A Novel Methodology for the Synthesis of Acyloxy Castor Polyol Esters: Low Pour Point Lubricant Base Stocks

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Abstract: Castor oil, a non-edible oil containing hydroxyl fatty acid, ricinoleic acid (89.3 %) was chemically modified employing a two step procedure. The first step involved acylation (C_2 - C_6 alkanolic anhydrides) of -OH functionality employing a green catalyst, Kieselguhr-G and solvent free medium. The catalyst after reaction was filtered and reused several times without loss in activity. The second step is esterification of acylated castor fatty acids with branched mono alcohol, 2-ethylhexanol and polyols namely neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) to obtain 16 novel base stocks. The base stocks when evaluated for different lubricant properties have shown very low pour points (-30 to -45°C) and broad viscosity ranges 20.27 cSt to 370.73 cSt, higher viscosity indices (144-171), good thermal and oxidative stabilities, and high weld load capacities suitable for multi-range industrial applications such as hydraulic fluids, metal working fluids, gear oil, forging and aviation applications. The study revealed that acylated branched mono- and polyol esters rich in monounsaturations is desirable for developing low pour point base stocks.

Key words: castor oil, acylation, Kieselguhr-G, acyloxy polyol esters, low pour point

1 Introduction

In the recent years, the increasing concern towards pollution and environmental health aspects has attracted the use of biodegradable resources. In this context, lubricants which find several applications in day-to-day life are mostly lost to the environment, water and soil being directly contaminated¹. The air is also affected by volatile lubricants or lubricant haze. The use of biodegradable lubricants significantly reduces this environmental pollution.

From a technical point of view, 90% of present day lubricants can be made rapidly biodegradable by using vegetable oil products as well as modified vegetable oil esters as base-stocks. Though natural triglycerides are rapidly biodegradable and highly effective lubricants, their thermal, oxidation and hydrolytic stability is limited, though some of the oils such as rapeseed and sunflower oils are used directly as lubricants in the European countries. They are limited to low thermal stress applications like mold release and chain saw oils¹.

On the other hand, the disadvantages associated with natural vegetable oils can be overcome with structural modification at the double bond elements in the fatty acid

part and the β -CH group of the alcoholic components. Also, natural esters have a tendency to hydrolyze in the presence of water^{2,3}.

The chemical modifications usually carried out on vegetable oils are epoxidation, acylation at the double bond, removal of β -hydrogen atom in the triglyceride by transesterification or esterification of vegetable oils with polyols such as PE, TMP, NPG etc. Several such modifications have been reported on large number of edible oils such as palm and palm kernel oil⁴⁻⁶, soybean oil^{7,8}, Rapeseed oil^{9,10}, Rapeseed, olive oil and animal fat¹¹, sal fat^{12,13}, Mustard oil¹⁴ and non-edible oils such as jatropha¹⁵⁻¹⁸, karanja^{19,20}, rubber²¹, milkweed²², Thumba²³, castor²⁴. These modifications resulted in a variety of base stocks with varied specifications suitable for hydraulic, metal working and other industrial applications.

However, the acyloxy modifications involved use of catalysts such as DMAP, BF_3 -etherate, pyridine, p-TSA, H_2SO_4 and the solvents such as xylene and toluene. The use of these solvents and reagents makes the process expensive and their disposal in turn contaminates the environment. Hence, the present study was aimed at the development of

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a process by employing a non-toxic, low cost, readily available green catalyst and a solvent free medium. The development of efficient and environmentally benign pathways that can produce valuable products is desirable²⁵⁾. Further, the availability of raw materials also adds to the cost of the process. In this context, castor oil, where India (0.55 million metric tons) is the major producer²⁶⁾ and a source of a number of oleochemicals²⁷⁾ has been used as a raw material.

Castor oil, an unusual hydroxy fatty acid, ricinoleic acid containing vegetable oil is a magic source used for the production of a number of value added products. A number of literature reports exist on the modification of ricinoleic acid for the development of base stocks with large number of applications. Some of the recent publications on castor oil-based lubricant base stocks are as described. Castor oil fatty acid methyl esters were epoxidized using acetic acid and hydrogen peroxides (H_2O_2) in the presence of strongly acidic cation ion-exchange resin, Amberlite IR 120²⁸⁾. The authors observed that the base-stocks showed better thermal stability compared to commercial grade lube oil. Amith Suhane²⁹⁾ used a blend of castor oil with mahua oil as lubricant base stocks for automotive applications. The researchers found that the blend possessed good wear reducing property compared to servo gear oil. Castor based lubricant base stocks by reacting castor oil with hexanol, octanol, and dodecanol with high yields useful for a number of industrial applications were prepared by Deepika *et al.*³⁰⁾ employing *Candida antarctica* lipase (Novozyme 435). Ricinoleic based mono- tri- and tetra esters were synthesized by salih *et al.*³¹⁾, where the base stocks with low coefficient of friction were obtained. Estolide esters of ricinoleic acid with fatty acids of varying chain lengths were prepared and these base stocks exhibited good biodegradability with superior low temperature properties, viscosity index and cost comparable to petroleum oils³²⁾. Acylated ricinoleate esters with short chain acids were prepared by Yao *et al.*³³⁾, and the base stocks exhibited low melting temperatures, viscosities and good lubricity.

However, most of the modifications using castor oil included estolide esters³⁴⁾, straight chain esters³⁰⁾ or acylated esters³¹⁾. No reports are available on castor acyloxy polyol esters. In our previous work, we have prepared acyloxy derivatives of branched mono- and polyol esters of sal fat which resulted in multi viscosity grade base stocks suitable for high temperature and varied applications¹³⁾. The base stocks exhibited high pour points, which could be due to high degree of saturation. Most of the acylation processes involved introduction of hydroxyl groups by reacting double bonds at the unsaturation giving partially saturated derivatives, in turn resulting in high pour points. Also, the acylated products were prepared using DMAP as catalyst and xylene as solvent under high temperature at 140°C. With this background and an idea that castor oil with hy-

droxyl fatty acid and high degree of unsaturation, >98% if acylated at hydroxy, followed by esterification with branched mono alcohol and polyols may result in base stocks with broad range of viscosities and low pour points. An attempt was also made to develop green processes by acylating castor fatty acids employing heterogeneous, recyclable catalyst Kieselguhr-G, under solvent free conditions at low temperatures. The prepared acylated

derivatives of castor fatty acids were evaluated for basic physico-chemical and lubricant properties.

2 EXPERIMENTAL

2.1 Materials

Castor oil (BSS grade) obtained from M/s Ramcharan Industries Pvt. Ltd., (Hyderabad, India) was used without any purification. 2-ethylhexanol (2-EtH), NPG, TMP, PE, p-toluenesulfonic acid (p-TSA), acetic anhydride, xylene, aluminum oxide active basic, sodium hydroxide (NaOH) and sodium sulphate were purchased from M/s S.D. Fine chemicals Pvt. Ltd., (Mumbai, India). Kieselguhr-G, propionic, butyric and hexanoic anhydrides were procured from Sigma-Aldrich (St. Louis, MO, USA). Hexane, methanol, and ethyl acetate were procured from Industrial Solvents and Chemicals Pvt. Ltd. (Mumbai, India). All the solvents and reagents were of analytical grade and used directly without any further purification.

2.2 Methods

2.2.1 Spectral analysis

Infrared (IR) spectra were obtained using a 1600 FT-IR Perkin-Elmer Spectrometer (Norwalk, CT) with a liquid film between NaCl cells. The spectra were recorded in a transmittance mode. Proton nuclear magnetic resonance (1H NMR) spectra were recorded on Avance (300, 500 MHz) equipment in $CDCl_3$. Chemical shift values relative to TMS as internal standard are given as δ values in ppm. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in $CDCl_3$ on a Varian (75 MHz) spectrometer. (Thermogravimetric analysis) TGA studies were 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 a rate of 10°C/min up to 600°C. The TGA degradation onset temperature was obtained by extrapolating the horizontal base line and intercept of this line with tangent to the downward portion of the weight curve which was taken as onset temperature.

2.2.2 Physico-chemical analyses

Total acid number, iodine value (IV), oxirane value and hydroxyl value were determined using standard AOCS methods. The lubricant base stocks were evaluated for lubricant properties, such as density, specific gravity, kine-

matic viscosity, viscosity index, pour point, flash point, copper corrosion, TGA onset temperature, oxidative stability, weld load and wear using standard ASTM methods. All the analyses were carried out in duplicates and the results are an average of the two independent analysis.

2.2.3 Preparation of castor fatty acids (CFA)

Castor oil (300 g, 0.324 mol) and sodium hydroxide solution (51.88 g, 1.297 mol in 650 mL water) was stirred mechanically at 80–90°C for 5 h. The progress of the reaction was monitored by TLC using hexane/ethyl acetate (90/10 vol). Then 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. The solvent was removed using rotary evaporator followed by drying under reduced pressure (3–5 mm Hg) to obtain 279.5 g, (97.5%) of castor fatty acids (CFA).

2.2.4 Acylation of castor fatty acids

CFA (300 g, 1.01 mol), alkanolic anhydride (1.52 mol), and Kieselguhr-G (120 g, 40% based on weight of CFA) were taken in a three necked reaction flask, and were stirred mechanically at 60°C for 7 h. The course of the reaction was monitored by TLC using solvent system hexane/ethyl acetate (80/20 vol) and IR. After completion of the reaction, the resultant crude product was filtered to remove the Kieselguhr-G. The filtrate was distilled to remove excess alkanolic anhydride and alkanolic acid by applying reduced pressure at 140°C and 5 mm Hg, to get pure acylated CFA. The product was analyzed for acid value and hydroxyl value. The formation of the product was confirmed by spectral techniques such as IR, ¹H NMR, and ¹³C NMR.

2.2.4.1 Acetylated castor fatty acids

IR (neat, cm⁻¹): 3020 (=C-H), 2931, 2858 (C-H), 1737 (-C(O)-), 1715 (-C(O)-), 1181 (-C-O-).

¹H NMR (CDCl₃, δ ppm): 0.88 (t, CH₃-CH₂-), 1.19–1.39 (m, (-CH₂)_n), 1.49–1.57 (m, -CH₂-CH₂-CH₂-CH-O-), 1.58–1.69 (m, -CH₂-CH₂-C(O)-O-), 1.98–2.08 (m, -O-CH-CH₂-CH=CH-CH₂-CH₂-, CH₃-C(O)-O-), 2.22–2.32 (m, -OCH-CH₂-CH=CH-CH₂-CH₂-, 2.35 (t, -CH₂-CH₂-C(O)-O-), 4.84–4.91 (m, -CH₂-CH₂-O-C(O)-), 5.29–5.37 (m, -CH₂-CH=CH-CH₂-CHO-), 5.43–5.51 (m, -CH₂-CH=CH-CH₂-CHO-).

¹³C NMR (CDCl₃, δ ppm): 14.04, 21.24, 22.54, 24.61, 25.06, 25.31, 27.25, 28.97, 29.01, 29.46, 29.63, 31.70, 31.87, 33.54, 34.01, 34.63, 74.01, 124.17, 132.57, 170.93, 179.92.

2.2.4.2 Propionoylated castor fatty acids

IR (neat, cm⁻¹): 3012 (=C-H), 2929, 2857 (C-H), 1734 (-C(O)-), 1711 (-C(O)-), 1183 (-C-O-).

¹H NMR (CDCl₃, δ ppm): 0.88 (t, CH₃-CH₂-), 1.13 (t, CH₃-CH₂-C(O)-O-), 1.19–1.47 (m, (-CH₂)_n), 1.49–1.57 (m, -CH₂-CH-O-C(O)-), 1.57–1.75 (m, -CH₂-CH₂-C(O)-O-), 1.96–2.11 (m, -CH₂-CH=CH-CH₂-), 2.22–2.44 (m, -CH₂-CH₂-C(O)-, CH₃-CH₂-C(O)-), 4.84–4.96 (m, -CH₂-CH₂-O-C(O)-), 5.29–5.38 (m, -CH₂-CH=CH-CH₂-CHO-), 5.42–5.52 (m, -CH₂-CH=CH-CH₂-CHO-).

¹³C NMR (CDCl₃, δ ppm): 9.24, 14.03, 22.54, 24.15, 24.63,

25.08, 25.31, 27.26, 27.86, 28.79–29.64, 31.70, 31.94, 33.60, 33.94, 34.63, 35.22, 73.73, 124.28, 132.47, 169.54, 174.24, 179.42.

2.2.4.3 Butanoylated castor fatty acids

IR (neat, cm⁻¹): 3012 (=C-H), 2929, 2857 (C-H), 1734 (-C(O)-), 1711 (-C(O)-), 1183 (-C-O-).

¹H NMR (CDCl₃, δ ppm): 0.88 (t, CH₃-CH₂-), 0.94 (t, CH₃-CH₂-CH₂-C(O)-O-), 1.20–1.40 (m, (-CH₂)_n), 1.49–1.56 (m, -CH₂-CHO-), 1.57–1.69 (m, -CH₂-CH₂-C(O)-O-), 1.97–2.08 (m, -CH₂-CH=CH-CH₂-), 2.27 (t, -CH₂-CH₂-C(O)-), 2.35 (t, CH₃-CH₂-CH₂-C(O)-), 4.85–4.92 (m, -CH₂-CH₂-O-C(O)-), 5.29–5.37 (m, -CH₂-CH=CH-CH₂-CHO-), 5.41–5.49 (m, -CH₂-CH=CH-CH₂-CHO-).

¹³C NMR (CDCl₃, δ ppm): 13.65, 14.04, 18.53, 22.54, 24.62, 25.06, 25.31, 27.26, 29.10, 29.46, 29.63, 31.70, 31.94, 33.58, 33.98, 34.62, 36.53, 73.67, 124.27, 132.47, 173.48, 179.70.

2.2.4.4 Hexanoylated castor fatty acid

IR (neat, cm⁻¹): 3019 (=C-H), 2931, 2958 (C-H), 1733 (-C(O)-), 1715 (-C(O)-), 1184 (-C-O-).

¹H NMR (CDCl₃, δ ppm): 0.84–0.93 (m, CH₃-CH₂-), 1.20–1.41 (m, (-CH₂)_n), 1.49–1.57 (m, -CH₂-CHO-), 1.57–1.71 (m, -CH₂-CH₂-C(O)-O-), 1.97–2.08 (m, -CH₂-CH=CH-CH₂-), 2.27 (t, -CH₂-CH₂-C(O)-), 2.35 (t, CH₃-(CH₂)₃-CH₂-C(O)-), 4.85–4.93 (m, -CH₂-CH₂-O-C(O)-), 5.29–5.37 (m, -CH₂-CH=CH-CH₂-CHO-), 5.41–5.51 (m, -CH₂-CH=CH-CH₂-CHO-).

¹³C NMR (CDCl₃, δ ppm): 13.89, 14.03, 22.31, 22.53, 24.62, 24.76, 25.06, 25.31, 27.26, 28.97, 29.29, 29.46, 29.65, 31.28, 31.70, 31.94, 33.58, 34.01, 34.61, 73.66, 124.27, 132.46, 173.66, 179.87.

2.2.5 Esterification of acylated castor fatty acids

Acylated CFA derivatives were esterified with different branched mono alcohol, 2-ethylhexanol, and polyols such as NPG, TMP, and PE to obtain corresponding acylated branched mono- and polyol esters.

2.2.5.1 Typical procedure for the preparation of 2-ethylhexyl esters of acetylated castor fatty acids

Acetylated castor fatty acids (300 g, 0.902 mol), 2-ethylhexanol (175.9 g, 1.35 mol), p-TSA (3.0 g, 1% wt of acetylated castor fatty acids) and xylene were placed in a three necked round-bottomed flask, fitted with Dean and Stark water separator and thermometer. The reaction was performed under magnetic stirring at 135–140°C, until theoretical amount of water was collected. When the reaction was complete, xylene and excess of 2-EtH was removed from the reaction mixture at 135–140°C by applying the reduced pressure, 2–3 mm Hg. The reaction mixture was extracted with ethyl acetate and washed with water until free from acid. The solvent was removed by rotary evaporator and dried under vacuum to afford AC2-EtHE. The crude product was passed 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 formation of the product was confirmed by spectral techniques

such as IR, ^1H NMR, and ^{13}C NMR.

Similar procedure was followed for the esterification of propionylated CFA, butanoylated CFA and hexanoylated CFA with 2-EtH.

2.2.5.1.1 Acetylated 2-EtH esters (AC2-EtHE)

IR (neat, cm^{-1}): 3013 ($=\text{C-H}$), 2929, 2858 (C-H), 1736 ($-\text{C}(\text{O})-$), 1184 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , 300 MHz, δ ppm): 0.84-0.93 (m, $-\text{CH}_2-\text{CH}_3$); 1.20-1.39 (m, $-(\text{CH}_2)_n$); 1.43-1.48 (m, $-\text{CH}_2-\text{CH}-\text{CO}$); 1.49-1.69 ($-\text{CH}_2-\text{CH}_2-\text{C}=\text{O}$); 1.94-2.11 (m, $-\text{CH}-\text{CH}_2-\text{OCO}-$, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$); 2.26-2.40 (m, $-\text{CH}_2-\text{CH}_2-\text{C}=\text{O}$); 3.94-4.02 (m, $-\text{CH}-\text{CH}_2-\text{O}-\text{CO}-$); 4.84-4.91 (m, $(\text{OC})-\text{O}-\text{CH}-$); 5.27-5.51 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 10.96, 14.04, 21.24, 22.55, 22.95, 23.74, 25.10, 25.32, 25.58, 25.70, 27.15, 27.30, 28.88, 29.11, 29.32, 29.50, 30.37, 31.71, 31.95, 33.58, 34.39, 34.63, 36.81, 38.69, 66.58, 73.61, 124.27, 132.47, 173.50, 174.04.

2.2.5.1.2 Propionylated 2-EtH esters (PC2-EtHE)

IR (neat, cm^{-1}): 3012 ($=\text{C-H}$), 2929, 2858 (C-H), 1737 ($-\text{C}(\text{O})-$), 1185 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , 300 MHz, δ ppm): 0.84-0.93 (m, $-\text{CH}_2-\text{CH}_3$); 1.14 (t, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.21-1.39 (m, $-(\text{CH}_2)_n$); 1.43-1.49 (m, $-\text{CH}_2-\text{CH}(\text{O}-\text{C}(\text{O})-)-$); 1.50-1.69 (m, $-(\text{CH}_2-\text{CH}_2-\text{C}=\text{O})$), 1.98-2.08 (m, $-\text{CH}-\text{CH}_2-\text{OCO}-$, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$); 2.20-2.36 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 3.95-4.02 (m, $-\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$); 4.85-4.91 (m, $(\text{O})-\text{C}-\text{O}-\text{CH}-$); 5.29-5.59 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 9.21, 10.96, 14.01, 22.54, 22.94, 23.76, 24.99, 25.32, 25.69, 27.30, 27.64, 27.85, 28.88-29.66, 30.39, 31.71, 31.87, 31.96, 33.60, 34.39, 34.63, 35.33, 36.82, 37.71, 66.70, 71.46, 73.69, 124.27, 125.18, 132.47, 133.29, 173.51, 174.04.

2.2.5.1.3 Butanoylated 2-EtH esters (BC2-EtHE)

IR (neat, cm^{-1}): 3011 ($=\text{C-H}$), 2928, 2858 (C-H), 1737 ($-\text{C}(\text{O})-$), 1183 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.85-0.92 (m, CH_3-CH_2-), 0.96 (t, $\text{CH}_3-(\text{CH}_2)_2-\text{C}(\text{O})-\text{O}-$), 1.20-1.40 (m, $-(\text{CH}_2)_n$), 1.44-1.70 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.98-2.08 (m, $>\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$); 2.19-2.34 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 3.95-4.01 (m, $>\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$), 4.85-4.92 (m, $(\text{O})-\text{C}-\text{O}-\text{CH}<$); 5.29-5.60 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 10.96, 13.66, 14.02, 18.54, 22.54, 22.94, 23.77, 25.00, 25.32, 25.67, 27.16, 27.34, 28.86-29.66, 30.39, 31.71-31.96, 33.61, 34.39, 34.63, 35.33, 36.54, 36.82, 38.71, 66.60, 71.46, 73.62, 124.29, 125.18, 132.47, 133.29, 173.51, 174.04.

2.2.5.1.4 Hexanoylated 2-EtH esters (HC2-EtHE)

IR (neat, cm^{-1}): 3011 ($=\text{C-H}$), 2930, 2858 (C-H), 1737 ($-\text{C}(\text{O})-$), 1183 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.89 (t, CH_3-CH_2-), 1.18-1.41 (m, $-(\text{CH}_2)_n$), 1.44-1.70 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.95-2.09 (m, $>\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$); 2.18-2.37 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 3.93-4.04 (m, $>\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$), 4.83-4.93 (m, $-(\text{O})-\text{C}-\text{O}-\text{CH}<$); 5.26-5.52 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$).

CH_2-).

^{13}C NMR (CDCl_3 , δ ppm): 10.96, 14.03, 22.31, 22.54, 22.95, 23.74, 24.77, 25.00, 25.32, 27.29, 28.87, 29.11, 29.50, 30.37, 31.29, 31.71, 31.95, 33.60, 34.38, 34.61, 38.69, 66.58, 73.60, 124.27, 132.47, 173.56, 174.05.

2.2.5.2 Typical procedure for the preparation of NPG esters of acetylated castor fatty acids

Acetylated castor fatty acids (300 g, 0.902 mol), NPG (37.53 g, 0.36 mol), p-TSA (3 g, 1% wt of acetylated CFA) and xylene were placed in a three necked reaction flask, fitted with Dean and Stark water separator and thermometer. The reaction was performed under magnetic stirring at 135-140°C until theoretical amount of water was collected. When the reaction was complete, xylene was removed from the reaction mixture at 135-140°C by applying the reduced pressure of 2-3 mm Hg. The reaction mixture was extracted with ethyl acetate and washed with water until it was free of acid, and the solvent was removed by rotary evaporator and dried under vacuum to obtain ACNPG. 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 spectral studies using IR, ^1H NMR, and ^{13}C NMR.

Similar procedure was followed for the esterification of alkanoylated CFA with TMP and PE. The structures of all the acylated polyol ester products were analyzed by spectral techniques using IR, ^1H NMR, and ^{13}C NMR.

2.2.5.2.1 Acetylated castor NPG esters (ACNPG)

IR (neat, cm^{-1}): 3011 ($=\text{C-H}$), 2928, 2856 (C-H), 1738 ($-\text{C}(\text{O})-$), 1174 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $-\text{CH}_2-\text{CH}_3$), 0.97 (s, $\text{CH}_3-\text{C}-\text{CH}_3$), 1.20-1.38 (m, $-(\text{CH}_2)_n$), 1.49-1.56 (m, $-\text{CH}_2-\text{CH}-\text{CO}$), 1.57-1.67 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-$), 1.97-2.08 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-\text{C}(\text{O})-$, $\text{CH}_3-\text{C}(\text{O})-\text{O}-$); 2.24-2.36 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-\text{C}(\text{O})-$), 3.88 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.84-4.91 (m, $-(\text{O})-\text{C}-\text{O}-\text{CH}-$), 5.28-5.50 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 14.03, 21.23, 21.71, 22.54, 24.93, 25.08, 25.32, 27.29, 29.11, 29.49, 31.70, 31.94, 33.58, 34.23, 34.63, 68.97, 73.96, 124.19, 132.55, 170.77, 173.67.

2.2.5.2.2 Propionylated castor NPG esters (PCNPG)

IR (neat, cm^{-1}): 3013 ($=\text{C-H}$), 2930, 2857 (C-H), 1737 ($-\text{C}(\text{O})-$), 1179 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $-\text{CH}_2-\text{CH}_3$); 0.97 (s, $\text{CH}_3-\text{C}-\text{CH}_3$); 1.14 (t, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.21-1.37 (m, $-(\text{CH}_2)_n$), 1.49-1.56 (m, $-\text{CH}_2-\text{CHO}-$), 1.57-1.66 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.97-2.07 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.22-2.37 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 3.88 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.85-4.90 (m, $\text{O}=\text{C}-\text{O}-\text{CH}-$), 5.29-5.37 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.42-5.49 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 9.25, 14.03, 21.72, 22.54, 24.93, 25.08, 25.31, 27.30, 27.52, 27.85, 29.11, 29.50, 31.70, 31.95,

33.60, 34.24, 34.62, 68.97, 73.62, 124.27, 132.46, 173.48, 173.67.

2.2.5.2.3 Butanoylated castor NPG esters (BCNPGE)

IR (neat, cm^{-1}): 3011 ($=\text{C-H}$), 2929, 2856 (C-H), 1736 ($-\text{C}(\text{O})-$), 1180 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $-\text{CH}_2-\text{CH}_3$); 0.94 (t, $\text{CH}_3-(\text{CH}_2)_2-\text{C}(\text{O})-\text{O}-$), 0.96 (s, $\text{CH}_3-\text{C}-\text{CH}_3$); 1.21-1.38 (m, $(-\text{CH}_2)_n$), 1.49-1.56 (m, $-\text{CH}_2-\text{CHO}-$), 1.57-1.70 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.97-2.08 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.22-2.35 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-$), 3.88 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$), 4.85-4.92 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.29-5.37 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.42-5.49 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 13.66, 14.04, 18.44, 18.54, 21.72, 22.55, 24.94, 25.07, 25.32, 27.17, 27.30, 29.11, 29.32, 29.51, 29.66, 29.73, 31.71, 31.97, 33.61, 34.24, 34.63, 36.16, 36.53, 68.96, 73.61, 124.29, 132.46, 173.49, 173.66.

2.2.5.2.4 Hexanoylated castor NPG esters (HCNPGE)

IR (neat, cm^{-1}): 3010 ($=\text{C-H}$), 2928, 2856 (C-H), 1735 ($-\text{C}(\text{O})-$), 1181 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.85-0.93 (m, CH_3-CH_2- , $-\text{CO}-(\text{CH}_2)_4-\text{CH}_3$), 0.96 (s, $\text{CH}_3-\text{C}-\text{CH}_3$), 1.20-1.39 (m, $(-\text{CH}_2)_n$), 1.49-1.56 (m, $-\text{CH}_2-\text{CHO}-$), 1.57-1.68 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-$), 1.97-2.08 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.23-2.35 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-$), 3.88 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$), 4.85-4.91 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.29-5.37 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.42-5.50 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 13.89, 14.03, 21.72, 22.30, 22.53, 24.63, 24.76, 24.93, 25.07, 25.31, 27.30, 29.10, 29.50, 29.65, 31.29, 31.70, 31.96, 33.59, 34.23, 34.61, 68.96, 73.59, 124.28, 132.44, 173.53, 173.65.

2.2.5.2.5 Acetylated castor TMP esters (ACTMPE)

IR (neat, cm^{-1}): 3012 ($=\text{C-H}$), 2930, 2857 (C-H), 1738 ($-\text{C}(\text{O})-$), 1178 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $-\text{CH}_2-\text{CH}_3$), 1.19-1.39 (m, $(-\text{CH}_2)_n$), 1.39-1.68 ($-\text{C}-\text{CH}_2-\text{CH}_3$, $-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.96-2.01 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.18 (s, $\text{CH}_3-\text{C}(\text{O})-\text{O}-$), 2.23-2.37 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 4.02 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.84-4.91 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.29-5.38 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.42-5.50 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 7.32, 14.05, 20.78, 21.24, 22.54, 24.86, 25.06, 25.31, 27.29, 29.11, 29.50, 31.70, 31.93, 33.56, 34.14, 34.61, 40.45, 63.57, 73.95, 124.26, 132.46, 170.81, 173.52.

2.2.5.2.6 Propionylated castor TMP esters (PCTMPE)

IR (neat, cm^{-1}): 3011 ($=\text{C-H}$), 2929, 2858 (C-H), 1737 ($-\text{C}(\text{O})-$), 1180 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $\text{CH}_3-\text{CH}_2-\text{CH}_2-$, $\text{CH}_3-\text{C}-$), 1.13 (t, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.20-1.41 (m, $(-\text{CH}_2)_n$), 1.44-1.68 ($-\text{C}-\text{CH}_2-\text{CH}_3$, $-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.93-2.09 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.22-2.38 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 4.02 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.84-4.95 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.28-5.39 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.42-5.51 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 7.33, 9.05, 9.24, 14.03, 22.53, 22.94, 24.86, 25.07, 25.30, 27.15, 27.28, 27.45, 27.84, 29.10, 29.30, 29.50, 29.65, 29.72, 31.70, 31.94, 33.59, 34.14, 34.61, 40.56, 63.60, 73.61, 124.27, 132.45, 173.48, 174.15.

2.2.5.2.7 Butanoylated Castor TMP Esters (BCTMPE)
IR (neat, cm^{-1}): 3011 ($=\text{C-H}$), 2929, 2856 (C-H), 1736 ($-\text{C}(\text{O})-$), 1180 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $\text{CH}_3-\text{CH}_2-\text{CH}_2-$, $\text{CH}_3-\text{C}-$), 0.94 (t, $-\text{C}(\text{O})-(\text{CH}_2)_2-\text{CH}_3$), 1.20-1.39 (m, $(-\text{CH}_2)_n$), 1.44-1.69 ($-\text{C}-\text{CH}_2-\text{CH}_3$, $-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.94-2.08 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.19-2.36 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 4.01 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.84-4.92 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.28-5.39 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.42-5.50 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 7.33, 13.66, 14.04, 18.38, 18.53, 22.54, 22.91, 24.86, 25.06, 25.31, 27.29, 29.11, 29.50, 31.70, 31.95, 33.58, 34.14, 34.61, 36.05, 36.51, 40.51, 63.59, 73.59, 124.27, 132.44, 173.35, 173.48.

2.2.5.2.8 Hexanoylated castor TMP esters (HCTMPE)

IR (neat, cm^{-1}): 3010 ($=\text{C-H}$), 2929, 2857 (C-H), 1735 ($-\text{C}(\text{O})-$), 1181 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $\text{CH}_3-\text{CH}_2-\text{CH}_2-$, $\text{CH}_3-\text{C}-$), 1.18-1.42 (m, $(-\text{CH}_2)_n$), 1.43-1.72 ($-\text{C}-\text{CH}_2-\text{CH}_3$, $-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.94-2.10 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.20-2.39 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 4.01 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.82-4.96 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.25-5.39 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.40-5.53 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 7.30, 13.85, 14.02, 22.23, 22.28, 22.52, 22.87, 24.55, 24.76, 24.85, 25.05, 25.31, 27.29, 29.09, 29.50, 29.65, 31.19, 31.27, 31.68, 31.94, 33.57, 34.13, 34.59, 40.47, 63.60, 73.60, 124.25, 132.43, 173.53, 173.59.

2.2.5.2.9 Acetylated castor PE esters (ACPEE)

IR (neat, cm^{-1}): 3012 ($=\text{C-H}$), 2929, 2858 (C-H), 1738 ($-\text{C}(\text{O})-$), 1179 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $\text{CH}_3-\text{CH}_2-\text{CH}_2-$), 1.20-1.39 (m, $(-\text{CH}_2)_n$), 1.48-1.56 ($-\text{CH}_2-\text{CHO}-$), 1.58-1.68 ($-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.96-2.10 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.22-2.36 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 4.11 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.84-4.92 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.29-5.38 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.40-5.53 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 14.05, 21.24, 22.54, 24.79, 25.06, 25.31, 27.29, 29.11, 29.50, 31.70, 31.94, 33.56, 34.00, 34.61, 41.65, 62.02, 73.95, 124.27, 132.46, 170.79, 173.51.

2.2.5.2.10 Propionylated castor PE esters (PCPEE)

IR (neat, cm^{-1}): 3011 ($=\text{C-H}$), 2929, 2857 (C-H), 1737 ($-\text{C}(\text{O})-$), 1180 ($-\text{C-O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $\text{CH}_3-\text{CH}_2-\text{CH}_2-$), 1.13 (t, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.19-1.39 (m, $(-\text{CH}_2)_n$), 1.48-1.67 ($-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.95-2.09 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.22-2.39 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $\text{CH}_3-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 4.12 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.84-4.92 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.28-5.37 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.41-

5.50 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 8.99, 9.25, 14.04, 22.54, 24.80, 25.07, 25.31, 27.16, 27.31, 27.85, 29.11, 29.51, 29.67, 31.71, 31.95, 33.59, 34.02, 34.63, 62.06, 73.62, 124.26, 132.46, 173.49, 174.17.

2.2.5.2.11 Butanoylated castor PE esters (BCPEE)

IR (neat, cm^{-1}): 3012 ($=\text{C}-\text{H}$), 2929, 2856 ($\text{C}-\text{H}$), 1737 ($-\text{C}(\text{O})-$), 1181 ($-\text{C}-\text{O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.88 (t, $\text{CH}_3-\text{CH}_2-\text{CH}_2-$), 0.94 (t, $\text{CH}_3-(\text{CH}_2)_2-\text{C}(\text{O})-\text{O}-$), 1.20-1.39 (m, $(-\text{CH}_2-)_n$), 1.49-1.70 ($-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 1.95-2.09 (m, $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 2.19-2.35 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$), 4.11 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$), 4.84-4.92 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$), 5.28-5.38 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$), 5.41-5.50 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 13.66, 14.05, 18.32, 18.54, 22.54, 24.79, 25.07, 25.31, 27.30, 29.11, 29.51, 29.65, 31.70, 31.95, 33.58, 34.01, 34.61, 35.92, 36.52, 62.04, 73.60, 124.27, 132.46, 173.18, 173.51.

2.2.5.2.12 Hexanoylated castor PE esters (ACPEE)

IR (neat, cm^{-1}): 3012 ($=\text{C}-\text{H}$); 2928, 2856 ($\text{C}-\text{H}$); 1736 ($-\text{C}(\text{O})-$); 1181 ($-\text{C}-\text{O}-$).

^1H NMR (CDCl_3 , δ ppm): 0.81-0.98 (m, $\text{CH}_3-\text{CH}_2-\text{CH}_2-$); 1.17-1.43 (m, $(-\text{CH}_2-)_n$); 1.45-1.73 ($-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$); 1.93-2.11 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$); 2.18-2.39 (m, $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-$); 4.11 (s, $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$); 4.82-4.95 (m, $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-$); 5.26-5.38 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$); 5.41-5.52 (m, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}-$).

^{13}C NMR (CDCl_3 , δ ppm): 13.89, 14.04, 22.24, 22.31, 22.54, 24.50, 24.77, 25.07, 25.31, 27.16, 27.31, 29.11, 29.51, 29.67, 31.20, 31.29, 31.71, 31.96, 33.59, 34.01, 34.61, 41.77, 62.07, 73.62, 124.28, 132.45, 173.16, 173.49.

3 Results and discussion

Castor oil is one of the most abundant oils in the world with composition (palmitic acid, 0.9%; stearic acid, 1.2%; oleic acid, 4.0%; linoleic acid, 4.6%; ricinoleic acid, 89.3%). Castor oil was hydrolysed to obtain castor fatty acids with an acid value, 183.3 mgKOH/g. The hydroxyl functionality of ricinoleic acid in castor fatty acids was acylated using different anhydrides such as acetic, propionic, butyric and hexanoic in the presence of greener and recyclable catalyst Kieselguhr-G at 60°C . The acylated castor fatty acids were analyzed for acid value, hydroxyl value, and thoroughly characterized using spectral techniques. The products with lower hydroxyl value ≤ 2.9 , and decrease in acid value from 183.3 to 119/146 indicated almost complete acylation. The acylation of castor products were further confirmed by spectral studies like IR, ^1H NMR and ^{13}C NMR.

Acylated derivatives of the edible^{7, 13} and non-edible

oils^{17, 20, 22} resulted in base stocks with moderate to poor pour points. This is for the reason that the double bonds of the fatty acids are completely modified resulting in saturation and high pour points. With an idea to keep the double bonds intact, we have chosen, hydroxyl containing castor oil as raw material, so that the hydroxyl group in castor oil is only acylated keeping the double bond intact. Further, our work on oleic acid rich branched mono- and polyol esters of sal fat, resulted in multiviscosity base stocks suitable for a number of high temperature industrial applications¹³. Taking this fact into consideration, the hydroxyl functionality was acylated with varying anhydrides, followed by esterification using 2-ethylhexanol and polyols such as NPG, TMP and PE which resulted in a panel of 16 novel base stocks. The products appeared to be slightly dark colored liquids with the yields ranging from 85-94%. A representative Scheme is shown taking the synthesis of acyloxy castor TMP esters (Scheme).

Another novelty of the present work is to carry out acylation of the hydroxyl functionality using Kieselguhr-G, a diatomaceous earth composed of silica, with a small quantity of alumina, iron oxide and traces of other metal oxides, avoiding the use of expensive reagents such as DMAP required in conventional reactions. The reactions were carried out at 60°C lower temperature, compared to the routine reactions. The use of low temperatures also avoided the formation of side reaction i.e. estolide formation. After the reaction the contents were filtered and the Kieselguhr after filtration was washed with ethyl acetate, recycled several times, without losing its activity. Similar method was adapted by Balakrishna *et al.*³⁵, where the authors esterified the hydroxyl group of lyso phosphatidylcholine.

All the acylated products of CFA have some common peaks in FTIR, ^1H NMR and ^{13}C NMR as explained. IR spectra shows the appearance of two stretching bands at around 1710 cm^{-1} and 1737 cm^{-1} related to fatty acid chain carbonyl and acylated side chain carbonyl, in ^1H NMR spectra appearance of new peaks at around δ 4.8-4.9 ppm related to point of the substitution in the fatty acid chain $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-\text{R}$, multiplet at around δ 1.4-1.5 ppm related to C_{13} position CH_2 protons of the fatty acid chain and multiplet at around δ 5.4-5.5 ppm related to C_{10} position $=\text{CH}$ protons of the fatty acid chain confirmed acylation of CFA. In ^{13}C NMR spectra the peaks at around δ 73.6 ppm related to C_{12} carbon point of the substitution in the fatty acid chain $-\text{CH}_2-\text{CH}-\text{O}-\text{C}(\text{O})-\text{R}$, around δ 124.2, 132.4 ppm indicates the two different environmental olefinic carbons (C_9 and C_{10}) and peaks at around δ 173, 179 ppm related to acyl side chain carbonyl and fatty acid chain carbonyl further confirmed the almost complete acylation.

In case of acetylated CFA the presence of multiplet at δ 1.98-2.08 ppm related to methyl group protons of the acyl substituent $\text{CH}_3-\text{C}(\text{O})-$ in ^1H NMR and also characteristic

R= methyl, ethyl, propyl, pentyl

Scheme Synthesis of acylated castor TMP esters.

peaks at δ 21.24 ppm relating to acetate CH_3 in ^{13}C NMR confirmed the acetylation of CFA.

In case of propionylated CFA the presence of triplet at δ 1.13 ppm related to terminal methyl group of propionyl substituent, and an increase in the area of the peak at δ 2.22-2.44 ppm due to CH_2 protons α to the carboxy group of the propyl side chain in ^1H NMR and also characteristic peaks at δ 9.24 ppm related to methyl carbon on the end of propyl side chain, δ 35.22 ppm related to C_{11} carbon on fatty acid chain in ^{13}C NMR confirmed the propionylation of CFA.

In case of butanoylated CFA the presence of triplet at δ 0.94 ppm related to terminal methyl group protons of bu-

tanoyl side chain and presence of triplet at δ 2.35 ppm related to CH_2 protons α to the carboxy group of the acyl side chain in ^1H NMR and also characteristic peaks at δ 13.65 ppm related to methyl carbon on the end of butyl side chain, δ 36.53 ppm related to α to the carboxy group of the acyl side chain carbon in ^{13}C NMR confirmed the butanoylation of CFA.

In case of hexanoylated CFA the presence of multiplet at δ 0.84-0.93 ppm related to terminal CH_3 group protons of hexanoyl side chain and fatty acid chain and presence of triplet at δ 2.35 ppm related to CH_2 protons α to the carboxy group of the acyl side chain in ^1H NMR and also characteristic peaks observed in ^{13}C NMR at δ 13.89 ppm

related to methyl carbon on the end of the hexanoyl side chain, δ 34.61 ppm related to α to the carboxyl group of the acyl side chain carbon confirmed the hexanoylation of CFA.

In the second step the acylated castor products were esterified with branched mono- alcohol, 2-EtH, and polyols, NPG, TMP and PE to obtain 16 novel base stocks. All the 16 base stocks were thoroughly characterized using IR, ^1H NMR and ^{13}C NMR spectral techniques. The IR spectra of the base stocks did not exhibit acid carbonyl stretching band at around 1710 cm^{-1} and appearance of a prominent intensity, carbonyl functionality at $\sim 1735\text{ cm}^{-1}$ is due to increasing the ester functionality in all the products compared to acylated CFA confirmed esterification.

^1H NMR spectra, in case of acylated branched mono esters, 2-ethylhexyl esters presence of multiplet at δ 3.95-4.01 ppm related to $>\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$ confirmed the esterification. In case of acylated NPG esters presence of singlet at δ 0.96 ppm related to $\text{CH}_3-\text{C}-\text{CH}_3$, singlet at δ 3.88 ppm related to $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$, in case of acylated TMP esters presence of singlet at δ 4.02 ppm related to $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$ and prominent increasing area of the triplet at δ 0.88 ppm related to $-\text{C}-\text{CH}_2-\text{CH}_3$, in case of acylated PE esters presence of singlet at δ 4.11 ppm related to $-\text{C}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}_2-$, and also increasing the area of triplet at δ 0.88 ppm related to $\text{CH}_3-\text{CH}_2-\text{CH}_2-$ confirm the esterification.

In ^{13}C NMR spectra, in case of acylated castor 2-ethylhexyl esters characteristic peaks at δ 10.96 ppm related to $\text{CH}_3-\text{CH}_2-\text{CH}<$, δ 38.7 ppm related to $-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}<$, δ 66.5 ppm related to $-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}<$ and δ 174.04 ppm

related to carbonyl of the ester, in case of acylated castor NPG esters characteristic peaks at δ 21.71 ppm related to $\text{CH}_3-\text{C}-\text{CH}_3$ of NPG backbone, δ 68.97 ppm related to CH_2 of the NPG back bone and also appearance of ester carbonyl peak at δ 173.4 ppm along with the disappearance of acid carbonyl confirm the esterification. In case of acylated castor TMP esters characteristic peaks at δ 7.3 ppm related to $\text{CH}_3-\text{CH}_2-\text{C}-$ of TMP back bone, δ 40.5 ppm related to quaternary carbon of TMP back bone, δ 63.6 ppm related to $-\text{C}-\text{CH}_2-\text{O}-$ of TMP back bone and appearance of the peak at δ 173.5 ppm related ester carbonyl along with the disappearance of acid carbonyl confirm the formation of TMP esters. In case of acylated castor PE esters characteristic peaks at δ 62.0 ppm related to $-\text{C}-\text{CH}_2-\text{O}-$ of PE back bone and δ 173.5 ppm related to ester carbonyl along with the disappearance of acid carbonyl confirms the formation of PE esters.

All 16 base stocks were evaluated for their physico-chemical and lubricant properties following the standard AOCS and ASTM procedures (Tables 1, 2, 3 and 4). The base stocks exhibited low acid number <0.5 , hydroxyl value <7.2 indicating almost complete esterification and densities well within the required specifications for base stocks with industrial applications.

3.1 Lubricant properties

3.1.1 Kinematic viscosity

Castor fatty acids on acylation with varied chain lengths such as methyl, ethyl, propyl and pentyl followed by reaction with branched mono alcohol 2-EtH resulted in base stocks AC2-EtHE, PC2-EtHE, BC2-EtHE and HC2-EtHE,

Table 1 Physico-chemical and Lubricant Properties of AC2-EtHE, PC2-EtHE, BC2-EtHE and HC2-EtHE.

TEST		AC2-EtHE	PC2-EtHE	BC2-EtHE	HC2-EtHE
Total Acid Number (mgKOH/g)		0.12	0.21	0.29	0.35
Hydroxyl Value (mgKOH/g)		1.8	2.1	2.3	2.9
Density		0.90878	0.90736	0.90940	0.90643
Specific Gravity		0.90960	0.90818	0.91022	0.90722
Kinematic Viscosity (cSt) at	40°C	28.63	24.96	24.40	20.27
	100°C	5.71	5.23	5.27	4.81
Viscosity Index		144	146	155	170
Pour Point (°C)		− 39	− 42	− 42	− 45
Flash Point (°C)		165	172	179	191
TGA Onset Temperature (°C)		181	193	202	221
Copper Corrosion		1a	1a	1a	1a
Oxidative Stability (min) (RBOT)		15	20	18	15
Weld Load (kg)		150	150	155	155
Wear (mm)		0.73	0.75	0.79	0.81

Table 2 Physico-chemical and Lubricant Properties of ACNPGE, PCNPGE, BCNPGE and HCNPGE.

TEST		ACNPGE	PCNPGE	BCNPGE	HCNPGE
Total Acid Number (mgKOH/g)		0.19	0.23	0.35	0.41
Hydroxyl Value (mgKOH/g)		1.8	2.3	3.2	4.5
Density		0.94937	0.94885	0.94424	0.94045
Specific Gravity		0.95023	0.94971	0.94509	0.94130
Kinematic Viscosity	40°C	113.90	101.51	103.31	97.03
(cSt) at	100°C	15.84	15.62	16.22	14.84
Viscosity Index		148	164	170	161
Pour Point (°C)		−36	−36	−39	−42
Flash Point (°C)		243	249	259	272
TGA Onset Temperature (°C)		215	230.7	266	318
Copper Corrosion		1a	1a	1a	1a
Oxidative Stability (min) (RBOT)		15	18	20	16
Weld Load (kg)		160	160	165	165
Wear (mm)		0.78	0.81	0.85	0.91

Table 3 Physico-chemical and Lubricant Properties of ACTMPE, PCTMPE, BCTMPE and HCTMPE.

TEST		ACTMPE	PCTMPE	BCTMPE	HCTMPE
Total Acid Number (mgKOH/g)		0.15	0.23	0.29	0.49
Hydroxyl Value (mgKOH/g)		2.1	3.0	4.2	5.1
Density		0.96272	0.95808	0.95573	0.94924
Specific Gravity		0.96359	0.95894	0.95659	0.95007
Kinematic Viscosity	40°C	273.29	219.26	224.32	201.06
(cSt) at	100°C	29.59	27.01	28.71	25.93
Viscosity Index		145	158	166	162
Pour Point (°C)		−33	−33	−36	−36
Flash Point (°C)		275	281	290	303
TGA Onset Temperature (°C)		250	267	289	303
Copper Corrosion		1a	1a	1a	1a
Oxidative Stability (min) (RBOT)		20	20	20	20
Weld Load (kg)		170	170	175	175
Wear (mm)		0.83	0.85	0.91	0.95

with viscosities ranging from 20.27–28.63 cSt which are useful in low-viscosity grade industrial applications¹⁷⁾. The viscosities of the base stocks decreased compared to native castor oil due to monoester and lower molecular weight and branching. The different castor acylated products on further esterification with NPG, TMP and PE, the viscosities increased with increase in number of acyl groups as observed in most of the previous reports on polyol esters^{11,21)}. However, the increase in viscosities was less compared to other acyloxy polyol esters studied¹³⁾ for the reason that in

castor, only hydroxyl functionality is acylated unlike the other oils where the double bond is modified to obtain diacylated products.

Castor acylated, polyol esters with viscosities 97 to 371 cSt are suitable for a variety of industrial applications such as SN 500 grade mineral oil, forging, metal working and high temperature applications, SAE gear oil no. 80W-140, bearing lubricants and positive displacement blowers, forging lubricants and metal working fluids¹³⁾.

Table 4 Physico-chemical and Lubricant Properties of ACPEE, PCPEE, BCPEE, and HCPEE.

TEST		ACPEE	PCPEE	BCPEE	HCPEE
Total Acid Number (mgKOH/g)		0.15	0.29	0.38	0.53
Hydroxyl Value (mgKOH/g)		3.1	4.9	6.5	7.2
Density		0.96449	0.96318	0.96211	0.95630
Specific Gravity		0.96536	0.96498	0.96298	0.95716
Kinematic Viscosity	40°C	359.03	342.61	346.83	370.73
(cSt) at	100°C	37.65	38.17	40.32	42.83
Viscosity Index		153	161	169	171
Pour Point (°C)		−30	−33	−33	−36
Flash Point (°C)		309	317	328	341
TGA Onset Temperature (°C)		263	283	311	338
Copper Corrosion		1a	1a	1a	1a
Oxidative Stability (min) (RBOT)		18	15	15	16
Weld Load (kg)		175	175	180	180
Wear (mm)		0.86	0.89	0.91	0.93

3.1.2 Viscosity index

The viscosity index of these mono acylated 2-ethylhexyl and polyol esters ranged between 144–171 displaying a wide range in values indicating that their viscosities suffer lower changes with temperature, suitable for multirange applications^{24, 36}. However, viscosity index values were more than most of the reported acylated derivatives^{13, 17, 22}.

3.1.3 Pour point

The castor branched mono acylated 2-ethylhexyl and branched mono acylated polyol esters exhibited much lower and a wide range of values. In case of 2-ethylhexyl acylated products the pour points ranged between −39 to −45°C, suitable for most of the industrial applications with stringent properties such as aviation lubricants³⁷. The reason being, firstly castor is acylated at −OH functionality with the double bond intact unlike other acylated products^{7, 17, 20, 22} and acylated 2-ethylhexyl ester of oleic rich sal fatty acids¹³.

On the other hand, not much difference in the pour point was observed on esterification of the acylated castor fatty acids with NPG. On further reaction with TMP and PE the pour points increased (Tables 3 and 4), which could be due to high molecular weight, and less number of acyl groups as seen in acylated 2-ethylhexyl and acylated NPG esters. However, with the increase in the chain lengths of the acylated groups (acyl to hexyl) the pour points were slightly affected. Overall all the base stocks exhibited very low pour points, indicating that presence of mono unsaturation and acylation at −OH functionality is responsible for the decrease in the pour points³⁸.

3.1.4 Flash point

This value indicates the highest temperature at which test material catches fire. This value is useful in determin-

ing the volatility and fire resistance of the lubricant required during transportation and storage. All the base stocks exhibited flash points in the range 165 to 341. All the acylated derivatives with flash point of ≥165°C lie well within the range of hydraulic oils¹⁰. The flash point increases with increase in chain lengths of the acylated groups (acylated to hexanoylated)⁷. Further the flash points were found to increase with number of acylated groups i.e. PE>TMP>NPG>2-ethylhexyl of the polyols^{13, 21}. The flash point of acylated castor 2-ethylhexyl esters, showed values lower to those of 2-ethylhexyl dihydroxy lauryl, myristyl, palmitoyl, stearyl, behenyl esters and the values were higher than octyloxy and nonyloxy 2-ethylhexyl dihydroxy esters³⁹.

3.1.5 Thermal stability

The thermal stability of the 16 base stocks was determined from onset temperatures of thermal decomposition under nitrogen atmosphere. The value indicates the high temperature where the tri horizontal system fluid remains unimpaired. The thermal stabilities of acylated castor mono- and polyol esters were found to be lower compared to other acylated polyol esters¹³. This is due to the presence of unsaturation in castor, while the later being saturated in nature. Among all the base stocks, acylated branched 2-ethylhexyl esters exhibited lower values due to disturbance in crystalline packing⁴⁰. While, the values were found to increase with increase in number of acylated groups i.e. PE>TMP>NPG>2-EtH, and also increase in acyl chains reacted at the −OH functionality of ricinoleic acid in the castor oil. Over all, all the 16 base stocks exhibited very good thermal stabilities, suitable for a number high temperature applications, such as aviation, forging, metal working fluid applications.

3.1.6 Oxidation stability (RPVOT)

Resistance to oxidative degradation is another important attribute to a number of industrial materials such as lubricants, surfactants and fuels. The more resistance a lubricant is towards oxidation, the lower is its tendency to form deposits, sludge, corrosive by products in engine oil and industrial applications. This in turn imparts resistance to the undesirable increase in viscosity during usage. Oxidation takes place through a radical initiated chain mechanism leading to alcohols, ketones, aldehydes and carboxylic acids⁴¹⁾, in turn resulting in rancidity and toxicity^{42, 43)}. In general vegetable oil based esters are more stable towards oxidation and this increase with the removal of β -hydrogen in the triglyceride by reacting with polyols and branched polyols⁴⁴⁾. In the present study, though castor oil was mono- acylated keeping the double bond intact the oxidation stabilities were on par with other acylated branched mono and polyol esters¹³⁾ and diacylated oils^{17, 22)} which have more of saturation⁴⁵⁾. This indicates that mono acylation with unsaturation which is responsible for decrease in pour points, also resulted in good oxidation stability.

3.1.7 Wear scar diameter

It is an important tribological measurement, where the lubricant reduces the wear of one or both the surfaces in close proximity and moving relative to each other. An ideal lubricant allows smooth continuous operation of the equipment with only mild wear and without excessive stresses at the bearing. The process leading to loss of material of the surface is known as wear. Wear scar diameter is the average impression mark left over the three lower static balls due to the sliding action of the upper balls. It is measured using a microscopic after removing the balls from the balls fort.

Vegetable oils are known to exhibit excellent lubricity due to their ester functionalities. The wear scar diameter were found to be slightly higher compared to diacylated branched mono- and polyol esters¹³⁾, which could be due to presence of unsaturation and less branching i.e. mono acylation in the acylated castor branched mono- and polyol esters. Among all the base stocks under study, not much difference was observed in the wear values. However, the values were found to slightly increase with increase in alkyl chain lengths acylated at -OH functionality.

3.1.8 Weld load

The load carrying capacity of acylated castor branched mono- and polyol esters was higher compared to native castor oil, 135 kg due to the polar functional groups in the former. The values exhibited the highest load carrying capacity was in acylated castor PE esters (175-180 kg), followed by TMP esters (170-175 kg), NPG esters (160-165 kg) and 2-ethylhexyl esters (150-155 kg). This could be due to more number of acylated groups in PE esters¹³⁾. All the base stocks exhibited values comparable to other reported polyols^{12, 21, 23)}.

4 Conclusion

With an intention to develop lubricant base stocks with very low pour points and multi viscosity ranges, castor oil was selected as raw material. Castor oil fatty acids were acylated (C_2 - C_6 alkanolic anhydrides) employing a green and recyclable catalyst Kieselguhr-G and a solvent free medium at low temperatures. The use of low temperatures avoided the formation of estolides increasing the yield of acylated products. Kieselguhr-G after the reaction was filtered and reused several times without loss in activity. The acylated fatty acids were converted to the branched mono- and polyol esters. These novel base stocks exhibited very low pour points, multi viscosity ranges, good thermal and oxidative stabilities, anti wear and high load carrying capacities suitable for a number of industrial applications. Hence, polyols with acylation and mono unsaturation functionalities is desirable to obtain low pour point base stocks.

Supporting Information

This material is available free of charge via the Internet at <http://dx.doi.org/jos.64.10.5650/jos.ess.15133>

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