



Partially Dehydrated Castor Oil-Based Isoalkyl and Polyol Esters as Potential Base Stocks for Industrial Applications

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Partially dehydrated castor oil (PDCO) which is of less use in the paint and furniture coating formulations has been modified to develop biolubricant base stocks. PDCO (44.1%, non-conjugated linoleic acid; 32%, conjugated linoleic acid (18:2) isomers and 15.3% ricinoleic acid) obtained from a local industry was hydrolyzed under alkaline conditions. The fatty acids obtained (PDCFAs) in 98% yields were reacted with polyols namely 2-ethyl hexanol, neopentyl glycol, trimethylol propyl, pentaerythritol to obtain respective isoalkyl esters and esters of polyol with >95% yield. The base stocks exhibited very high viscosity indices (187.288 to 187.687), excellent pour point (-25 to -40 °C) and high flash points (212 to 317 °C) required for a variety of industrial applications namely metal working, hydraulic, forging, cutting fluid, gear oil applications. The tribological properties of PDCO, exhibited very low WSD (0.72-0.79 mm) and WSVs (0.82-0.83 mm³) with high load carrying capacities (180-220 kg) indicating low friction and less energy losses between the sliding surfaces. This was also accompanied by very high thermo-oxidation stabilities [Oxidation stability (230-242 °C); Onset temperature (300-381 °C)] of the base stocks due to branching. Overall all the PDCO isoalkyl and polyol esters exhibited excellent properties suitable for a wide range of industrial applications on par with mineral oil based lubricants.

Keywords: Partially dehydrated castor oil, Polyols, Lubricant base stocks, Oxidation stability, Wear scan.

INTRODUCTION

There is a constant fight against the use of environmentally hazardous, non-biodegradable lubricants entering into the ecosystem by the way of total loss applications and spillages. This thirst for environmentally friendly resources, led to the exploration of plant oil-renewable materials [1]. In this context several government directives and legislations have been fighting to overcome the above said crisis [2]. For a country like India, where major percentage of the edible oils is being imported 60% [3], making it impossible to use edible oils for other industrial formulations. Keeping in view the above fact, one has to look into non-edible oils or oils which are thrown away either after use or having non-suitable composition.

Castor is one such oil, the most commercially used, highly renewable source used in chemical industry [4,5]. It is a major source used in the preparation of a number of industrial formu-

lations such as paints, coatings, inks and lubricants. The hydroxy functionality of ricinoleic acid (87-90% of castor oil) makes the castor oil a natural polyol providing oxidation stability and relatively high shelf life. As ricinoleic acid contains dual functionality -OH and double bond can be exploited for a number of chemical modifications useful in the preparation of a variety of base molecules.

One of the most important modifications of the oil is the dehydration step where one -OH and neighboring -H are removed resulting in dehydrated castor oil (DCO). DCO contains conjugated 75-90% of 9, 11-linoleic acid and rest being isolated double bonds (composition and analysis of dehydrated castor oil [6]). It is used as drying oil by adducting with maleic anhydride and is extensively used in furniture coatings and paint industries. It was observed that when DCO was used in the formulations, improved the glossiness of the films and its flexibility by 60% [7]. The dehydrated oil alkyd based film

revealed the shortest drying time with greater hardness. This property of DCO is due to the presence of >90% conjugated linoleic acid and more number of double bonds exposed to oxidation compared to castor oil or any other oil [8].

However, during the process some amount of partially DCO (PDCO) with less conjugation and more ricinoleic acid is obtained which cannot be used as drying oil. In most of the industries, PDCO with less conjugated linoleic acid will be either thrown into waste or sold away at a throw-away-price. On the other hand, there is a rapid increase in the demand for biolubricants, so as to save the environment from hazardous leaks and spillages. In this context, a thought was given to use PDCO with poor conjugated linoleic acid and more ricinoleic acid for developing biolubricant base stock with superior properties, as there are numerous reports on castor oil modifications for developing biolubricant base stocks [9-12]. As ricinoleic acid is present to an extent of 87-90% in castor oil, biolubricant base stocks developed exhibited excellent pour point, superior wear and weld properties in most of the studies. However, due to less unsaturation in partially dehydrated castor oil (PDCO) compared to completely dehydrated castor oil (DCO), it is anticipated that base stocks prepared from partially dehydrated have better thermo-oxidation properties. This can add value to PDCO which does not find a place in coating applications. The chemistry of esterification of fatty acids with polyols has been widely used in several lubricant industries. This is due to the fact that, polyols due to lack of β -hydrogen in the triglyceride, exhibit superior thermo-oxidative, pour point, wear and weld load properties.

Taking this chemistry, PDCO (44.1%, non-conjugated linoleic acid; 32%, conjugated linoleic acid (18:2) isomers and 15.3% ricinoleic acid) obtained from a local industry was reacted with polyols namely 2-ethyl hexanol, neopentyl glycol, trimethylol propyl and pentaerythritol. The biolubricant base oil prepared was assessed for their physico-chemical and tribological characteristics.

EXPERIMENTAL

Partially dehydrated castor oil (PDCO) was purchased from M/s Rajeev Industries Pvt. Ltd., (Hyderabad, India). 2-Ethylhexanol, neopentyl glycol, trimethylol propane (TMP), pentaerythritol (PE), *p*-toluenesulfonic acid (*p*-TSA), Xylene, aluminum oxide active basic and sodium hydroxide were purchased from M/s S.D. Fine chemicals Pvt. Ltd., (India). Solvents (hexane, methanol and ethyl acetate) were obtained from M/s Industrial Solvents and Chemicals Pvt. Ltd. (Mumbai, India). All the solvents and reagents were of analytical grade and have been used without further purification.

Physico-chemical characteristics: PDCO and its derivatives (base stocks) were evaluated for acid [13], iodine [14], hydroxyl [15], saponification [16], oxirane [17], density [18], kinematic viscosity [19], viscosity index (vi) [20], flash point [21], pour point [22], copper strip corrosion [23], oxidative onset temperature (OOT) test [24], thermogravimetric analysis [25], weld load [26] and wear [27] values using standard AOCS and ASTM methods.

Fatty acid composition of partially dehydrated castor oil (PDCO): PDCO oil (100 mg) was refluxed with 2% H₂SO₄ in methanol (20 mL) for 2 h at 55 °C. The change in the reaction, esterification was checked by TLC eluted with the solvent system of hexane:ethyl acetate (90:10, v/v). The contents were extracted with ethyl acetate, washed with water until neutral, dried over anhydrous Na₂SO₄ to get fatty acid methyl esters analyzed using gas chromatography equipped with flame ionization detector (GC-FID).

GC analyses of PDCO-FAME were performed using Agilent 6890N (Agilent Technologies, USA) gas chromatograph equipped with a flame-ionization detector (FID). The injector and detector temperatures were maintained at 250 °C and 270 °C, respectively. The carrier gas (constant flow mode) used was nitrogen, at 1 mL/min with a split ratio of 1:50. The analyses were carried out on a CP-WAX 58 FFAP CB (Agilent Technologies, USA; 25 m × 0.53 mm i.d., 1.0 μ m film thickness) mega bore column. The oven temperature was initially set at 200 °C for 1 min then increased to 250 °C at 10 °C min⁻¹ and then maintained for a hold time of 15 min. The total run time was 21 min. Data acquisition and processing were developed using Agilent Chemstation software.

Thermogravimetric analysis: The polyol esters were determined for their thermal decomposition stability by employing thermogravimetric analysis (TGA), TA Q500 instrument in a non-isothermal mode using nitrogen atmosphere. An aluminum crucible was taken and around 5.0 mg of the sample was placed in it, applying heating at the rate of 10 °C/min at a temperature range of 35-500 °C.

Preparation of partially dehydrated castor fatty acids (PDCFA): PDCO (300 g, 0.34 mol) and NaOH solution (53.20 g, 1.33 mol in 650 mL water) were taken and reacted under mechanical stirring at temperatures 80-90 °C for 5 h. The change in the reaction was monitored by TLC using hexane/ethyl acetate (90/10 vol) solvent system. The reaction mixture was cooled to 50 °C and acidified with dilute HCl. The contents were extracted with ethyl acetate, washed with water to remove excess HCl. Solvent was removed using rotary evaporator followed by vacuum drying (3-5 mm Hg) to obtain 284.1 g, (94.7 %) of PDCFA.

Esterification of PDCFA: PDCFA were esterified with isoalkyl, 2-ethyl hexanol and polyols like NPG, TMP, and PE to obtain respective mono and branched polyol esters.

Preparation of 2-ethylhexyl esters of PDCFA: PDCFA (300 g, 0.34 mol), 2-ethylhexanol (67.0 g, 0.51 mol), *p*-TSA (3.0 g, 1 %wt. of dehydrated castor fatty acids) and xylene were taken into a three necked round-bottomed flask, fitted with Dean and Stark water separator and thermometer. The contents were stirred using a magnetic stirring at 135-140 °C, till theoretical amount of water was collected. On completion of the reaction, xylene was distilled out under vacuum. The contents were washed with water by taking into organic solvent ethyl acetate. The contents were passed over basic alumina column using hexane for the removal of unreacted fatty acids present in traces to obtain 2-ethylhexyl esters of PDCFA with an acid value < 0.1. The structure of 2-ethyl hexyl esters was confirmed by spectroscopic methods, infrared, ¹H & ¹³C NMR.

Preparation of neopentyl glycol esters of PDCFA:

PDCFA (300 g, 0.34 mol), neopentyl glycol (11.47 g, 0.11 mol), *p*-TSA (3 g, 1% wt. of PDCFA) and xylene were taken into a three-necked reaction flask with a provision to arrange a Dean and Stark water separator and thermometer. The contents were stirred magnetically at 135-140 °C until calculated amount of water was obtained. On completion of the reaction, xylene was distilled out at 135-140 °C by applying the reduced pressure of 2-3 mm Hg. The contents were taken in ethyl acetate and washed with water until it was acid free. Solvent was removed by rotary evaporator and dried under reduced pressure to obtain PDCNPGE. The product was further purified by passing over basic alumina column using hexane to remove traces of unreacted fatty acids to yield the desired product with an acid value of < 0.1. The structure of the product was confirmed by spectroscopy, IR, ¹H & ¹³C NMR.

PDCNPGE and PDCPE esters were prepared following a similar procedure by the esterification of PDCFA, trimethylol propyl (TMP) and pentaerythritol (PE). The structures of all the isoalkyl and polyol esters were characterized employing spectroscopic methods namely IR, ¹H & ¹³C NMR.

Spectral data

2-EtH ester: IR (neat, cm⁻¹): 3006 (=C-H), 2926, 2855 (C-H), 1738 (-C(O)-), 1172 (-C-O-). ¹H NMR (CDCl₃, δ ppm): 0.87-0.91 (t, CH₃-CH₂-CH₂-, CH₃-C-), 1.29 (m, (-CH₂-)_n), 1.60-1.75 (-CH₂-CH₂-C(O)-O-), 2.17 (s, CH₂-CH=CH-CH₂-CH=CH-CH₂-), 2.30 (m, -CH₂-CH₂-C(O)-O-), 4.11 (s, -C-CH₂-O-C(O)-CH₂-), 5.34-5.45 (m, -CH=CH-CH₂-CH=CH-), 5.92-6.02 (m, -CH=CH-CH=CH-). ¹³C NMR (CDCl₃, δ ppm): 10.98-14.10 (CH₃-); 22.58-32.57 (-CH₂-); 34.22 (-CH₂-C(O)); 40.61, 63.67 (O-CH₂-C-); 73.69 (-CH-OH); 126.96 (CH₂-CH=CH-CH₂-CH=CH-CH₂-); 128.07 (CH₂-CH=CH-CH=CH-CH₂-); 130.30 (-CH=CH-CH₂-CH=CH-); 132.49 (CH₂-CH=CH-CH=CH-CH₂-); 173.49 (-CH₂-C(O)). ESI-MS (*m/z*): 415.54 [M+Na], 433.46 [M+Na].

NPG ester: IR (neat, cm⁻¹): 3009 (=C-H), 2929, 2856 (C-H), 1743 (-C(O)-), 1166 (-C-O-). ¹H NMR (CDCl₃, δ ppm): 0.87-0.96 (t, CH₃-CH₂-CH₂-, CH₃-C-), 1.30 (m, (-CH₃-)_n), 1.62 (-CH₂-CH₂-C(O)-O-), 2.17 (s, CH₂-CH=CH-CH₂-CH=CH-CH₂-), 2.29-2.32 (m, -CH₂-CH₂-C(O)-O-), 3.88 (s, -C-CH₂-O-C(O)-CH₂-), 5.34-5.47 (m, -CH=CH-CH₂-CH=CH-), 5.92-6.02 (m, -CH=CH-CH=CH-). ¹³C NMR (CDCl₃, δ ppm): 14.10 (CH₃-); 22.58-32.57 (-CH₂-); 34.22 (-CH₂-C(O)); 40.61, 63.67 (O-CH₂-C-); 73.69 (-CH-OH); 126.96 (CH₂-CH=CH-CH₂-CH=CH-CH₂-); 128.07 (CH₂-CH=CH-CH=CH-CH₂-); 130.30 (-CH=CH-CH₂-CH=CH-); 132.49 (CH₂-CH=CH-CH=CH-CH₂-); 173.49 (-CH₂-C(O)). ESI-MS (*m/z*): 139.10, 389.41, 543.53, 651.92 [M+Na], 667.79, 824.01 and 932.69 [M+Na].

TMP ester: IR (neat, cm⁻¹): 3009 (=C-H), 2927, 2856 (C-H), 1742 (-C(O)-), 1169 (-C-O-). ¹H NMR (CDCl₃, δ ppm): 0.87-0.90 (t, CH₃-CH₂-CH₂-, CH₃-C-), 1.3 (m, (-CH₂-)_n), 1.60 (-CH₂-CH₂-C(O)-O-), 2.17 (s, CH₂-CH=CH-CH₂-CH=CH-CH₂-), 2.28-2.31 (m, -CH₂-CH₂-C(O)-O-), 4.01 (s, -C-CH₂-O-C(O)-CH₂-), 5.34-5.45 (m, -CH=CH-CH₂-CH=CH-), 5.92-6.02 (m, -CH=CH-CH=CH-). ¹³C NMR (CDCl₃, δ ppm): 14.10 (CH₃-); 22.58-32.57 (-CH₂-); 34.22 (-CH₂-C(O)); 40.61, 63.67

(O-CH₂-C-); 73.69 (-CH-OH); 126.96 (CH₂-CH=CH-CH₂-CH=CH-CH₂-); 128.07 (CH₂-CH=CH-CH=CH-CH₂-); 130.30-130.87 (-CH=CH-CH₂-CH=CH-); 132.49 (CH₂-CH=CH-CH=CH-CH₂-); 173.49 (-CH₂-C(O)). ESI-MS (*m/z*): 139.10, 352.32, 583.82, 682.00 [M+Na], 962.64.

PE ester: IR (neat, cm⁻¹): 3010 (=C-H); 2927, 2855 (C-H); 1743 (-C(O)-); 1164 (-C-O-). ¹H NMR (CDCl₃, δ ppm): 0.88 (t, CH₃-CH₂-CH₂-, CH₃-C-), 1.29 (m, (-CH₂-)_n), 1.60 (-CH₂-CH₂-C(O)-O-), 2.17 (s, CH₂-CH=CH-CH₂-CH=CH-CH₂-), 2.30 (m, -CH₂-CH₂-C(O)-O-), 4.11 (s, -C-CH₂-O-C(O)-CH₂-), 5.38-5.59 (m, -CH=CH-CH₂-CH=CH-), 5.92-6.02 (m, -CH=CH-CH=CH-). ¹³C NMR (CDCl₃, δ ppm): 14.10 (CH₃-); 22.58-32.57 (-CH₂-); 34.22 (-CH₂-C(O)); 40.61, 63.67 (O-CH₂-C-); 73.69 (-CH-OH); 126.96 (CH₂-CH=CH-CH₂-CH=CH-CH₂-); 128.07 (CH₂-CH=CH-CH=CH-CH₂-); 130.30-130.87 (-CH=CH-CH₂-CH=CH-); 132.49 (CH₂-CH=CH-CH=CH-CH₂-); 173.49 (-CH₂-C(O)). ESI-MS (*m/z*): 139.10, 413.33, 583.75, 639.71, 864.45 and 946.49 and 1185.07.

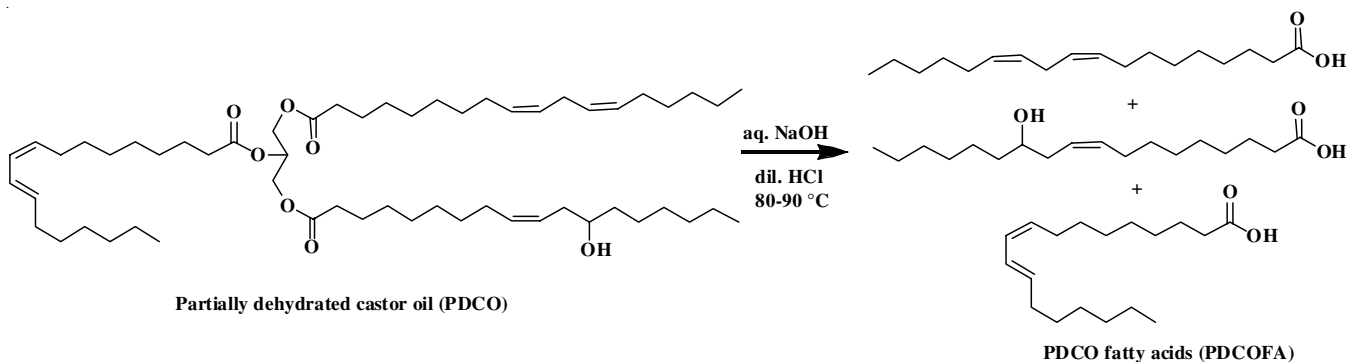
RESULTS AND DISCUSSION

Castor is a well known renewable source that has been utilized in the preparation of a number of lubricant base stocks with varied properties [9-11]. On the other hand, dehydrated castor oil (DCO) prepared by the dehydration of castor oil is exploited widely in paint and coating industry as a drying oil [5]. However, if the dehydration is not complete, resulting in partially dehydrated oil, the material is of less use and most of it is sold away at a throw away price. During the process of dehydration, sometimes partially dehydrated oil (PDCO) is also obtained in good quantities (Table-1). With an intention to value add PDCO, the material was chemically modified to polyol ester for application into lubricants. As PDCO contains non-conjugated linoleic acid (18:2), 44.1%; conjugated linoleic acid (18:2) isomers, 32.0%; ricinoleic acid (18:1-OH), 15.3% in major amounts with other fatty acids in minor quantities (Fig. 1), it is expected to possess high thermo-oxidative stabilities with low pour points and superior tribological properties.

TABLE-1
COMPOSITION OF FATTY ACIDS (wt%)
OF PDCO METHYL ESTERS

Fatty acids	Area (%)
Palmitic acid, 16:0	2.4
Stearic acid, 18:0	2.0
Oleic acid, 18:1	4.2
Non-conjugated linoleic acid, 18:2	44.1
Conjugated linoleic acid (18:2) isomers	32.0
Ricinoleic acid (18:1-OH)	15.3

Partially dehydrated castor oil (PDCO) was hydrolyzed using NaOH solution to obtain PDCO fatty acids, more than 95% purity. A representative structure of triglyceride containing non-conjugated linoleic acid, conjugated linoleic acid and ricinoleic acid hydrolyzed to PDCFA is shown in **Scheme-I**. The fatty acids were esterified with 2-ethyl hexanol, neopentyl glycol, trimethylol propyl and pentaerythritol with about 95-98% purity (**Scheme-II**).



Scheme-I: Preparation of partially dehydrated castor oil fatty acids (PDCFA)

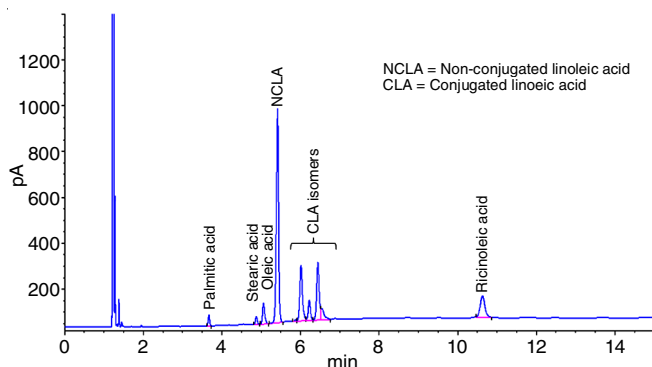
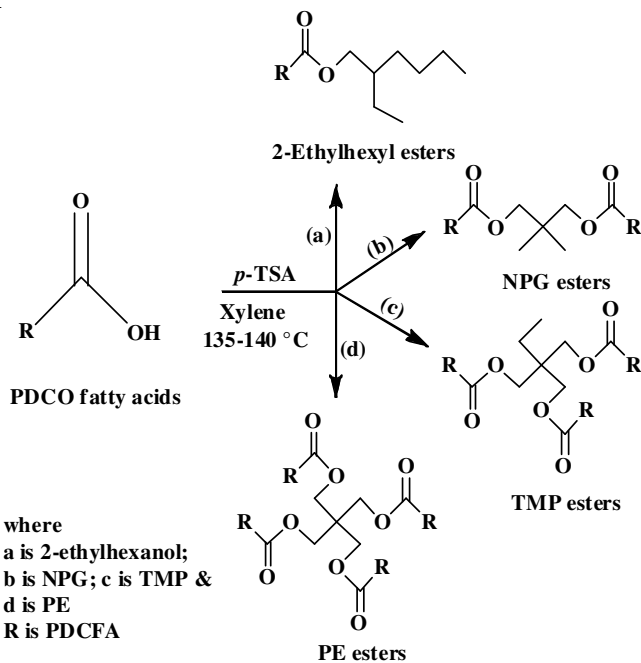


Fig. 1. GC chromatogram of Partially dehydrated castor oil methyl esters

singlet at δ 0.96; triplet at δ 2.3; singlet at δ 3.8 in case of neopentyl glycol esters; quartet at δ 1.43-1.47; triplet at δ 2.3 and singlet at δ 4.0 in case of trimethylol propyl esters; triplet at δ 2.3, singlet at δ 4.01 in case of pentaerythritol esters and presence of conjugated ^1H multiplet at δ 5.92-6.02 and non-conjugated ^1H multiplet at δ 5.34-5.45 confirmed the structures of isoalkyl, 2-ethyl hexanol and polyol esters of PDCO. Further the base oils were characterized for lubricant properties employing ASTM methods (Table-3).

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTICS OF THE PDCO

Parameter	Methods	Value
Acid value (mg KOH/g oil)	AOCS cd 3d-63	4.97
Free fatty acid content (% as oleic acid)	AOCS cd 3d-63	2.49
Peroxide value (meq O_2/kg oil)	AOCS cd 8-53	16.91
Iodine value (g of $\text{I}_2/100$ g oil)	AOCS cd 1-25	117.07
Hydroxyl value (mg KOH/g)	AOCS cd 13-60	87
Saponification number (mg KOH/g oil)	AOCS cd 3-25	183.63
Unsaponifiable matters content (% of oil)	AOCS ca 6a-40	0.5025
Refractive index	AOCS cd cc 7-25	1.4814
Moisture Content (%)	AOCS cd ca 2c-25	0.04
Phosphorous content	IUPAC 1987	22.85



Scheme-II: Preparation of branched mono- and polyol esters of PDCO fatty acids

The physico-chemical properties of 2-ethyl hexanol and polyol esters were carried out by employing AOCS methods (Table-2). Lower acid values of less than 0.5 mg KOH/g and low -OH values < 5mg KOH/g indicated that the esterification was almost completed. The structures of 2-EtH and polyol esters were confirmed by ^1H & ^{13}C NMR, ESI-Mass and FT-IR spectroscopy. Doublet at δ 4.0 ppm in case of 2-ethyl hexanol,

The high viscosity ranges VG-10 for isoalkyl ester to VG-240 for polyol esters at 40 °C, indicated that these base stocks find wide range of industrial applications namely SN 500 grade mineral oil, forging, metal working and high temperature applications [9]. Presence of high viscosity indices further indicated their potential use in wide industrial formulations [12,28,29]. Presence of very low pour point and high flash points make these base stocks excellent sources for very stringent formulations such as aviation lubricants [30].

The most important set of properties to be looked into while selecting a suitable lubricant is its tribological properties with respect to lubricity, friction and wear [1]. These tribological properties are assessed based on the wear scar diameter (WSD) or volume (WSV), further indicating the load carrying capacity (evaluated as weld load). A stable tribofilm at evaluated temperatures and heavy loads is ensured when the lubricant possesses high viscosity index and low WSD and WSV, respectively [31].

TABLE-3
LUBRICANT PROPERTIES OF PARTIAL DEHYDRATED CASTOR OIL POLYOLS

Test	Method	D2EHE	DNPGE	DTMPE	DPEE	
Density (g/cc)	15 °C	ASTM D 4052	0.8748	0.9219	0.9373	0.9467
	30 °C		0.8645	0.9119	0.9275	0.9368
Specific gravity	15 °C	ASTM D 4052	0.8756	0.9227	0.9382	0.9476
	30 °C		0.8683	0.9159	0.9315	0.9409
Kinematic viscosity (cSt)	40 °C	ASTM D 445	7.8026	56.7036	137.638	242.44
	100 °C		2.5953	11.1375	22.0443	33.967
Viscosity index		ASTM D 2270	187.687	193.54	187.288	187.288
Oxidation stability (min) DSC		ASTM E 2009-08	230.55	233.32	239.36	242.90
Onset temperature (OC) TGA		[25]	300.80	335.13	364.46	381.29
Pour point (°C)		ASTM D 97	-40	-37	-28	-25
Flash point (°C)		ASTM D 93	212	271	304	317
Copper strip corrosion		ASTM D 130	1a	1a	1a	1a
Weld load (Kg)		IP 239	180	180	210	220
Wear WSD (mm)		ASTM 4172	0.72	0.70	0.74	0.79
Wear WSV (mm ³)		ASTM 4172	0.83	0.82	0.80	0.82

These base oils were evaluated for their anti-wear properties, where very low WSD and WSV along with high viscosity indices was observed, indicating their excellent lubricity behaviour (Fig. 2). High molecular weights and branching in polyols is responsible for such a behaviour [32]. The resistance to friction as discussed in these base stocks is further reflected in their high load carrying capacity (Table-3). The excellent anti wear property and high load carrying properties of isoalkyl and polyol esters provides an upper hand to these PDCO esters over the mineral oil-based lubricants.

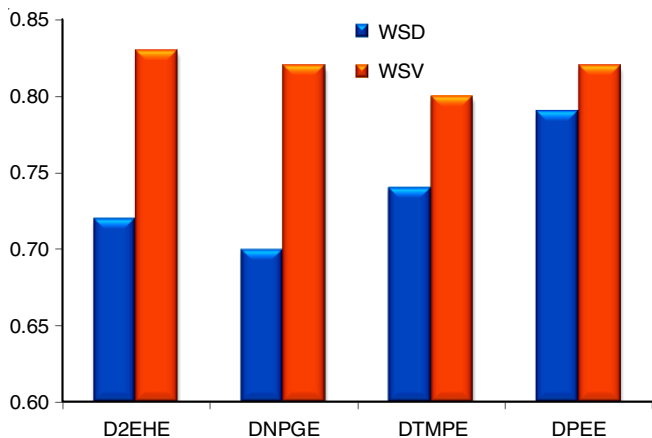


Fig. 2. Wear (WSD and WSV) values of mono and branched polyol esters

Further the stability and lubricity of a lubricant is also governed by its thermal and oxidative stabilities (Figs. 3 and 4). High thermo-oxidative stabilities are observed in highly branched molecules (due to steric hindrance) [1]. As polyol esters and iso alkyl esters of PDCO are highly branched, their thermo-oxidative stabilities were also very high indicating their wide range of industrial applications.

Conclusion

Partially dehydrated castor oil (PDCO) obtained from a local industry with good percentage of ricinoleic acid (15.3%), non-conjugated linoleic acid (44.1%) and conjugated linoleic acid isomers (32.0%) was chemically modified to 2-ethyl hexyl

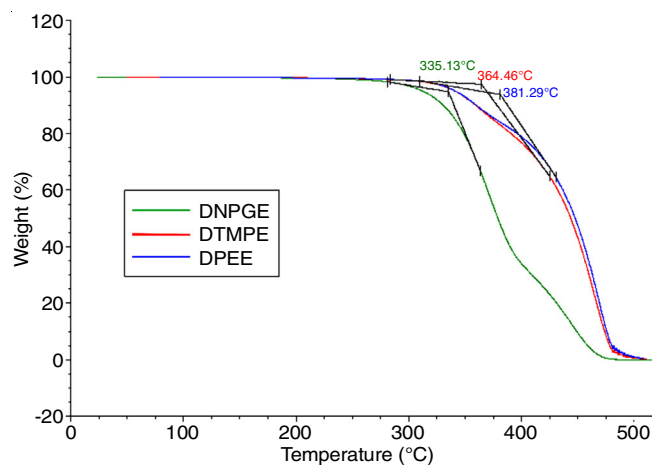


Fig. 3. Thermo-stability of partially dehydrated castor mono and branched alkyl esters

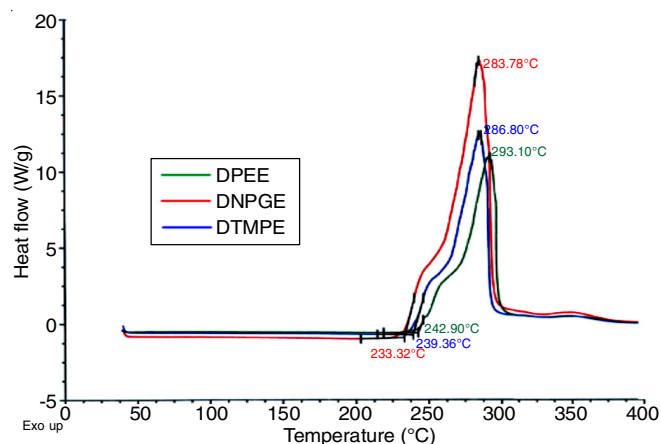


Fig. 4. DSC curves of partially dehydrated castor mono and branched alkyl esters

(iso alkyl) and neopentyl glycol (NPG), trimethylol propyl (TMP) and pentaerythritol (PE) ester (polyol ester) in >95% purity. The base stocks exhibited very high viscosity indices, excellent pour point and high flash points required for a variety of industrial applications namely metal working, hydraulic, forging, cutting fluid, gear oil applications. However, from

tribological point of view, good lubricant base stock can be judged in terms of its stability and the adhesiveness of its tribofilm reflected by low WSD and WSVs and high load carrying capacities. The prepared PDCO, exhibited very low WSD and WSVs with high load carrying capacities. This was also accompanied by high thermo-oxidation stability of the base stocks due to branching. Overall all the PDCO isoalkyl and polyol esters exhibited excellent properties suitable for a wide range of industrial applications on par with mineral oil based lubricants.

CONFLICT OF INTEREST

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

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