Chemical Modification of Camelina Oil based Unsaturated Fatty Acid for Renewable Biolubricant Base Stock

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A green and eco-friendly method for preparation of oleochemicals from Camelina oil was developed for possible application for bio-lubricant basestocks, The steps involved are consisting of epoxidation of Camelina oil based fatty acid followed by further branching with wide range of alcohol such as 2-propanol, *n*-butanol, isoamyl alcohol and 2-ethylhexanol. These products were evaluated with physico-chemical properties such as acid value, oxirane oxygen content (OOC), hydroxyl value, low temperature properties, viscosity at 40 and 100 °C, viscosity index and characterized by FTIR, ^{1}H NMR. The appearance of peak at 824 cm^{-1} in the FTIR spectra was due to the formation of epoxy group and broad peak appeared at 3500-3300 cm^{-1} is for hydrogen bonded O-H stretching vibration of hydroxy group. The ^{1}H NMR spectra showed a signal at 2.9-3.2 ppm region indicated CH-proton attached to the oxygen atom of the both epoxy group for epoxidized product, peaks for newly formed secondary alcohols emerged at 4.25-3.35 in alkoxy derivatives. The Camelina based synthetic product may find application in biolubricants base stock.

Keywords: Unsaturated fatty acid, Epoxidation, Chemical modification, Pour point, Viscosity index.

INTRODUCTION

Lubricants play important functions such as reducing friction by improving the smoothness between two moving surfaces, minimizing the heat generation due to friction, increasing the efficiency and minimizing energy losses. Currently, the most common types of lubricant available in the market are automotive transmission fluids, metal working fluids, hydraulic fluids, cold rolling oils, fire resistant hydraulic fluids, industrial gear oils and neat cutting oils [1-3]. The lubricants are consisting of about 70-99% of petroleum base oil and 1-30% of additives. The lubricant contaminates the environment by spillage accidently [4,5]. Lubricant has extensive environmental issue, dependency on fossils oil, non-renewable sources and low biodegradability.

Vegetables oils are triglycerides comprising three esters of fatty acids. Vegetable oils are the renewable resources, having good lubricity, biodegradability, low volatility, non-toxic, high flash point, high viscosity index over mineral oil. On the other hand, vegetable oil has poor oxidative, thermal stability, poor cold flow properties [6,7]. Unsaturated fatty acid is more susceptible to radical attack leads to oxidative degradation leading to deposits. The hydrocarbon ends of fatty acids are formed thin layer film around metal surfaces forming slid surface to prevent direct metal to metal contact [8]. The extend of adsorption on metal surfaces shows the efficiency of a lubricant's performance [9].

To minimize the problem associated with vegetable oil based lubricant modern approaches involves genetic modification, additive treatment or chemical modification [10]. Vegetable oils as considered as potential bio-lubricant based stock to replace conventional mineral oil based lubricating oil and synthetic esters. Salimon *et al.* [11] investigated synthetic ester oils as basestocks for lubricant applications by chemical modification of plant fatty acid, oleic acid with lower pour point. Castor oil contains high content of ricinoleic acid, which focused to chemical modification of hydroxyl groups through esterification [12]. The esterification of castor and lesquerella oil [13,14] to form estolides as alternate to bio-lubricant base-stock has been reported in the literature.

Camelina sativa is an oil seed crop, member of *Brassicaceae* family grown in some parts of the Europe and North America. It is commonly known as false flax or gold-of-pleasure and considered as weed in Europe [15]. The oil content in Camelina seed is twice (36-47%) than soybean oil (18-22%) [16]. The content of unsaturated fatty acids in Camelina oil is about 90%, with an average of 5.8 double bonds per triglyceride [17]. Both the unsaturated fatty acid content and the degree of unsaturation of Camelina oil are higher than that of soybean oil (84% and 4.6% respectively). Camelina oil contains high percentage of unsaturated fatty acid which is further revealed from its iodine value *i.e.* 140 g I_2/100 g as a result, it is less favourable for biodiesel feedstock.

Epoxidation is a key step for preparation of various bio-lubricants from vegetables oils. For instance, Petrovic *et al.* [18] has developed a process for production of epoxidized vegetables oils. In present study, it has been focused on synthesis of epoxidized fatty acid followed by ring opening with different alcohols. Various biolubricants prepared and correlated with reaction conditions and properties. The products are characterized by FT IR and ^{1}H NMR spectra.

EXPERIMENTAL

The *Camelina sativa* seeds were growing from its inter-cropping with *Jatropha curcas* plantation at DIBER-DRDO Project site Secunderabad. Reagents such as concentrated sulfuric acid (98%), 2-propanol (99.9%), 1-butanol (99.5%), iso-amyl alcohol (98%), 2-ethyl hexanol (99%) were purchased from Merck India. All other chemicals and reagents were obtained from Sigma-Aldrich (India) and used without any further purification. All the experiments were carried out using a single lot of Camelina oil.

Characterization: The physico-chemical properties such as acid value, iodine value, hydroxyl value of sample were estimated according to IS-548 1964 (Part I) [19] and oxirane oxygen content (OOC) was estimated as per AOCS official method Cd 9-57 [20,21]. The percentage of conversion of double bond to oxirane ring was quantified as per eqn. 1:

$$\text{Relative conversion to oxirane} = \left(\frac{\text{OOC}_{exp}}{\text{OOC}_{the}} \right) \times 100 \quad (1)$$

where experimental value of oxirane oxygen content denotes by OOC_{exp} and theoretical value maximum oxirane oxygen content in 100 g of Camelina oil denotes by OOC_{the} calculated by eqn. 2:

$$\text{OOC}_{the} = \frac{IV_o/2A_i}{100 + (IV_o/2A_i)A_o} \times A_o \times 100 \quad (2)$$

where, A_i and A_o are the atomic weights of iodine and oxygen respectively and IV_o are the initial iodine value of the Camelina oil.

The FT-IR spectra of Camelina oil based unsaturated fatty acid and final products were recorded using a Thermo Fisher FT-IR (NICOLET 8700) with an attenuated total reflectance (ATR) crystal accessory. The angle of incidence of the germanium ATR crystal used was characteristically 45° the spectra was recorded in the wavelength range 4000-600 cm^{-1}.

^{1}HNMR spectroscopic analysis of the unsaturated fatty acid, epoxy fatty acid and ring opened products was recorded on Bruker AVIII 600 MHz NMR spectrometer equipped with a 5 mm broadband (BBFO) probe (Bruker Biospin, Fallenden, Switzerland). Instrument was controlled and chemical shift (δ) was recorded using Topspin 3.2 software (Bruker Biospin, Fallenden, Switzerland). The samples were allowed to equilibrate for 5 min inside the NMR probe which preheated to the respective temperature. To achieve good line shape and reduce signal-to-noise (S/N), the signals were field frequency locked and shimmed using TopShim gradient shimming tool of the Topspin 3.2 software. The samples were dissolved in CDCl$_3$ solvent. The deuterated chloroform chemical shift peak at 7.26 ppm was considered as internal reference.

The pour point was measured according to ASTM D-97-96a Method. The pour point was observed in 3 °C increments until sample stopped pouring. The pour point is determined as the sample of test jar did ceases to flow.

Viscosity index (VI) is an arbitrary measure for the change of viscosity with temperature. The kinematic viscosity of branched fatty acid was measured using 20 mL of branched fatty acid at 40 and 100 °C directly with a Cannon-Fenske U-tube Viscometer. The viscosities were estimated using ASTM methods D 445-97 [22]. The temperature of the viscometer was maintained at ±0.1 °C via an external temperature controller.

Epoxidation of unsaturated fatty acid: Epoxidation of Camelina oil based unsaturated fatty acid (UFA) were performed in round bottom flask (250 mL capacity), placed in a thermostatic water bath which could control the reaction temperature up to ± 1 °C attached with a magnetic stirrer. In a typical experiment, UFA sample is taken in a flask known molar ratio of formic acid was added followed by dropwise addition of hydrogen peroxide to the flask cooled at 4 ºC (ice bath). The reactions were conducted at desired temperature in a water bath with rapid stirring. Samples were withdrawn at regular time interval to access the extent of completion of reaction. The reaction parameter such as molar ratio of UFA:HCOOH, molar ratio of UFA:H$_2$O$_2$, reaction temperature and reaction time were varied during the study. The collected sample was cooled down at room temperature, washed with distilled water and dried under vacuum to obtain colorless, transparent, viscous liquid.

The epoxidation of UFA was optimized by response surface methodology (RSM) [23] for maximum conversion of double bond of unsaturated fatty acid to epoxy fatty acid. The response was affected by three experimental variables such as molar ratio of (UFA) to HCOOH (x_1), molar ratio of UFA to H$_2$O$_2$ (x_2) and temperature (x_3). The OOC of epoxy fatty acid (Y) is expressed as a mathematical function of three variables, *i.e.* Y = f (x_1, x_2, x_3). The design expert software version 10 with a 3-factor, 2-level of full factorial central composite design (CCD) was utilized for experimental setup. The predicted response of experimental data is represented in term of a quadratic polynomial eqn. 3 [21] with independent variables of experiment.

$$Y = \beta_o + \Sigma\beta_i x_1 + \Sigma\beta_{ii} x_1^2 + \Sigma\beta_{if} x_1 x_2 \quad (3)$$

where, Y is predicted response of OOC, β_o is constant, β_i the linear effect, β_{ii} the squared effect and β_{if} is the interaction effect.

The results showed the experimental data were well fitted in RSM model with CCD experiment design, generated a second-order polynomial eqn. 4 in terms of coded factor and obtained predicted value which was successfully correlated to the experimental value.

Oxirane oxygen content = $+7.75 + 0.79A + 0.73B + 0.47C - 0.76AB + 0.26AC - 0.11BC - 0.63A^2 - 0.74B^2 - 0.14C^2$ [23]   (4)

where, A: molar ratio of UFA to HCOOH, B: molar ratio of UFA to H_2O_2, C: temperature.

The adequacy of the model was analyzed using analysis of variances (ANOVA) and results have been discussed in our previous study [23]. Study revealed that the maximum yield of OOC (8.11 %) was observed with the molar ratio of UFA to HCOOH (1:0.75) and molar ratio of UFA to H_2O_2 (1:1.5) stirring at 42.5 °C at 600 rpm for 6 h. The 3D response surface plots [23] between the effect of molar ratio of UFA to HCOOH also H_2O_2, temperature and their interaction on OOC were discussed. The predicted response from the quadratic model [23] between the predicted values and experimental values were shown linearly.

Ring opening of oxirane moiety in epoxy fatty acid: The opening of oxirane in epoxy fatty was conducted with short chain alcohols. The epoxy fatty acid (1 mol) was taken in 100 mL flat bottom flask, the reaction was conducted with different alcohol such as propanol, *n*-butanol, isoamyl alcohol (1.3 mol) catalyzed with 1.5 mL of H_2SO_4 dropwise and the mixture was heated at 70-80 °C for 4 h with stirring at 600 rpm. In case of ring opening of oxirane with 2-ethyl hexanol, epoxidized fatty acid (1 mol) was taken in 100 mL flat bottom, addition of 2-ethyl hexanol (2 mol) catalyzed with 2 mL of H_2SO_4 dropwise and the mixture heated at 100 ºC for 6 h with stirred at 800 rpm. The reaction mixture was cooled and washed with distilled water to remove the acid and excess alcohol. The remaining alcohol was recovered by rotary evaporator to obtain ring opened product.

RESULTS AND DISCUSSION

Physico-chemical analysis: The physico-chemical properties of camelina oil such as iodine value was 143 g I_2/100 g and acid value was 198 mg KOH/g. Further, Camelina oil based UFA was characterized for iodine value which was 162 g I_2/100 g. The physico-chemical properties changed after epoxidation, namely the acid value was 178 mg KOH/g, the iodine value decreased up to 9.49 g I_2/100 g with oxirane value is 8.11%. The iodine value decreased from 162 to 9.49 g I_2/100 g which further revealed more than 94% conversion during epoxidation (Table-1). The ring opening of epoxy fatty acids was carried out with different alcohol such as propanol, butanol, isoamyl alcohol, ethyl hexanol with sulfuric acid as catalyst at 80-100 ºC for 4-6 h (**Scheme-I**). The obtained propoxy fatty acid, butoxy fatty acid, isoamoxy fatty acid, ethyl hexoxy fatty acid having iodine value were 7.9, 7.6, 7.8 and 7.9 g I_2/100 g, respectively, oxirane oxygen content 0.18, 0.19, 0.17 and 0.13%, respectively indicated the presence of low unsaturation in it. The acid values of propoxy fatty acid, butoxy fatty acid, isoamoxy fatty acid, ethyl hexoxy fatty acid were 39.92, 26.51, 26.62 and 7.86, respectively which was decrease from 178 mg KOH/g (Table-1).

Viscosity index: The viscosity of propoxy, butoxy, iso-amoxy fatty acid were in the range of 152-168 cSt at 40 ºC, 19-21 cSt at 100 ºC and viscosity index was 142-159. The viscosity of ethyl hexoxy fatty acid was 11.65 cSt at 40 ºC, 3.3 cSt at 100 ºC and viscosity index was 166 (Table-1), the viscosity index increases with an increasing number of alkyl chains at mid and end points are considered to be more complex structure of products with high molecular weight which leads to increase viscosities. Ethyl hexoxy fatty acid is having high viscosity index with low viscosity change with temperature. It has been reported bio-lubricants having low viscosity change with the temperature attribute the stable viscosity temperature relation [24].

Hydroxyl value: The hydroxyl value of epoxy fatty acid was 2-3 mg KOH/g. The hydroxyl value of ring open derived

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF CAMELINA OIL BASED UNSATURATED FATTY ACID AND THEIR DERIVATIVES

Product	Iodine value (g I_2/100 g)	Acid value (mg KOH/g)	OOC (wt.%)	Hydroxyl value (mg KOH/g)	Pour point (°C)	Viscosity (cst)		Viscosity index
						40 °C	100 °C	
Unsaturated fatty acid	162	212	-	-	-9	22.4	6	238
Epoxidized fatty acid	9.49	178	8.11	2.5	0	257.7	37	194
Propoxy fatty acid	7.9	39.92	0.18	88.83	-10	168.9	20.5	142
Butoxy fatty acid	7.6	26.51	0.19	83.85	-18	152.9	19.9	151
Iso-amoxy fatty acid	7.8	26.62	0.17	83.91	-21	153.4	20.8	159
Ethyl hexoxy fatty acid	7.9	7.86	0.13	10.37	-40	11.65	3.32	169
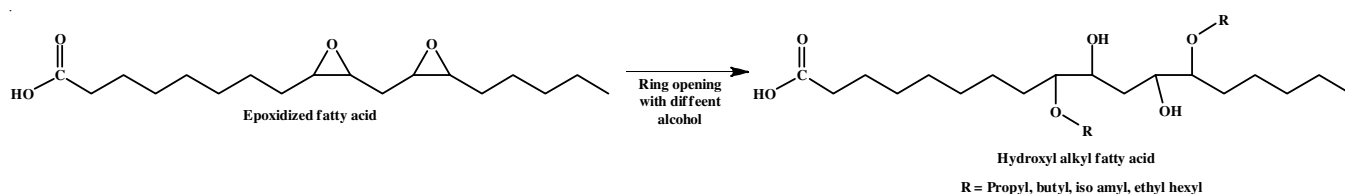
Scheme-I: Ring opening of epoxy fatty acid using different alcohol

product such as propoxy fatty acid, butoxy fatty acid, iso-amoxy fatty acid, ethyl hexoxy fatty acid were 88.83, 83.85, 83.91 and 10.37, respectively. The hydroxyl value is best suited as precursor to derive estolide with free –OH group to impart better lubricity. All the different alcohols required different conditions to complete the ring opening reaction. Longer or bulkier alcohols required longer reaction times and higher temperatures to complete the ring-opening reaction. For example, at 70-80 ℃, 4 h time was required to complete the reaction with propanol, *n*-butanol, isoamyl alchol, while a longer reaction time of 6 h at 100 ℃ was required for the higher molecular weight alcohols such as 2-ethylhexanol.

Pour point: The pour point is characteristics of bio-lubricant basestock for its use in cold climate. The pour point of unsaturated fatty acid was -9 ℃ and after chemical modification such as epoxy fatty acid, the pour point was 0 ℃, ring opening of epoxidized fatty acid to derive alkyl hydroxy fatty acid have low temperature operatablity. The pour point of propoxy fatty acid was -10 ℃, butoxy fatty acid was -18 ℃, iso amoxy fatty acid was -21 ℃ and ethyl hexoxy fatty acid was -40 ℃. It has been assumed that the presence of the large branching group in the chain of fatty acid attributed steric barrier around the individual molecule indicates to slow down the process of crystallization. The result (Table-1) shows the lowering of the pour point of individual molecule.

Effect of reaction time on ring opening reaction with different alcohols: The molar ratio of epoxy fatty acid to butanol::1:1.3 stirring at 600 rpm revealed the oxirane oxygen content decreased from 0.4724 to 0.2719 and decreased the hydroxyl value from 92.26 to 83.85 mgKOH/g at 80 ℃ for 240 min (Fig. 1). The acid value remained unchanged throughout for 240 min *i.e.* 26-27 mgKOH/g. The iodine value of butoxy fatty acid was 7.6 g I_2/100 g. The molar ratio of epoxy fatty acid:propanol::1:1.3 stirring at 600 rpm revealed the oxirane oxygen content decreased from 0.3492 to 0.1791 and the hydroxyl value from 152.33 to 88.83 mgKOH/g at 80 ℃ for 240 min (Fig. 2). The acid value is decreased from 82.64 to 39.92 mg KOH/g for 240 min while the iodine value of propoxy fatty acid was 7.9 gI_2/100 g. The molar ratio of epoxy fatty acid to isoamyl alcohol (1:1.3) stirred at 600 rpm revealed the oxirane oxygen content decreased from 0.2776 to 0.1252 and the
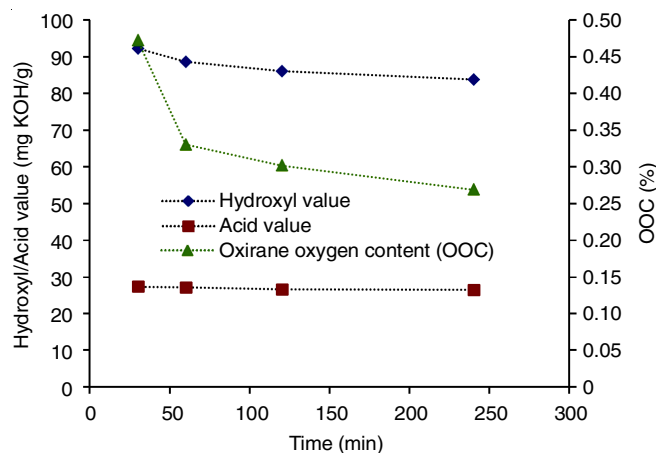
hydroxyl value from 122.89 to 63.91 mg KOH/g at 80 ℃ for 240 min (Fig. 3). The acid value is decreased from 104.48 to 26.62 mg KOH/g for 240 min and the iodine value of isoamoxy fatty acid was 7.8 g I_2/100 g. The molar ratio of epoxy fatty acid to ethyl hexanol (1:2) stirred at 800 rpm revealed the oxirane oxygen content decreased from 0.1988 to 0.133 and the hydroxyl value increases from 32.80 to 39.01 mgKOH/g at 100 ℃ for 360 min (Fig. 4). The acid value is increased from 6.46 to 7.86 mgKOH/g for 360 min and the iodine value of ethyl hexoxy fatty acid 7.9 g I_2/100 g.
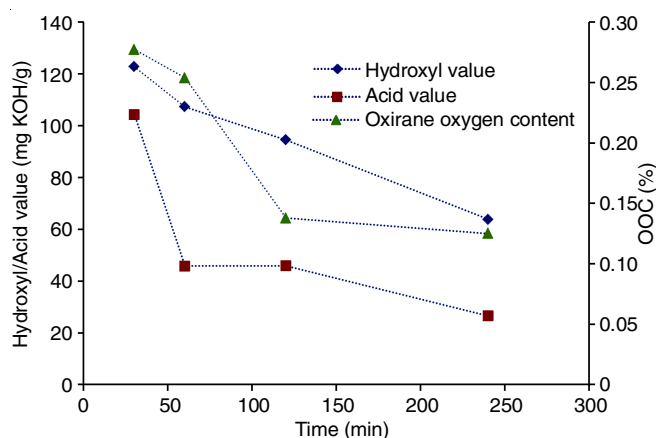

Fig. 2. Scheme of ring opening of epoxy fatty acid using propanol

Fig. 3. Scheme of ring opening of epoxy fatty acid using isoamyl alcohol

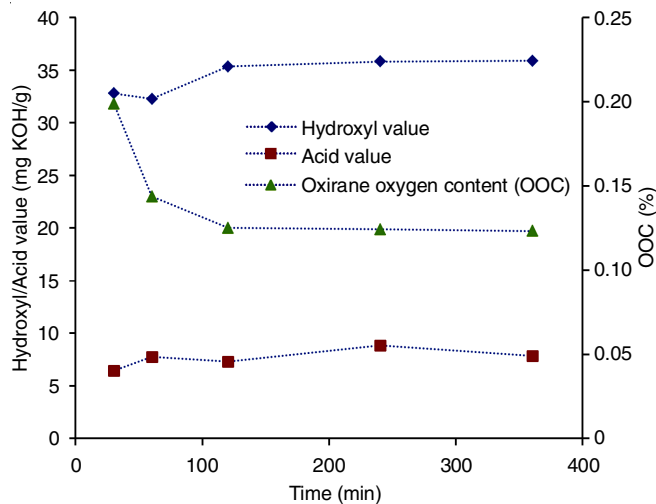Fig. 1. Scheme of ring opening of epoxy fatty acid using butanol

Fig. 4. Scheme of ring opening of epoxy fatty acid using 2-ethyl hexanol

FT-IR spectra: The FTIR spectra of unsaturated fatty acid (UFA), epoxy fatty acid (EFA), propoxy fatty acid (PFA), butoxy fatty acid (BFA), isoamoxy fatty acid (IAFA), ethyl hexoxy fatty acid (EHFA) are represented in Fig. 5. In all fatty acid, a sharp absorption band appears at 1708.48 cm^{-1} for -C=O of carboxylic group. The bands at 2853, 2923-2975 and 3009 cm^{-1} were appeared due to CH$_3$, CH$_2$ and CH stretching vibrations respectively, whereas band intensity ~721, 1155-1370 and 1370-1470 cm^{-1} showed the bending vibrations of above groups. The signals at 3009 and 721 cm^{-1} appeared due to the –C=C- bonds of camelina oil based UFA. After epoxidation of UFA, new signal appeared at 824.3 cm^{-1} which shows the presence of epoxy group of epoxy fatty acid. Velck and Petrovic [25] reported that the presence of epoxy group was attributed due to a signal at 833-822 cm^{-1}. After ring opening reaction occurs a broad peak appeared at 3500-3300 cm^{-1} attributed to hydrogen bonded and O-H stretching vibration of hydroxy group. Camelina oil based UFA shows CH$_2$ bending vibration around 1465-1462 cm^{-1}, CH$_3$ symmetrical bending vibration around 1378-1367 cm^{-1}, CH$_2$ rocking vibration 721 cm^{-1} and additional peak at 1282, 1180, 1160 cm^{-1} due to stretching vibration of the carbonyl group of ester. The signals at 2923 and 2853 cm^{-1} are due to the presence of methylene asymmetric stretching.
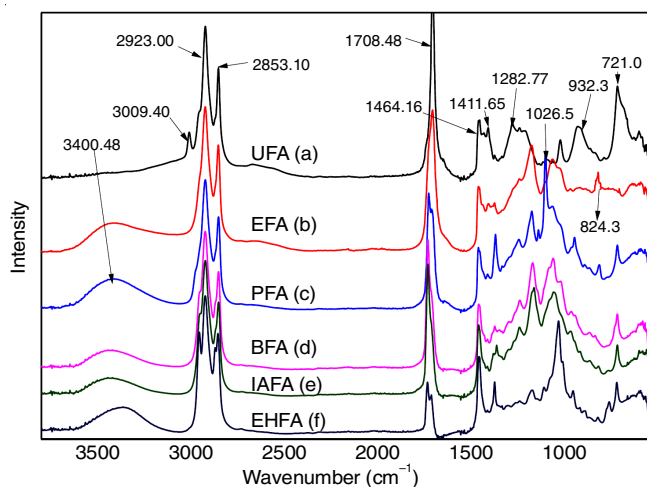

Fig. 5.   FT-IR spectroscopy of unsaturated fatty acid, epoxy fatty acid and ring opened product by using different alcohol such as propanol, butanol, iso amyl alcohol, ethyl hexanol

^{1}H NMR spectra: ^{1}H NMR spectrum of camelina oil based unsaturated fatty acid reveals with several characteristic peaks such as allylic protons of 3.05-2.60 ppm, α-CH$_2$ protons of 2.50-2.30 ppm, CH$_2$–CH=CH protons of ~2.0 ppm and the (CH$_2$)$_n$ and CH$_3$ protons in the regions of 1.60-1.2 and 0.98-0.86 ppm, respectively. The olefinic protons, –CH=CH–, of unsaturated fatty acids appear mainly in the region of 5.2-5.5 ppm. These peaks have been disappeared in epoxy fatty acid which reveals that C=C is converted to epoxy group in the unsaturated moiety. A peak at 2.9-3.2 ppm region is due to the presence of CH-proton attached to the oxygen atom of the both epoxy group. Two epoxide groups of proton were appeared at 1.48 and 1.72 ppm due to presence of vicinal methylene proton in accordance with the literature [26].

The reaction of epoxy fatty acid with an alcohol catalyzed with sulfuric acid to synthesis the ring-opened products as well as many other types of products. For evaluation of the alkyl group effect on the low-temperature properties, different alcohols including propanol, *n*-butanol, isoamyl alcohol and 2-ethyl hexanol were used in the reaction. The reaction completion was further confirmed by examine disappearance of peaks at 2.9-3.2 ppm in the ^{1}H NMR spectra corresponding to hydrogen in the epoxy ring. Besides, the tertiary proton of the -CH$_2$**CH**CH$_2$ backbone appears at 5.2-5.3 ppm, the methylene proton of the -**CH$_2$**- CHCH$_2$- backbone appears at 4.1-4.4 and the terminal -**CH$_3$** groups appears at 0.8-1.0 ppm region [27,28]. The peaks emerge at 4.1-4.2 ppm corresponds to -**CH$_2$**-CHCH$_2$- and peaks for newly formed secondary alcohols (R'R.**H**COH and R'R.HCO**H**) emerged at 4.25-3.35 ppm.

Conclusion

The vegetable bio-based products are important part of developing new strategies, policies and subsidies that aid in reducing the dependence on mineral oils and other non renewable sources. By chemical modifications of vegetable oil (through epoxidation and ring opening of epoxidized fatty acid with different alcohols) to form bio-lubricant basestocks with low temperature application such as propoxy fatty acid was -10 °C, butoxy fatty acid was -18 °C, isoamoxy fatty acid was -21 °C and ethyl hexoxy fatty acid was -40 °C. The ethyl hexoxy fatty acid exhibited better pour point compared to other products. Camelina oil based hydroxy fatty acid with high hydroxyl value is best suited as precursor to derive estolide. All the derived products exhibit better viscosity index and expected to have improved affinity for better adsorption on metal surfaces. These derive product have ability to replace of mineral or synthetic oil.

CONFLICT OF INTEREST

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

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