 22.6 (CH$_3$-C$\underline{H}_2$-), 25.5 (-CO-CH$_2$-C$\underline{H}_2$-), 27.1-29.6 (-(C$\underline{H}_2$)$_n$-), 31.5-31.8 (-C$\underline{H}_2$-HC=HC-CH$_2$-CH=CH-C$\underline{H}_2$-), 34.0 (-CO-C$\underline{H}_2$-), 41.8 (-HC=HC-C$\underline{H}_2$-CH=CH-), 66.0 (-CO-O-C$\underline{H}_2$-CH-), 128.0 (-CH=C$\underline{H}$-CH$_2$-C$\underline{H}$= CH-), 174 (-CO-); IR (neat, cm^{-1}) 3008.37, 1747.24, 1163.74, 757.15; LC-MS: [*m/z* of (M + Na$^+$)] ions: 657 (16:0 + 18:1), 681 (18:1 + 18:2), 683 (18:1 + 18:1; 18:2 + 18:0), 687 (18:0 + 18:0), 713 (20:0 + 18:1).

Preparation of trimethylolethane esters of jatropha fatty acids (JTME): Jatropha fatty acid (400 g, 1.43 mol), TME (49.3g, 0.41mol), *p*-TSA (4g) and yield obtained 93%. ^{1}H NMR (CDCl$_3$, δ ppm): 0.9 (m, -CH$_3$), 1.0 (s, -CH$_3$), 1.2-1.4 (m, -CH$_2$-), 1.6-1.7 (m-C-CH$_2$-C$\underline{H}_2$-), 2.0 (m, -CH=CH-C$\underline{H}_2$), 2.3 (t, -C-C$\underline{H}_2$-), 4.0 (s, -C$\underline{H}_2$-O-), 5.3-5.4 (m, -CH=CH-); ^{13}C NMR (CDCl$_3$, δ ppm): 14.0 (C$\underline{H}_3$), 22.6 (CH$_3$-C$\underline{H}_2$-), 25.5 (-CO-CH$_2$-C$\underline{H}_2$-), 27.1-29.6 (-(C$\underline{H}_2$)$_n$-), 31.5-31.8 (-C$\underline{H}_2$-HC=HC-CH$_2$-CH=CH-C$\underline{H}_2$-), 34.0 (-CO-C$\underline{H}_2$-), 41.8 (-HC=HC-C$\underline{H}_2$-CH=CH-), 66.0 (-CO-O-C$\underline{H}_2$-CH-), 128.0 (-CH=C$\underline{H}$-CH$_2$-C$\underline{H}$=CH-), 175 (-CO-); IR (neat, cm^{-1}) 2928, 1732, 756; LC-MS: [*m/z* of (M + Na$^+$)] ions: 907 (18:1 + 18:2 + 16:0); 909 (18:0 + 18:2 + 16:0); 931 (18:1 + 18:2 + 18:2); 935 (18:1 + 18:1 + 18:1); 967 (18:0 + 18:1 + 20:0).

Preparation of trimethylolpropane esters of jatropha fatty acids (JTMP): TMP esters of jatropha fatty acid (400 g, 1.43 mol), TMP (51.4 g, 0.38 mol) and yield obtained 92.6%. ^{1}H NMR (CDCl$_3$, δ ppm): 0.9 (m, -CH$_3$), 1.5 (q, -CH$_3$-C$\underline{H}_2$-), 1.2-1.4 (m, -CH$_2$-), 1.6-1.7 (m, C-C$\underline{H}_2$-CH$_2$-), 2.0 (m, -CH=CH-C$\underline{H}_2$), 2.3 (t, -C-CH$_2$-), 2.7-2.8 (t, =CH-C$\underline{H}_2$-CH=), 2.7-2.8 (t, =CH-C$\underline{H}_2$-CH=), 4.0 (s, -CH$_2$-O-) and 5.3-5.4 (m, -CH=CH-); ^{13}C NMR (CDCl$_3$, δ ppm): 14.0 (C$\underline{H}_3$), 22.6 (CH$_3$-C$\underline{H}_2$-), 25.5 (-CO-CH$_2$-C$\underline{H}_2$-), 27.1-29.6 (-(C$\underline{H}_2$)$_n$-), 31.5-31.8 (-C$\underline{H}_2$-HC=HC-CH$_2$-CH=CH-C$\underline{H}_2$-), 34.0 (-CO-C$\underline{H}_2$-), 41.8 (-HC=HC-C$\underline{H}_2$-CH=CH-), 66.0 (-CO-O-C$\underline{H}_2$-CH-), 128.0 (-CH=C$\underline{H}$-CH$_2$-C$\underline{H}$= CH-), 174 (-CO-); IR (neat, cm^{-1}): 2925, 1741, 767; LC-MS: [*m/z* of (M + Na$^+$)] ions: 657 (18:2 + 16:0); 659 (18:1 + 16:0); 685 (18:1 + 18:1, 18:2 + 18:0); 949 (18:1 + 18:1 + 18:1); 951 (18:0 + 18:1 + 18:1); 953 (18:0 + 18:0 + 18:1); 1009 (18:1 + 20:0 + 20:0); 1011 (18:0 + 20:0 + 20:0).

Preparation of pentaerythritol esters of jatropha fatty acids (JPE): Jatropha fatty acid (400 g, 1.43 mol), PE (48 g, 0.35 mol), *p*-TSA (4 g) and yield obtained 90%. ^{1}H NMR (CDCl$_3$, δ ppm): 0.9 (m, -CH$_3$), 1.2-1.4 (m, -CH$_2$-), 1.6-1.7 (m, -C-CH$_2$-C$\underline{H}_2$-), 2.0 (m, -CH=CH-C$\underline{H}_2$), 2.3 (t, -C-CH$_2$-), 4.0 (t, -CH$_2$-O-), 5.3-5.4 (m, -CH=CH-); ^{13}C NMR (CDCl$_3$, δ ppm):14.0 (C$\underline{H}_3$), 22.6 (CH$_3$-C$\underline{H}_2$-), 25.5 (-CO-CH$_2$-C$\underline{H}_2$-), 27.1-29.6 (-(C$\underline{H}_2$)$_n$-), 31.5-31.8 (-C$\underline{H}_2$-HC=HC-CH$_2$-CH=CH-C$\underline{H}_2$-), 34.0 (-CO-C$\underline{H}_2$-), 41.8 (-HC=HC-C$\underline{H}_2$-CH=CH-), 66.0 (-CO-O-C$\underline{H}_2$-CH-), 128.0 (-CH=C$\underline{H}$-CH$_2$-C$\underline{H}$-CH-), 174 (-CO-); IR (neat, cm^{-1}): 3008, 1747.24, 1163, 757; LC-MS: [*m/z* of (M + Na$^+$)] ions: 925 (18:1

+ 18:1 + 16:0); 951 (18:1 + 18:1 + 18:1); 1161 (18:1 + 18:2 + 16:0 + 16:0); 1190 (18:1 + 18:1 + 18:0 + 16:0); 1216 (18:1 + 18:1 + 18:0 + 18:2); 1246 (18:1 + 18:1 + 18:1 + 20:0); 1276 (18:1 + 18:1 + 20:0 + 20:0).

Preparation of isoalcohol mono esters of jatropha fatty acids (JTMH and JETH): Jatropha fatty acid (400 g, 1.43 mol), alcohol (278 g, 1.93 mol of 3,5,5-trimethyl-1-hexanol and 251 g, 1.93 mol of 2-ethyl-hexanol), *p*-TSA (4 g) and yield obtained for JTMH 96.5% and 96.7% for JETH.

3,5,5-Trimethyl-1-hexyl mono esters of jatropha fatty acids: ^{1}H NMR (CDCl$_3$, δ ppm): 0.9 (m, -CH$_3$), 1.2-1.4 (t, -CH$_3$), 1.6-1.7 (m, -C-CH$_2$-C$\underline{H}_2$-), 2.0 (m, -CH=CH-C$\underline{H}_2$), 2.3 (t, -C-CH$_2$-), 2.7-2.8 (t, =CH-C$\underline{H}_2$-CH=), 3.5 (t-C$\underline{H}_2$-CH$_2$-), 3.9-4.0 (t, -CH$_2$-O-), 5.3-5.4 (m, -CH=CH-); ^{13}C NMR (CDCl$_3$, δ ppm): 14.0 (C$\underline{H}_3$), 22.6 (CH$_3$-C$\underline{H}_2$-), 25.5 (-CO-CH$_2$-C$\underline{H}_2$-), 27.1-29.6 (-(C$\underline{H}_2$)$_n$-), 31.5-31.8 (-C$\underline{H}_2$-HC=HC-CH$_2$-CH=CH-C$\underline{H}_2$-), 34.0 (-CO-C$\underline{H}_2$-), 41.8 (-HC=HC-C$\underline{H}_2$-CH=CH-), 66.0 (-CO-O-C$\underline{H}_2$-CH-), 128.0 (-CH=C$\underline{H}$-CH$_2$-C$\underline{H}$=CH-), 174 (-CO-); IR (neat, cm^{-1}): 3008.37, 1747.24, 1163.74, 757; LC-MS: [*m/z* of (M + Na$^+$)] ions: 405 (16:0); 429 (18:2); 431 (18:1).

2-Ethyl-1-hexyl mono esters of Jatropha fatty acids: ^{1}H NMR (CDCl$_3$, δ ppm): 0.9 (m, -C$\underline{H}_3$), 1.0-1.2 (t, -CH$_3$), 1.4 (m, -CH$_2$), 1.6-1.7 (m-C-CH$_2$-C$\underline{H}_2$-), 2.0 (m, -CH=CH-C$\underline{H}_2$), 2.3 (t, -C-CH$_2$-), 2.7-2.8 (t, =CH-C$\underline{H}_2$-CH=), 3.9-4.0 (t, -CH$_2$-O-), 5.3-5.4.0 (m, -CH=CH-); ^{13}C NMR (CDCl$_3$, δ ppm): 14.0 (C$\underline{H}_3$), 22.6 (CH$_3$-C$\underline{H}_2$-), 25.5 (-CO-CH$_2$-C$\underline{H}_2$-), 27.1-29.6 (-(C$\underline{H}_2$)$_n$-), 31.5-31.8 (-C$\underline{H}_2$-HC=HC-CH$_2$-CH=CH-C$\underline{H}_2$-), 34.0 (-CO-C$\underline{H}_2$-), 41.8 (-HC=HC-C$\underline{H}_2$-CH=CH-), 66.0 (-CO-O-C$\underline{H}_2$-CH-), 128.0 (-CH=C$\underline{H}$-CH$_2$-C$\underline{H}$=CH-), 174 (-CO-); IR (neat, cm^{-1}): 3008, 1747 (-C=O); 1163 (C-O). 757; LC-MS: [*m/z* of (M + Na$^+$)] ions: 391 (16:0); 415 (18:2); 417 (18:1).

RESULTS AND DISCUSSION

Jatropha oil containing oleic acid (45.7%) and linoleic acid (33%) was hydrolyzed to obtain the corresponding fatty acids. Fatty acids from jatropha (acid value, 193 mg KOH/g) were esterified with various alcohols namely, NPG, TMP, TME, PE, MPPD, 3,5,5-trimethyl-1-hexanol and 2-ethyl-1-hexanol using *p*-TSA as catalyst (**Scheme-I**). Synthesis of jatropha polyols and branched mono-alcohol esters was done affording high yield (90-96.5%) of corresponding esters. The physico-chemical and structural characterization of the resulting compounds was carried out. Low hydroxyl values of all the esters (0.3-0.9 mg KOH/g) indicated almost complete esterification of alcohols. The formation of ester groups was confirmed by FTIR absorption at 1745-1738 cm^{-1} wavenumber (Fig. 1). The peaks in the ^{1}H NMR spectra at δ 2.28-2.30 ppm (CH$_2$CH=CH-), δ 3.9-4.0 ppm (CH$_2$O-C=O), δ 2.21-2.25 ppm (CH$_2$C=O), 1.6-1.2 ppm (CH$_2$) and 0.85-0.93 ppm (CH$_3$), while the ^{13}C NMR supported the terminal methyl carbon at 14 ppm. The LC-MS revealed the corresponding molecular ion peaks of JNPG, JMPPD, JTME, JTMP, JTMH and JEH, which further confirmed the formation of corresponding branched, mono-, di-, tri- and tetra-esters, respectively. All the physico-chemical properties, lubricant and tribological properties like wear (ASTM D-4172) and weld load (IP 239) properties were also evaluated (Table-1).
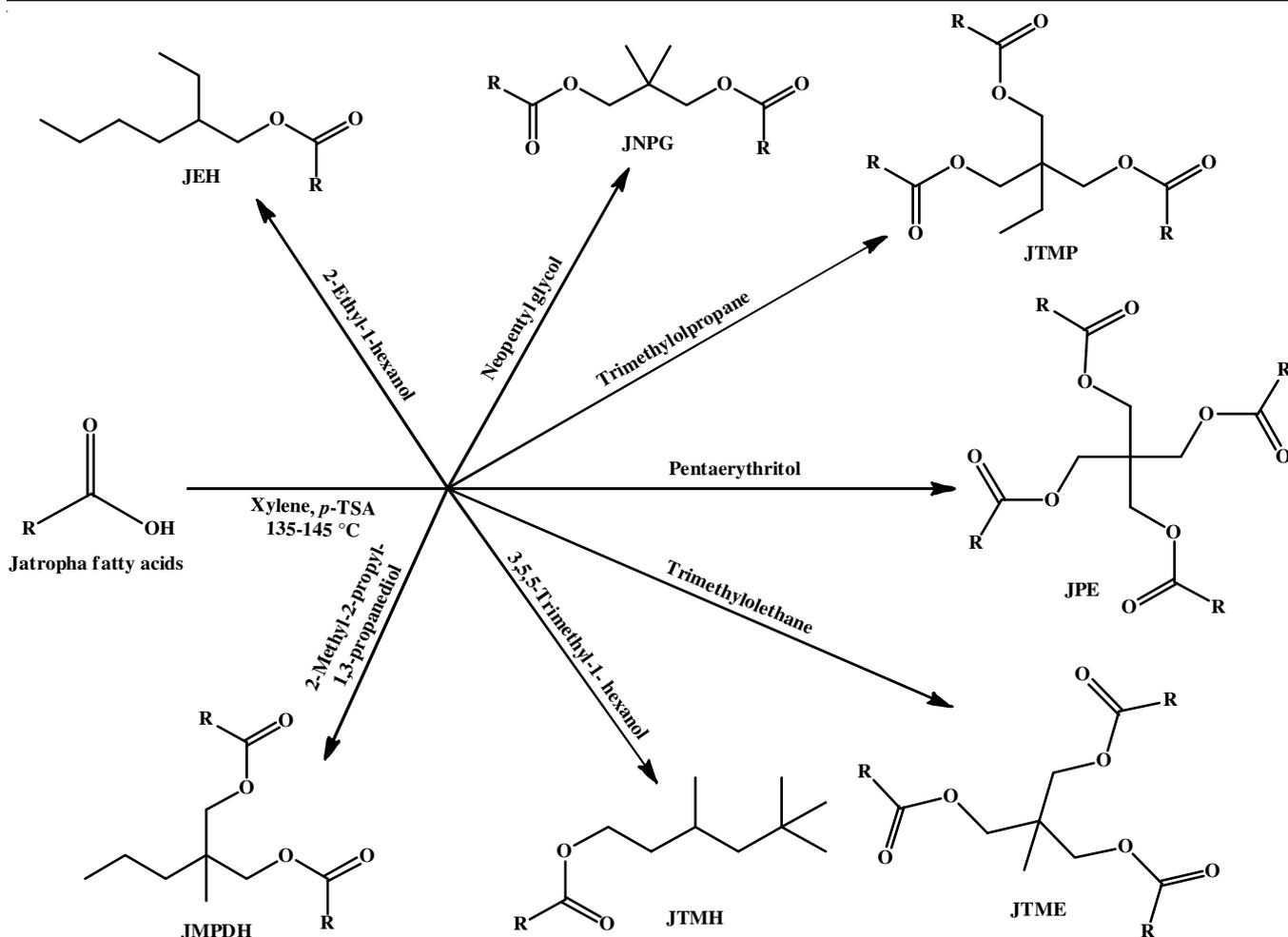
Scheme-I: Preparation of mono and branched jatropha polyol esters

TABLE-1
JATROPHA POLYOL AND BRANCHED MONO ALCOHOL ESTERS HAVE LUBRICATING AND PHYSICAL CHARACTERISTICS

Property		JNPG	JMPDH	JTME	JTMP	JPE	JTMH	JEH	ISO 10532
Total acid number (mg) KOH/g		0.3	0.6	0.4	0.6	0.7	0.41	0.64	2.0
Hydroxyl value (mg) KOH/g		0.4	0.4	0.6	0.9	0.8	0.4	0.4	–
Density		0.906	0.9031	0.922	0.921	0.9292	0.8680	0.8753	–
Specific gravity		0.907	0.9039	0.923	0.922	0.9300	0.8688	0.8761	–
Viscosity	40 °C	25.36	26.48	48.77	49.73	74.87	11.29	8.73	[a]
(cSt)	100 °C	6.13	6.32	9.99	9.91	13.6	3.39	2.78	–
Viscosity index		205	204	196	190	187	176	184	175
RPVOT value (min)		10	10	15	15	18	10	10	–
Flash point (°C)		288	290	300	302	310	162	154	250
Pour point (°C)		-15	-12	-10	-12	-9	-12	-18	[b]
Weld load (kg)		150	155	160	160	165	145	140	–
Wear scar dia. (mm)		0.684	0.694	0.584	0.589	0.556	0.566	0.576	0.5
Copper corrosion		1a	1a	1a	1a	1a	1a	1a	1a
Foam	Sequence 1	nil/nil	nil/nil	10/nil	nil/nil	nil/nil	30/nil	80/nil	150/10
stability	Sequence 2	nil/nil	nil/nil	10/nil	10/nil	nil/nil	40/nil	20/nil	300/10
(mL)	Sequence 3	nil/nil	nil/nil	10/nil	nil/nil	nil/nil	20lnil	80/nil	150/10
TGA (on set point °C)		337	334	376	378	398	233	228	–
Auto ignition temperature (°C)		425	423	435	437	485	405	403	370

[a]Viscosity grade: ISO VG 22 at 40 °C = 19.8-24.2 cSt; ISO VG 46 at 40 °C = 41.4-51.6 cSt; ISO VG 68 at 40 °C = 61.2-74.8 cSt.
[b]Pour point: ISO VG 22 = -12 °C; ISO VG 46 = -09 °C; ISO VG 68 = -09 °C.
JNPG: Jatropha neopentylglycol esters; JMPPD: Jatropha 2-methyl, 2-propyl, 1,3-propane diol esters; JTME: Jatropha trimethylolethane esters; JTMP: Jatropha trimethylolpropane esters; JPE: Jatropha pentaerythritol esters; JTMH:Jatropha 3,5,5-tri methyl-1-hexanol esters; JEHE: Jatropha 2-ethyl-1-hexanol esters.
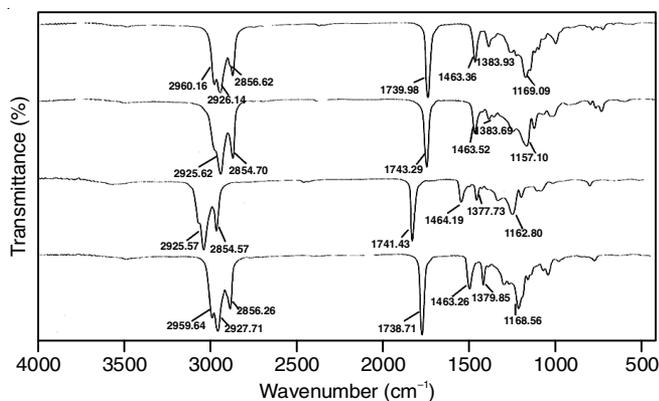
Fig. 1.   FT-IR spectrum of jatropha polyol esters (a) J-EHE, (b) JNPG J, (c) JTMP and (d) JPE

Increased molecular weight and reduced molecular flexibility due to branching or presence of ring structures generally increases viscosity. The ester molecular weight increases with an increase in either the amount of carbon atoms or the number of ester groups per molecule. Jatropha esters are not different from this trend. The viscosities and densities of seven esters were found to decrease as the number of ester groups per molecule decreased. The pentaerythritol (PE) esters which have the most ester groups, fall under ISO VG 68 of IS 10532 (Part 5) fire resistant hydraulic fluids followed by TMP and TME esters, which showed their kinematic viscosity at 40 °C in the range of ISO VG 46. The JNPG and JMPPD esters can be classified as ISO VG 22 grade although their viscosities are slightly higher than the required viscosity range. Due to their low molecular weights, the branched mono alcohol esters JTMH and JEH displayed low viscosities and are classified as ISO VG 10 viscosity grade fluids. The products' viscosities ranged from 2.71 to 13.6 cSt at 100 °C.

All the seven synthesized esters showed high viscosity indices, ranging from 176 to 205, which is a desirable characteristic for a lubricant as a high viscosity index attributes little change over a wide temperature range and these products can be used further for high temperature applications. According to API categorization, jatropha fatty acid esters fall into the group III category of base fluids based on viscosity index. These viscosity indices fall well within the parameters needed to produce hydraulic fluids that are fire resistant.

Pour point is used to gauge a lubricant's low-temperature fluidity. Vegetable oils have a high pour point because they may easily develop a packed structure at low temperatures by uniformly stacking the long chain fatty acids of triacylglycerol. Due to steric interactions, the presence of a polyol and branched mono alcohol attached to the fatty acid prevents easy stacking of the individual molecules, improving the fluidity of the final product. The low pour points of all the polyol and branched mono alcohol esters ranged from -6 to -18 °C. Esters JNPG and JMPPD, which fall under the ISO VG 22 category, satisfy the IS 10532 specification requirement of -12 °C. The base fluid of JPE satisfies the criteria of ISO VG 68 grade (-9 °C). While JTMP's pour point of -6 °C falls short of -3 °C, ester JTME, which belongs to the ISO VG 46 category, meets the requirement of -9 °C. Further formulation with pour point depres-

sant can facilitate the deficiency. Due to the branching in the alkyl chain, the branched chain esters JTMH and JEH both had low pour points.

It was observed that all the polyol esters had high flash points. As predicted, the compounds' flash points rose as ester groups per molecule increased. Due to their low viscosity and low molecular weights both JTMH and JEH exhibited lower flash points (162 and 154 °C). A high flash point is a highly desirable criterion for fire resistant hydraulic fluids because it ensures better safety in the handling and storage of lubricant. All polyol esters with flash points greater than 175 °C (288-310 °C) fall well within the range of IS 10532 fire resistant hydraulic fluids.

The auto-ignition temperature is the point at which the oil vapour ignite spontaneously without the help of an external igniters such as a spark or pilot flame under specific conditions. All the jatropha esters with auto ignition point above 400 °C (403-485 °C) fall within the prescribed range of IS 10532 fire resistant hydraulic fluids. Polyols esters with higher molecular weight exhibited higher values.

The tendency of oils to foam can be a severe problem in hydraulic systems and frequently result in air-entrainment issues like cavitations and poor fluid compressibility and slow hydraulic reaction. Among the polyol esters, JNPG, JMPPD and JPE esters did not display foaming. However, JTME only displayed a 20 mL of very little foam at sequences 1, 2 and 3, while TMP esters only displayed 20 mL of foam at sequence 2. JTMH esters have shown improved foam stability among the two branched mono esters.

Ability to withstand high temperatures is a vital characteristic of a hydraulic fluid. Good thermal stabilities of the polyesters can be attributed to the absence of hydrogen atoms on the β-carbon atom of the alcohol portion of ester. In comparison to polyols based on TMP, which are more stable than those based on NPG, pentaerythritol-based polyols have a tendency to be very thermally stable [24]. Similar pattern is observed in case of jatropha polyol esters, JPE esters exhibited highest TGA onset temperature at 398 °C followed by JTMP and JTME esters with onset temperatures 378 and 376 °C, correspondingly followed by JNPG and JMPPD with 337 and 334, respectively. As branched chain esters are less stable than linear alkyl chain esters, they exhibit less stability [25]. All the jatropha polyol esters are potential base stocks for fire resistant hydraulic fluids due to their high thermal stability.

Oxidation stability: Oxidation stability is another important property, which refers to how resistant a lubricant is to oxidation. The removal of β-hydrogen atom during the chemical conversion of triglycerides to polyol and branched mono esters increases the oxidation stability. The pentaerythritol (PE) esters are typically much more stable than TMP esters, NPG and branched mono esters. Similar pattern is noticeable in the case of jatropha esters. Among the esters, oxidative stability was greater for JPE esters, (18 min) followed by TME and TMP (15 min) and the rest exhibited RPVOT value of 10 min. The oxidative stability for jatropha esters is comparable to that of unsaturated rich fatty acid esters like TMP trioleate [26].

Corrosion test: The copper corrosion test establishes a material's tendency to deteriorate metal. The findings show that all the jatropha fatty acid-based esters fall under class 1a (slight tarnish). According to the colour of the copper strip, the term "class" denotes the characteristic of copper corrosion. As a result, there was little corrosion caused by any of the esters used in this study on metals.

Load capacity: The jatropha ester's ability to support the weld loads was also evaluated using an extreme pressure test. Esters typically have weld load between 140 and 165 kg. Due to the presence of more polar functional groups in the molecule and their interactions with the metallic surfaces, the PE esters of jatropha oil had a higher weld load (165 kg) than other esters. When compared to NPG and MPPD esters, whose respective weld load capacities were 150 and 155 kg, both TMP and TME esters showed improved weld load capacities (160 kg). Both the monoesters exhibited weld load below 150 kg.

Anti-wear property: This property describes the anti-wear capabilities of lubricant in preventing dimensional loss of a single solid between two moving surfaces, with or without real decoupling and material loss. It is well known that polyol esters exhibit appealing tribological characteristics, particularly with regard to boundary and anti-wear properties, which are attributed in large part to the presence of ester groups whose presence results in good anti-wear property. Among the polyol esters JPE exhibited better anti-wear property followed by TMP, TME esters, followed by NPG and MPPD esters. This feature is imparted by an increase in the amount of ester groups, which results in a higher binding of the molecules and a greater resistance to shear pressures. Branched monoesters display anti-wear property due to better flexibility of the molecule, which promotes binding to the surface [27].

Conclusion

In this study, jatropha oil was chemically altered to produce branched mono and polyol esters that closely matched the requirements of ISO VG 22 grade and IS 10532 (Part 5) fire resistant hydraulic fluids in the case of trimethylolpropane (TMP) and tri-methylolethane (TME) esters and ISO VG 46 grade in the case of TMP and TME esters. In conclusion, all base-stocks exhibiting rigorous qualities could be used to make fire-resistant hydraulic fluids.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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