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Vegetable oil-based ethanolamides as potential anti-oxidant additives for lubricant formulations

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Novel antioxidant mono- and diethanolamide, eight additives have been prepared from castor oil, coconut oil, thumba oil and sal fat. These have been evaluated for antioxidant efficacy taking epoxy karanja oil as base oil at 0.5-5% concentration. Antioxidant tests have been performed on Rotating Pressure Vessel Oxidation Test RPVOT and Differential Scanning Calorimetry DSC. Among the prepared mono and diethanolamides, only diethanolamide-based additives have exhibited potential anti-oxidant behavior. Coconut diethanolamides containing saturated medium chain fatty acids have exhibited excellent stabilities, followed by diethanolamides of sal rich containing saturated long chain fatty acids. The castor based diethanolamides, which are rich in mono unsaturated hydroxy fatty acid show slightly lower stabilities, while thumba with polyunsaturation exhibits poor oxidation stabilities. Both the methods have shown that the fatty diethanolamides exhibit extraordinary stabilities compared to commercial antioxidant, butylated hydroxy toluene BHT at 1-5% concentration. The study indicates that the presence of saturation and medium chain fatty acids in the diethanolamide-based additives improves the oxidation stability of the base oils.

Keywords: Vegetable oil-based ethanolamides, Anti-oxidant additives, Rotating Pressure Vessel Oxidation Test, Differential Scanning Calorimetry, Epoxy esters, Lubricant base stocks

The use of vegetable oils as lubricants by man dates back to ancient times. It has been known that environmental pollution caused by petroleum-based lubricants is severe due to their inherent toxicity and non-biodegradable nature[1,2]. This motivated the researchers all over the world to focus on the use of renewable vegetable oils to save energy, protect the environment and reduce the dependency on petroleum based lubricating oils. Seed oils are renewable and sustainable sources of fatty acids which can be used to prepare a number of oleochemicals that can replace petrochemicals for industrial applications[3].

Despite the many favorable attributes of biolubricants, the largest drawbacks to them are their poor thermo-oxidative stability, which is due to the high degree of multiple C-C unsaturation in fatty acid chain and the bis-allyic protons[4]. One of the important modifications of olefinic group is epoxidation which is more vulnerable to oxidation. Further, the epoxy products are being used for a number of potential applications such as fuel, lubricant additives and in the preparation of a number of polymers[5,6]. Epoxidized fatty acids are particularly useful in metal working formulations[7] and also used as high-temperature lubricants[8].

Lubricant base stocks are generally used in presence of air whereby oxidative chemical reactions take place leading to failures in lubrication. This is accompanied by decomposition of lubricant base stocks that can severely limit the operating life and effectiveness of the fluid, resulting in the damage of machines. During oxidation the oil becomes darker and thicker, hence, the addition of lubricating additives is necessary to all lubricating oils to prevent the formation of such compounds[9]. Today, practically all types of lubricants and hydraulic fluids are composed of at least one additive, and some oils contain additives of several different types. The amount of additive used varies from a few hundredths of a percent to 30% or more. Typically, additives are used as antioxidants, metal deactivators, detergents, dispersants, rust corrosion inhibitors, de-emulsifiers, wear reducers, pour point depressors, antiwear additives, extreme pressure additives, viscosity improvers, and hydrolysis inhibitors[10-13].

The most widely used additives are phosphorus, sulphur, zinc dialkyldithiophosphates (ZDDP) common in mineral and plant oils[14]. On the other hand, the content of heavy metals like zinc and phosphorus are not suitable for machines in food industries and in agriculture[15,16] due to environmental toxicity. Thus, efforts are being made to find more environmentally benign replacements for industrial applications. In case of naturally occurring antioxidants such as tocopherols vitamin E, L-ascorbic acid vitamin C, esters of gallic acid, propyl gallate, citric acid derivatives, and synthetic antioxidants, that is: lipid-modified ethylenediaminetetraacetic acid (EDTA) derivatives, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), mono-*tert*-butylhydroquinone (TBHQ), or 4,4′-methylene-bis-2,6-di-*tert*-butylphenol (MBP), which serve as synthetic metal scavengers may be used to formulate environmentally friendly lubricants as alternatives to the currently used toxic antioxidants[17-19]. Some of these natural antioxidants were found to contain sulfur or nitrogen-bearing functional groups.

Fatty acids and their derivatives have also been attractive, renewable resources for the replacement of petrochemical based additives. A whole new series of oleochemical products are being manufactured for use as base fluids, additives, *etc.*[20] In previous studies Chen *et al*. used oleic acid alkanolamide phosphates as additives for enhanced biodegradability, lubricity and corrosiveness of lubricating oil[21]. Quinchia *et al.* used natural and synthetic antioxidants to improve the oxidative stability of high oleic sunflower oil and castor oil based lubricant formulations[22]. Castor oil was used as an additive to improve the oxidative stability of soya bean oil fatty acid methyl esters[23]. Hydroxylamines were also used as antioxidant additives as reported by Hras *et al.*[17] Epithio compounds from alkyl epoxy undecanoates were used as antioxidants, displaying extreme pressure and anti wear properties in different base fluids such as epoxy jatropha fatty acid *n*-butyl esters, di-2-ethylhexyl sebacate and mineral oil S-105[24]. Among the different alkyl-11-anilino-10-hydroxyundecanoate ester additives, *n*-butyl ester exhibited best stabilizing effect on epoxy karanja fatty acid 2-ethylhexyl esters[25]. Fatty acid sulfide derivatives were tested for their antioxidant behavior taking epoxy jatropha fatty acid *n*-butyl esters as base fluid. The products were found to exhibit antioxidant efficacy comparable to BHT[26]. Amino acid-based thioglycolic derivatives prepared from methyl oleate were found to be potential multifunctional additives towards epoxy jatropha fatty acid *n*-butyl esters as base fluid[27].

Fatty ethanolamides are another group of compounds that contain physically and chemically stable nitrogen containing compounds[28]. These exhibit low reactivity and high thermal stability, some of which were used in making friction reducing additives[29]. Fatty acid ethanolamides find a variety of applications particularly in lubricants, detergents and cosmetic formulations such as foam boosters, viscosity builders, emulsifiers, wetting agents and as conditioning agents[3,30-32]. Diethanolamine based hexanamide-mono and di-linoleniate esters were used as a synthetic ester-based mud for oil-well drilling fluids[33]. Khalker *et al.* demonstrated the use of fatty acid amides as friction modifier additives in petroleum base stock[34]. Diethanolamides were also used in the composition of lyotropic liquid crystal metal working lubricants[35]. Fatty acid ethanolamides or esters of diethanolamine were used as crankcase lubricants in internal combustion engines as friction reducing agents[29].

However, the fatty diethanolamides were not studied for antioxidant behavior. Hence, with this background, the fact that nitrogen and sulphur containing fatty compounds exhibit potential antioxidant behavior and also are readily soluble in lubricating oils[29], an attempt was made to prepare different fatty ethanolamides and evaluate their efficacy in the base oil. Keeping this in view, the importance of epoxy base oils as widely used lubricating oils, epoxy karanja oil was chosen as base oil. As the importance of biodegradation is rapidly increasing, the use of bio-based ingredients in lubrication can lead to economic benefits to farmers as well as the rural economy.

The objective of the present study was to prepare antioxidant additives employing four different oils widely grown globally with variation in the nature of the fatty acids, such as *Citrullus colocynthis*, thumba containing unsaturated-rich fatty acids, 80.6%, *Ricinus communis*, castor containing ricinoleic acid, a hydroxy fatty acid 89.3%, coconut containing medium chain fatty acids, 80% and *Shorea robusta*, sal fat containing saturated-rich fatty acids, 56.5% for the preparation of mono- and diethanolamides. Further to check the antioxidant efficacy of the prepared additives taking epoxy karanja oil as base oil in different percentages 0-5 wt% on the basis of base oil. The anti-oxidant tests were performed using Rotating Pressure Vessel Oxidation Test (RPVOT) and Differential Scanning Calorimetry (DSC).

Experimental Section

Thumba seeds were procured from M/s Sanjeevani Herbal Health Society, Hyderabad, castor oil from

M/s Ramcharan Industries Pvt. Ltd., Hyderabad and sal fat was procured from M/s Paras Vanaspathi, Raipur. Coconut oil was purchased from local super market. Hydrogen peroxide 30%, formic acid 85%, acetic acid, 4N hydrobromic acid, iodine monochloride, potassium hydroxide, hydrochloric acid, *n*-butanol, pyridine, chloroform, acetic anhydride, diethanolamine (DEA), monoethanolamine (MEA), sodium hydroxide (NaOH), diethyl ether, sodium chloride and sulfuric acid were purchased from SD Fine Chem. Pvt. Ltd., Mumbai, TLC silica gel 60 F_{254} plates were purchased from Merck, Germany. All the chemicals were of reagent grade and were used directly without further purification.

Gas chromatographic analysis

GC analysis of the methyl ester was carried out using the GC 6890N series of Agilent and DB-225 column i.d. 0.25 mm, length 30 m. The injector and flame ionization detector were at 250°C and 270°C. The oven temperature was programmed at 160°C for 2 min and then increased to 230°C at 5°C min^{-1}. The carrier gas used was nitrogen at a flow rate of 1.0 mL min^{-1}. The GC-MS analyses were recorded using an Agilent 6890N gas chromatograph with an HP-1 MS capillary column 30 m. 0.25 mm. 0.25 µm connected to an Agilent 5973N mass spectrometer at –70 eV *m/z* 50-600, source at 230°C and quadrupole at 150°C in the EI mode.

Spectral analysis

Infrared spectra IR on sodium chloride (NaCl) disks were recorded in dichloromethane on a Perkin-Elmer FT-IR instrument Model: Spectrum BX, Perkin-Elmer, Connecticut, USA. ^{1}H NMR and ^{13}C NMR spectral data were recorded on Avance 300 MHz, 500 MHz and 75 MHz spectrometer, ^{1}H at 300 MHz and 500 MHz and ^{13}C at 75 MHz in deuterated chloroform ($CDCl_3$) solution and Tetramethylsilane (TMS) was used as an internal standard. The chemical shift values were reported in units of δ (ppm) downfield from TMS. Mass spectra were recorded using electrospray ionization on ESI-MS using Waters e2695 separators module Waters, Milford, MA, USA mass spectrometer. All high-resolution spectra were recorded on QSTARXL hybrid MS/MS system Applied Biosystems, USA under electrospray ionization.

Oxidation stability test

The oxidative stability of the products was measured using a Koehler Inc., USA Rotating Pressure Vessel Oxidation Test, RPVOT apparatus as per the ASTM D 2272 test method. The experiment was carried out at 150°C, with a Cu catalyst, 55.5 g, sample, 50 g and water, 5 mL. The vessel was sealed and charged with oxygen to 90 psi pressure. The test was completed once the pressure dropped more than 25 psi below the maximum pressure. Antioxidant activity of the additives was determined employing differential scanning calorimeter DSC, Q-100 thermal analyzer TA instruments under oxygen atmosphere according to ASTM E 2009-08. The DSC instrument was calibrated using pure indium, and an empty open aluminium pan was used to obtain the base line correction. Typically, 1.5-3.0 mg is placed in open aluminium pans and oxygen flow is maintained at 50 mL min^{-1}. The cell temperature was raised to750°C, at a heating rate of 10°C min^{-1}. The analysis was carried out in duplicates and the average of two measurements is reported. The stabilities are compared with the commercial antioxidant, BHT. DSC provides the onset temperature OT and signal maximum SM. They correspond to the temperatures when oxidation begins and reached maximum, respectively.

Preparation of Lubricant Base Stock Base oil

Epoxy karanja oil was prepared from karanja oil[36] in 99% yield. The fatty acid composition of the base oil was determined by GC and spectral studies, ^{1}H NMR, IR and ^{13}C NMR.

Synthesis of Antioxidant Additives Mono- and Diethanolamides of Thumba, Castor, Coconut, and Sal Fat

Fatty acid composition of the thumba seed oil, castor oil, coconut oil and sal fat

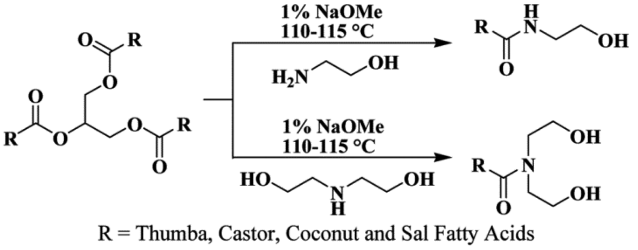
Fatty acid methyl esters of the oils were prepared by refluxing the oil at 70°C for 4 h in 2% sulfuric acid in methanol. The esters were extracted into ethyl acetate, washed with water until free of acid and the ethyl acetate layer was passed over anhydrous sodium sulfate. The ethyl acetate extracts were further concentrated using rotary evaporator to obtain a fatty acid methyl ester. The composition of fatty acid methyl esters was analyzed by GC and GC-MS. The fatty acid compositions of the oils are shown in Table 1.

A typical procedure for the synthesis of monoethanolamides of thumba seed oil TMEA

Thumba seed oil 35 g, 0.04 mol was taken in a 250 mL two necked round bottomed flask, connected

Table 1 — Fatty acid composition (wt %) of thumba seed oil, castor oil, coconut oil and sal fat

Fatty acids	Fatty acid composition (wt %)			
	Thumba seed oil	Castor oil	Coconut oil	Sal fat
8:0	–	–	7.0	–
10:0	–	–	5.4	–
12:0	–	–	48.9	–
14:0	–	–	20.2	–
16:0	10.3	0.9	8.4	5.5
18:0	8.0	1.2	2.5	43.2
18:1	24.5	4.0	5.2	41.0
18:2	55.9	4.6	1.4	1.7
18:3	0.2	–	–	–
20:0	0.4	–	–	7.3
20:1	0.2	–	–	–
22:0	0.2	–	–	–
22:1	0.1	–	–	–
24:0	0.2	–	–	0.5
Ricinoleic acid	–	89.3	–	–



Scheme 1 — Preparation of fatty ethanolamides

with a calcium chloride guard tube and dropping funnel. The temperature of the medium was maintained at 110-115°C, followed by addition of sodium methoxide 0.35 g, 1% wt of oil and the contents were stirred magnetically. Monoethanolamine 8.5 g, 0.14 mol was taken in a dropping funnel was added drop-wise to the reaction mixture over a period of 30 min and stirred at 110-115°C for 4 h. The reaction was monitored by TLC using chloroform/methanol 95/5, by vol. After the reaction, the reaction mixture was cooled to RT, dissolved in chloroform 150 mL, washed with brine solution repeatedly till the mixture was free of sodium methoxide and monoethanolamine. The reaction mixture was passed over anhydrous sodium sulfate, concentrated using rotary evaporator followed by drying under reduced pressure. The pure monoethanolamide was isolated using silica gel 60-120 mesh column chromatography to remove the traces of impurities namely amine esters and free fatty acids. The eluent being chloroform / methanol 98/2, by vol. Thumba monoethanolamide obtained was 35.5 g, 92% yield.

Similar procedure was followed for the preparation of castor, coconut and sal fat monoethanolamides. The formation of monoethanolamides is as shown in Scheme 1. All the compounds were characterized using IR, ^{1}H and ^{13}C NMR, and ESI-MS spectral studies.

Monoethanolamides of thumba seed oil, TMEA

IR (neat): 3303 (-OH), 3094 (-NH), 3006 (=C-H), 2925 (-C-H), 1642 (-C=O of amide), 1064 cm^{-1} (-C-O- of OH); ^{1}H NMR (CDCl$_3$): δ 0.88 (t, -C*H*$_3$), 1.21-1.34 (m, - C*H*$_2$ $_n$-), 1.56-1.68 (m, -C*H*$_2$-CH$_2$-C O -), 1.98-2.09 (m, -C*H*$_2$-CH=CH-), 2.23 (t, -C*H*$_2$-CO-), 2.71 (s, -CH$_2$-O*H*), 2.77 (t, -CH=CH-C*H*$_2$-CH=CH-), 3.41-3.47 (m, -HN-C*H*$_2$-), 3.67-3.75 (m, -NH-CH$_2$-C*H*$_2$-OH), 5.39-5.45 (m, -CH$_2$-C*H*=C*H*-CH$_2$-C*H*=C*H*-CH$_2$-), 5.94 (s, -CO-N*H*-CH$_2$-); ^{13}C NMR (CDCl$_3$): δ 14, 22.5, 25.4, 25.69, 27.1, 29-33.9, 36.5, 42.3, 62, 127.8, 129.9, 174.6; ESI-MS: *m/z* 300 16:0+H$^+$, 322 16:0+Na$^+$, 324 18:2+H$^+$, 326 18:1+ H$^+$, 346 18:2+Na$^+$, 348 18:1+Na$^+$, 350 18:0+Na$^+$.

Monoethanolamides of castor oil, CMEA

IR (neat): 3298 (-OH), 3096 (-N-H), 3010 (=C-H), 2926 (-C-H), 1645 (-C=O of amide), 1060 cm^{-1} (C-O of –OH); ^{1}H NMR (CDCl$_3$): δ 0.89 (t, -C*H*$_3$), 1.24-1.39 (m, - C*H*$_2$ $_n$-), 1.41-1.52 (m, -C*H*$_2$-CH-OH), 1.54-1.68 (m, -C*H*$_2$-CH$_2$-C O -), 1.97-2.1 (m, -C*H*$_2$-CH=CH- and -CH=CH-C*H*$_2$-CH OH), 2.18 (t, -C*H*$_2$-CO-), 3.28-3.41 (m, -CH$_2$-C*H*-OH), 3.52-3.61 (m, -NH-C*H*$_2$-), 3.61-3.69 (m, -NH-CH$_2$-C*H*$_2$-OH), 5.29-5.39 (m, -CH$_2$-C*H*=CH-CH$_2$-), 5.52 (-CH$_2$-CH=C*H*-CH$_2$-CH OH -), 6.1 (s, -CO-N*H*-CH$_2$-); ^{13}C NMR (CDCl$_3$): δ 14, 22.6, 25.1, 25.6, 27.2, 28.9-36.8, 42.3, 62.1, 71.5, 125.3, 133.2, 174.5; ESI-MS: *m/z* 324 18:1+H$^+$, 342 Ricinoleic acid+H$^+$, 364 18:1+Na$^+$ Ricinoleic acid +Na$^+$.

Monoethanolamides of coconut oil, CNMEA

IR (neat): 3303 (-OH), 3094 (-NH), 2924 (-C-H), 1641 (-C=O of amide), 1061 cm^{-1} (-C-O- of OH); ^{1}H NMR (CDCl$_3$): δ 0.88 (t, -C*H*$_3$), 1.23-1.39 (m, - C*H*$_2$ $_n$-), 1.54-1.65 (m, -C*H*$_2$-CH$_2$-CO-), 2.04 (m, -C*H*$_2$-CH=CH-), 2.23 (t, -C*H*$_2$-C O -), 2.71 (s, -CH$_2$-O*H*), 3.41-3.47 (m, -HN-C*H*$_2$-), 3.67-3.75 (m, -NH-CH$_2$-C*H*$_2$-OH), 5.29-5.34 (m, -CH$_2$-C*H*=C*H*-CH$_2$-), 5.94 (s, -CO-N*H*-CH$_2$-); ^{13}C NMR (CDCl$_3$): δ 14, 22.5, 25.4, 25.69, 27.1, 29-33.9, 36.5, 42.3, 62, 127.8-129.9, 174.6; ESI-MS: *m/z* 188 8:0+H$^+$, 210 8:0+Na$^+$, 216 10:0+H$^+$, 244 12:0+H$^+$, 266 12:0+Na$^+$, 272 14:0+H$^+$, 294 14:0+Na$^+$, 300 16:0+H$^+$, 322 16:0+Na$^+$, 326 18:1+H$^+$, 348 18:1+Na$^+$.

Monoethanolamides of sal fat, SMEA

IR (neat): 3297 (OH), 3094 (-NH), 2926 (-C-H), 1643 (-C=O of amide), 1053 cm^{-1} (C-O of OH); ^{1}H NMR (CDCl$_3$): δ 0.88 (t, -CH_3), 1.21-1.34 (m, - CH_2 $_n$-), 1.53-1.68 (m, -CH_2-CH$_2$-CO-), 1.95-2.10 (m, -CH_2-CH=CH-), 2.2 (t, -CH_2-CO-), 3.38-3.45 (m, -NH-CH_2-), 3.67-3.76 (m, -NH-CH$_2$-CH_2-OH), 5.26-5.39 (m, -CH$_2$-C*H*=C*H*-CH$_2$-), 6.1 (s, -CO-N*H*-CH$_2$-); ^{13}C NMR (CDCl$_3$): δ 14.1, 22.7, 25.7, 27.2, 29-31.9, 36.7, 42.4, 62.4, 129.7-130.1, 175.7; ESI-MS: *m/z* 300 16:0+H$^+$, 322 16:0+Na$^+$, 326 18:1+H$^+$, 328 18:0+H$^+$, 348 18:1+Na$^+$, 350 18:0+Na$^+$, 378 20:0+Na$^+$.

A typical procedure for the synthesis of diethanolamides of thumba seed oil, TDEA

Thumba seed oil 35 g, 0.04 mol was taken in a 250 mL two necked round bottomed flask, connected with a calcium chloride guard tube and a dropping funnel. The temperature of the medium was maintained at 110-115°C, followed by the addition of sodium methoxide 0.35 g, 1% wt of oil and the contents were stirred magnetically. Diethanolamine 14.7 g, 0.14 mol was taken in a dropping funnel added drop-wise to the reaction mixture over a period of 30 min and stirred at 110-115°C for 4 h. The reaction was monitored by TLC eluted with chloroform/methanol 95/5, by vol. After the reaction, the reaction mixture was cooled to RT, dissolved in chloroform 150 mL, washed with brine solution repeatedly till the contents were free of sodium methoxide and DEA. The reaction mixture was dried over anhydrous sodium sulfate, concentrated using rotary evaporator followed by drying. The pure diethanolamide was isolated using silica gel 60-120 mesh column chromatography to remove the traces of impurities namely amine esters and free fattyacids. The eluent being chloroform / methanol 98/2, by vol. Thumba diethanolamide obtained was 36.97 g, 89% yield.

Similar procedure was followed for the preparation of castor, coconut, and sal fat diethanolamides. The formation of diethanolamides is as shown in Scheme 1. The compounds were characterized using IR, ^{1}H and ^{13}C NMR, and ESI-MS spectral studies.

Diethanolamides of thumba seed oil, TDEA

IR (neat): 3359 (-OH), 3009 (=C-H), 2925 (-C-H), 1620 (-C=O of amide), 1061 cm^{-1} (C-O of –OH); ^{1}H NMR (CDCl$_3$): δ 0.89 (t, -CH_3), 1.24-1.39 (m, -CH_2 $_n$-), 1.55-1.64 (m, -CH_2-CH$_2$-C O -), 1.93-2.09 (m, -CH_2-CH=CH-), 2.38 (t, -CH_2-C O -), 2.77 (t, -CH=CH-CH_2-CH=CH-), 3.45-3.55 (m, -N-CH_2-), 3.73-3.81 (m, -N-CH$_2$-CH_2-OH), 4.15 (s, -CH$_2$-O*H*), 5.27-5.41 (m, -CH$_2$-C*H*=C*H*-CH$_2$-C*H*=C*H*-CH$_2$-); ^{13}C NMR (CDCl$_3$): δ 14.02, 22.91, 25.23, 25.61, 27.24, 29.05-33.73, 50.61, 52.35, 60.71, 61.41, 127.83-128.16, 129.81-130.20, 175.73; ESI-MS: *m/z* 344 16:0+H$^+$, 366 16:0+Na$^+$, 368 18:2+H$^+$, 370 18:1+H$^+$, 372 18:0+H$^+$, 390 18:2+Na$^+$.

Diethanolamides of castor oil, CDEA

IR (neat): 3410 (-OH), 3292 (-OH), 3010 (=C-H), 2924 (-C-H), 1618 (-C=O of amide), 1054 cm^{-1} (C-O of –OH); ^{1}H NMR (CDCl$_3$): δ 0.88 (t, -CH_3), 1.3 (m, - CH_2 $_n$-), 1.45 (m, -CH_2-CH-OH), 1.62 (m, -CH_2-CH$_2$-CO-), 2.04 (m, -CH_2-CH=CH-), 2.2 (m, -CH=CH-CH_2-CH OH -), 2.38 (t, -CH_2-CO-), 3.5 (m, -N-CH_2-), 3.6 (m, -CH$_2$-C*H* OH -), 3.78 (m, -N-CH$_2$-CH_2-OH), 5.39 (m, -CH$_2$-C*H*=CH-CH$_2$-), 5.54 (-CH$_2$-CH=C*H*-CH$_2$- CHOH -), 4.02 (s, -CH$_2$-O*H*); ^{13}C NMR (CDCl$_3$): δ 14.03, 22.51, 25.14, 25.67, 27.21, 28.01-36.65, 50.31, 52.11, 60.51, 61.09, 71.45, 125.21, 133.13, 175.51; ESI-MS: *m/z* 368 18:2+H$^+$, 386 Recinoleic acid+H$^+$, 372 18:0+H$^+$, 408 Recinoleic acid+Na$^+$.

Diethanolamides of coconut oil, CNDEA

IR (neat): 3361 (-OH), 3013 (=C-H), 2926 (-C-H), 1621 (-C=O of amide), 1062 cm^{-1} (C-O of –OH); ^{1}H NMR (CDCl$_3$): δ 0.88 (t, -CH_3), 1.21-1.36 (m, - CH_2 $_n$-), 1.54-1.68 (m, -CH_2-CH$_2$-CO-), 2.02 (m, -CH_2-CH=CH-), 2.39 (t, -CH_2-CO-), 3.52 (m, -N-CH_2-), 3.81 (m, -N-CH$_2$-CH_2-OH), 5.31-5.39 (m, -CH$_2$-C*H*=C*H*-CH$_2$-), 3.91 (s, -CH$_2$-O*H*); ^{13}C NMR (CDCl$_3$): δ 14.05, 22.62, 25.29, 27.15, 29.13-30.24, 31.85, 33.57, 50.49, 52.18, 60.67, 61.24, 175.67; ESI-MS: *m/z* 232 8:0+H$^+$, 254 8:0+Na$^+$, 260 10:0+H$^+$, 282 10:0+Na$^+$, 288 12:0+H$^+$, 310 12:0+Na$^+$, 316 14:0+H$^+$, 338 14:0+Na$^+$, 344 16:0+H$^+$, 366 16:0+Na$^+$, 370 18:1+H$^+$, 392 18:1+Na$^+$.

Diethanolamides of sal fat, SDEA

IR (neat): 3361 (-OH), 3013 (=C-H), 2926 (-C-H), 1621 (-C=O of amide), 1062 cm^{-1} (C-O of –OH); ^{1}H NMR (CDCl$_3$): δ 0.88 (t, -CH_3), 1.26 (m, - CH_2 $_n$-), 1.62 (m, -CH_2-CH$_2$-CO-), 2.02 (m, -CH_2-CH=CH-), 2.39 (t, -CH_2-CO-), 3.52 (m, -N-CH_2-), 3.81 (m, -N-CH$_2$-CH_2-OH), 5.35 (m, -CH$_2$-C*H*=C*H*-CH$_2$-), 3.9 (s, -CH$_2$-O*H*); ^{13}C NMR (CDCl$_3$): δ 14.01, 22.6, 25.2, 27.1, 29.1-33.6, 50.5, 52.2, 60.7, 61.2, 129.6-129.9, 175.6; ESI-MS: *m/z* 344 16:0+H$^+$, 366 16:0+Na$^+$, 370 18:1+H$^+$, 372 18:0+H$^+$, 392 18:1+Na$^+$, 394 18:0+Na$^+$, 422 20:0+Na$^+$.

Results and Discussion

The fatty acid composition of the prepared epoxy karanja oil includes palmitic (12%); oleic (52%); linoleic (16%) and linolenic (3%) acids. The base oil being rich in unsaturation has poor oxidation stability; hence an attempt was made to improve its oxidation stability using the synthesized ethanolamide based additives.

Synthesis of antioxidant additives mono- and diethanolamides of thumba, castor, coconut, and sal fat

Four vegetable oils namely thumba seed oil, castor oil, coconut oil, and sal fat were used for preparation of mono- and diethanolamides[37]. The fatty acid composition of these oils was determined as methyl esters using GC. The composition showed that thumba was rich in unsaturated fatty acids 80.9%, castor oil contained hydroxyl fatty acid, ricinoleic acid 89.3%, coconut oil was rich in saturated medium chain fatty acids 80%, while sal fat was rich in saturated fatty acids 56.5% (Table 1). The triglycerides of the thumba seed oil, castor oil, coconut oil, and sal fat were converted into mono- and diethanolamides, Scheme 1.

The structure of mono- and diethanolamides was confirmed by IR (Fig. 1), ^{1}H NMR (Fig. 2), ^{13}C NMR (Fig. 3) and ESI-MS (Fig. 4). The characteristic absorption bands at 3094 cm^{-1} TMEA (Fig. 1), 3096 cm^{-1} CMEA, 3094 cm^{-1} CNMEA and 3094 cm^{-1} SMEA due to –NH-, 1642 cm^{-1} TMEA (Fig. 1), 1645 cm^{-1} CMEA, 1641 cm^{-1} CNMEA and 1643 cm^{-1} SMEA in IR spectra due to the amide bond of –CON- confirmed the formation of monoethanolamides. The characteristic absorption band at 1620 cm^{-1} TDEA, 1621.4 cm^{-1} CDEA, 1621 cm^{-1} CNDEA and 1618 cm^{-1} SMEA in IR spectra due to the –CON- further confirmed the formation of diethanolamides.

The presence of multiplet at δ 3.41-3.47 TMEA (Fig. 2), 3.52-3.61 CMEA, 3.41-3.47 CNMEA and 3.42 SMEA ppm due to -NH-CH_2- and 3.67-3.75

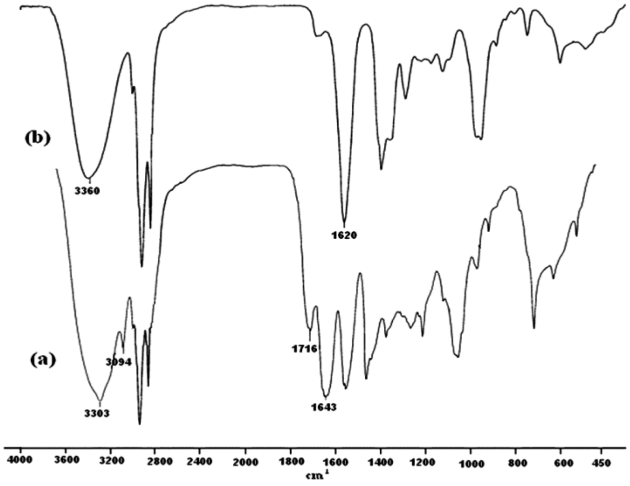


Fig. 1 — IR Spectra of thumba ethanolamides (a) Monoethanolamide (TMEA) (b) Diethanolamide (TDEA)

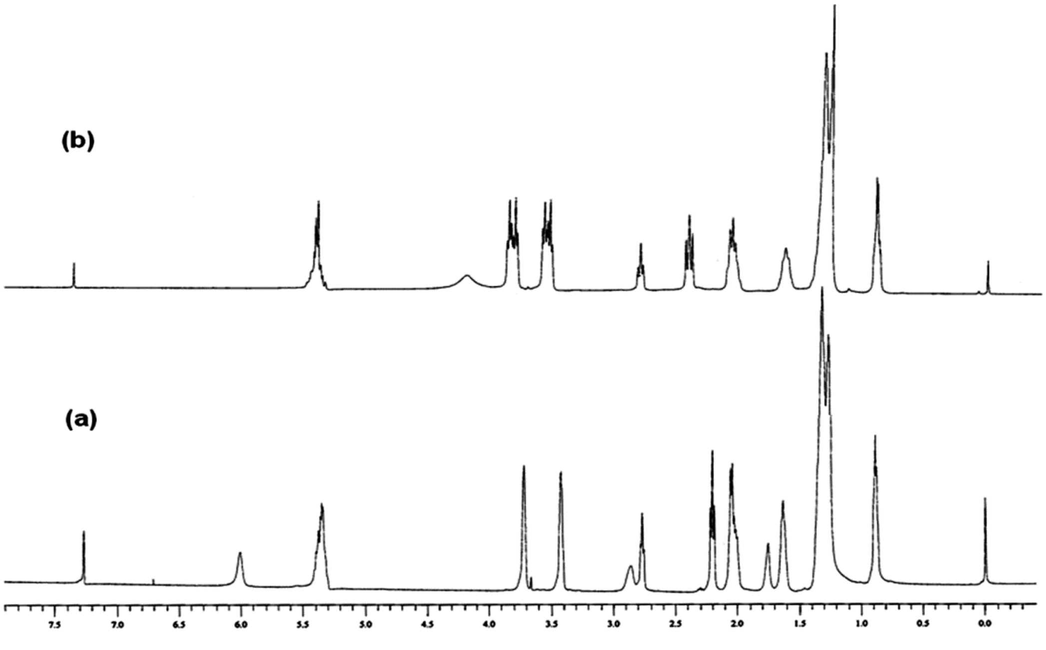


Fig. 2 — ^{1}H NMR Spectra of thumba ethanolamides (a) Monoethanolamide (TMEA) (b) Diethanolamide (TDEA)

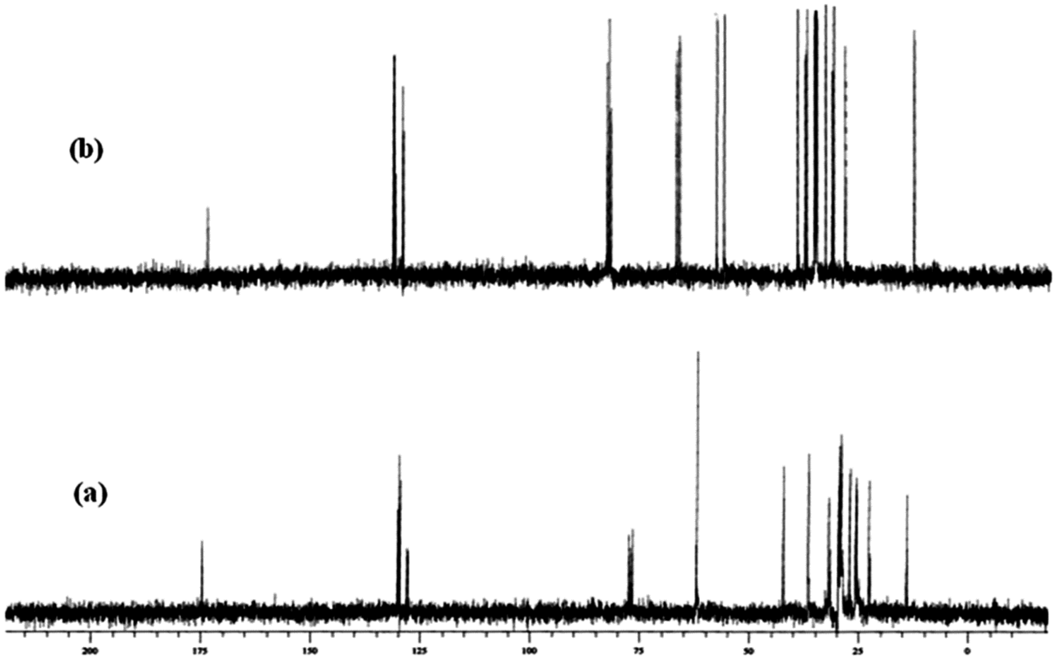


Fig. 3 — ^{13}C NMR Spectra of thumba ethanolamides (a) Monoethanolamide (TMEA) (b) Diethanolamide (TDEA)

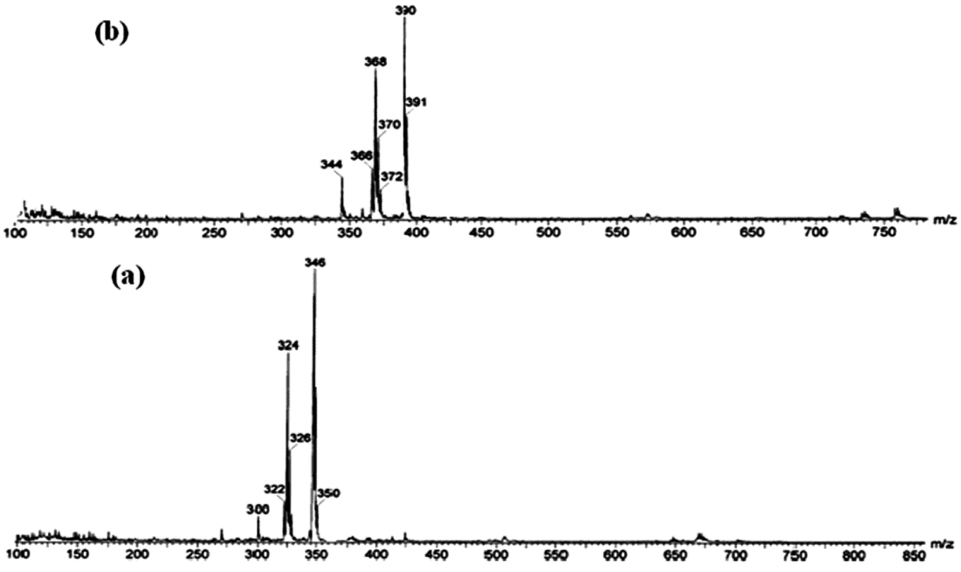


Fig. 4 — Mass spectra of thumba ethanolamides (a) Monoethanolamide (TMEA) (b) Diethanolamide (TDEA)

TMEA, 3.61-3.69 CMEA, 3.67-3.75 CNMEA and 3.67-3.76 m, -NH-CH_2-CH_2-OH, SMEA ppm due to -NH-CH_2-CH_2-OH in ^{1}H NMR spectra further confirmed the formation of monoethanolamides. While the peaks at 3.5 TDEA (Fig. 2), 3.51 CDEA, 3.52 CNDEA and 3.52 SDEA ppm due to -N-CH_2- and 3.78 TDEA, 3.79 CDEA, 3.81 CNDEA, and 3.8 SDEA ppm -N-CH_2-CH_2-OH in ^{1}H NMR spectra further confirmed the formation of diethanolamides.

The structures were also confirmed using ^{13}C NMR which showed characteristic peaks at 42.3 TMEA (Fig. 3), 42.3 CMEA, 42.3 CNMEA and 42.4 SMEA ppm due to -NH-CH_2- and 62, 62.1 CMEA, 62 CNMEA and 62.4 SMEA ppm due to -NH-CH_2-CH_2-OH in ^{13}C NMR spectra further confirmed the formation of monoethanolamides. The presence of peaks at 50.6, 52.3, 50.3, 52.1 CDEA, 50.49, 52.18 CNMEA and 50.5, 52.2 SDEA ppm due to -N-CH_2-

and 60.7, 61.4 TDEA, 60.5, 61.1 CDEA, 60.67, 61.24 CNMEA and 60.7, 61.2 SDEA ppm due to -N-CH_2-CH_2-OH in ^{13}C NMR spectra further confirmed the formation of diethanolamides.

The structure of the products was further confirmed by ESI-MS spectral technique. The spectra of the fatty mono- and diethanolamides are given by taking TMEA and TDEA as representative Fig. 4. The aim of the present study was to check the effect of chain length and nature of fatty acids unsaturation, saturation, chain length, hydroxyl functionality of the fatty acids on the antioxidant efficacy of additives. Antioxidant substrates were so chosen that the nature of fatty acids varied from medium chain as seen in coconut to long chain fatty acids as observed in thumba oil, castor oil, and sal fat. The fatty acids in thumba were unsaturated-rich, castor is rich in hydroxy fatty acid, while sal fat is rich in saturation. The study of these covered almost the whole range of fatty acids found in most of the vegetable oils.

Evaluation of ethanolamides as antioxidants

The antioxidant behaviour of the synthesized additives and commercial antioxidant, BHT in base oil, epoxy karanja oil was determined employing RPVOT and DSC. It is known that nitrogen and hydroxyl group containing fatty acids behave as antioxidant additives[22]. The antioxidant behavior of diethanolamides can be explained based on the two alkyl hydroxy groups and a tertiary nitrogen group, which provoke the release of hydrogen free radical which in turn captures the active oxygen species preventing oxidation of double bonds. Hence, an attempt was made to add the synthesized castor, thumba, coconut and sal fat mono- and diethanolamides to the base fluid, epoxy karanja oil and evaluate their antioxidant efficacy.

RPVOT

The prepared antioxidants were added in the base oils ranging from 0.5-5%. The stability of the base oil with and without addition of antioxidant was measured. The results are shown in Fig. 5.

It was observed that among the ethanolamide derivatives only diethanolamide-based additives exhibited antioxidant property. In the series among the thumba, castor, coconut and sal diethanolamides the oxidation stability was more when CNDEA was used. CNDEA with saturated medium chain fatty acids and polar -OH groups had better solubility, binding the surface of the base fluids, rendering more stability towards oxidation. This was followed by castor diethanolamides which are more polar due to more number of –OH groups and also were known to be very good surface active agents[30] this could be the reason for better solubility of the additive in the base oil. The additive is attached to the surface of the base fluid by adsorption forces governed by their polarity[11, 12] resulting in stability towards oxidation.

On the other hand, sal-based diethanolamides with saturated long chain fatty acids is sparingly soluble in the base fluids resulting in poor oxidation stability values at lower concentrations, 0.5 to 2%. However, as the concentration of the additive increased from 3 to 5%, its solubility has improved resulting in high oxidation stability compared to castor based diethanolamides. In case of all diethanolamides, the stabilities were lower compared to commercial antioxidant BHT at 0.5 wt% of base oil. On further increase in concentration, the oxidation stabilities have increased about 2 to 3 times, the effect compared to BHT. Thumba diethanolamides being rich in polyunsaturation and due to the position of allylic and bisallylic carbons adjacent to double bonds[4], are responsible for poor anti-oxidant activity. Fig. 6 shows RPVOT graph of base oil, epoxy karanja oil and epoxy karanja oil with CDEA (3%) as a representative.

DSC

The trend in the oxidation stability of ethanolamides as observed employing RPVOT was further confirmed using DSC. In this study also, the base stock, epoxy karanja oil with diethanolamides exhibited good to extraordinary oxidation stabilities compared to BHT. Coconut diethanolamides with

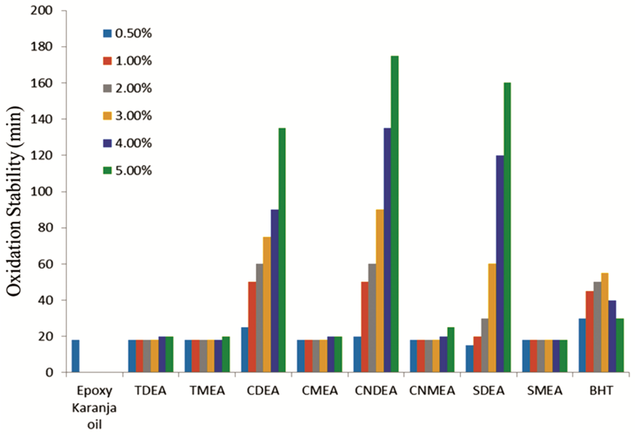
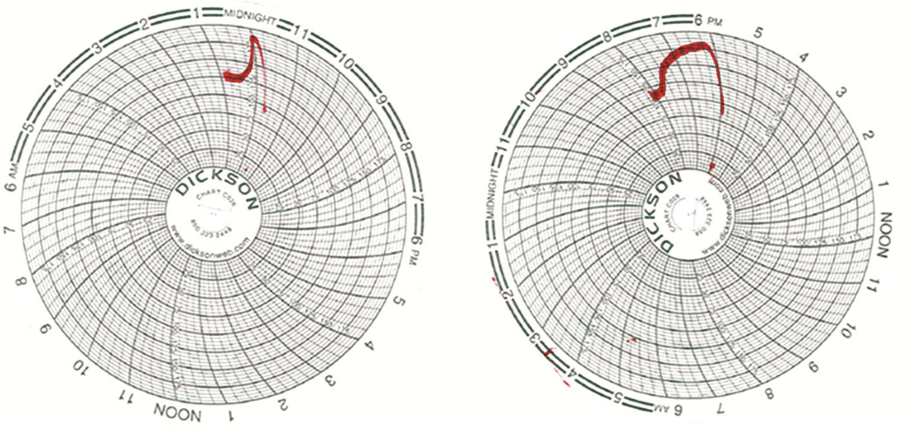


Fig. 5 — Oxidative stability (RPVOT) of epoxy karanja oil with the addition of ethanolamides



Base oil (EOSnBE)

Base oil (EOSnBE) + 3% Castor Diethanolamides (CDEA)

Fig. 6 — RPVOT Graphs of base oil (epoxy karanja oil) and base oil (epoxy karanja oil) with castor diethanolamides (3%, CDEA)

Table 2 — Oxidative onset temperature (OOT) of base oil with antioxidants as determined by DSC method

Test Compd	Oxidative onset temperature (OOT, °C)					
	*Base oil + additive					
	0.5%	1%	2%	3%	4%	5%
TDEA	181.03	181.1	181.13	181.2	181.25	181.51
CDEA	181.01	218.13	221.35	225.0	230.0	232.0
CNDEA	182.35	218.13	221.3	230.0	235.0	242.0
SDEA	181.05	202.3	210.5	221.3	228.0	232.0
BHT	187.32	211.43	203.64	201.19	192.3	188.03

*Epoxy Karanja Oil

saturated and medium chain fatty acids 80% exhibited high oxidation stabilities as seen by their high OT and SM values compared to sal, thumba and castor diethanolmaides (Table 2). The stabilities were found to increase with increase in concentration, much superior to commercial antioxidant BHT. However, the stability was found to decrease gradually beyond 5% concentration. The good emulsification power of diethanolamides could be responsible for very high oxidation stabilities[37]. Further their extraordinary oxidation stabilities can be explained based on their functionalities and nature of fatty acids present. Also, it was observed that in case of thumba diethanolamides, which is poly-unsaturated rich, it was more prone to oxidation resulting in lower oxidation stability. Hence, presence of saturation and medium chain is essential for the oxidation stability.

Mechanism of action of ethanolamide-based antioxidant additives

The present study has established that fatty diethanolamide-based additives are excellent to good anti-oxidants. Whereas, monoethanolamide-based additives do not exhibit any anti-oxidant property which can be explained based on tautomerization mechanism involved in case of monoethanolamides.

Conclusions

Novel class of antioxidants with excellent antioxidant activity behavior have been developed from renewable vegetable oils namely coconut, sal, thumba and castor oil. The effect of nature and chain length of the additives has been extensively studied in the present work. It is observed that diethanolamides exhibit better oxidation stability in comparison to monoethanolamides. On the other hand, saturated medium chain fatty diethanolamides, as seen in case of coconut, are better additives, followed by saturated long chain fatty diethanolamides in sal. The castor based diethanolamides with hydroxy, monounsaturation exhibited slightly inferior activity compared to the above two. Thumba based diethanolamides with polyunsaturation rendered poor oxidation stability. The study reveals that in addition to a variety of additive applications such as friction reducing agents, foam boosters, viscosity builders, emulsifiers, *etc*., fatty diethanolamides are also potential anti-oxidant additives.

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