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ORIGINAL PAPER

Synthesis of Carbonated Vernonia Oil

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Abstract The research objective was to determine whether naturally occurring epoxy functional vernonia oil would result in lower viscosity compounds after converting the virgin oil into the cyclic carbonate using supercritical carbon dioxide as the reactant. The cyclic carbonate was produced using relatively mild conditions as described in the paper. Carbonated vernonia oil retains the characteristic low viscosity of vernonia oil, and offers potential as a valuable, biobased intermediate for synthesizing low viscosity resins.

Keywords Vernonia oil · Carbonation · Epoxidized vegetable oils

Introduction

Carbonates, i.e., esters of carbonic acid (H_2CO_3), are increasingly used as solvents and reactive intermediates [1] and in metal ion extraction [2]. Several carbonation techniques are described in the literature, e.g., reacting phosgene with dihydroxy compounds [3, 4], ammonium hydrogen carbonate with chlorohydroxy compounds [5], or reacting a 1,2-diol or 1,3-diol with dialkyl carbonate in the presence of basic catalysts [6]. A more attractive method of synthesizing carbonates is by reacting carbon dioxide with an epoxide. The chemistry of carbon dioxide is of interest because of its potential as an abundant carbon source, and its transformation into useful organic substances represents an attractive area of study in both organic and green chemistry [7]. Carbon dioxide insertion into the carbon-oxygen bond of an oxirane (epoxide) usually requires high temperature and pressure, and a variety of catalysts have been evaluated to ameliorate the processing conditions [8]. Doll and Erhan [9, 10] have well documented the use of supercritical carbon dioxide in combination with catalytic amounts of tetrabutylammonium bromide (TBAB) to facilitate epoxide to carbonate conversion of epoxidized soybean oil and fatty acid methyl esters, respectively.

Epoxidized vegetable oils are widely used as plasticizers and stabilizers in plastics and rubber products. The commercial process for epoxidizing vegetable oil generally reacts the unsaturated sites with petroleum derivatives such as performic acid or peracetic acid to insert oxygen into the double bond. Epoxidized oils possess higher viscosity than their parent vegetable oils and carbonation increases their viscosity even further, thus limiting their utility in synthesizing polymers with low volatile organic compound (VOC) content [9].

Alternative crop development provides reliable and generally sustainable sources of uniquely functional vegetable oils to reduce our dependence on imported petroleum and its derivatives. Vegetable oils, i.e., triglyceride esters of fatty acids, are one of the oldest polymer precursors. Vernonia oil is a naturally occurring epoxidized oil obtained from the seeds of the plant, *Vernonia galamensis*, an annual herb and native of Africa that grows in areas with as little as 20 cm of seasonal rainfall. Plantings in Virginia, Arizona, and other states have confirmed that vernonia is extremely resistant to insects and diseases. Vernonia seeds contain up to 40% oil by weight, with fatty acid distributions averaging 6% oleic acid, 12% linoleic acid, and 80% vernolic acid (*cis*-12,13-epoxy oleic acid) (Fig. 1) [11].

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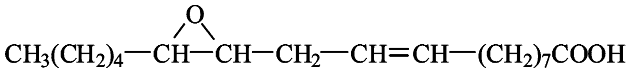


$$\mathrm{CH_3(CH_2)_4{-}\overset{O}{\overbrace{CH{-}CH}}{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOH}$$

Fig. 1 Vernolic acid

A key feature of vernonia oil is its relatively low viscosity compared to synthetic epoxidized oils of similar composition (Table 1). Due to its intrinsic low viscosity, vernonia oil is an attractive raw material for synthesizing vegetable oil carbonates that can serve as low viscosity precursors for isocyanate-free urethanes by reacting with amines or amino alcohols.

Experimental Procedures

Materials

Vernonia oil was purchased from Vertech, Inc. (Bethesda, MD) while epoxidized soybean oil (ESO, Vikoflex 7170) was purchased from Arkema, Inc. (Philadelphia, PA). Carbon dioxide (50 lb siphon-type high pressure cylinder, bone-dry, CO51) was obtained from Nordan Smith (Hattiesburg, MS) while TBAB (99%) was purchased from Sigma-Aldrich (St Louis, MO). Glacial acetic acid, tetraethylammonium bromide, perchloric acid, and crystal violet indicator were obtained from Fisher Scientific. All materials were used as received.

Instrumentation

A Parr (Moline, IL) 4560 mini benchtop stainless steel unit (600 mL) equipped with a Parr 4843 controller and thermocouple was used for the carbonation reactions. The reactor was heated using a 780 W, 115 V high temperature fabric heating mantle.

FTIR spectra were obtained on sodium chloride plates from 32 scans using a Varian 1000 Scimitar^{TM} Series FTIR spectrometer at 2 cm^{-1} resolution. ^{1}H- and ^{13}C-NMR spectra were obtained using a Varian Mercury NMR spectrometer operating at a frequency of 300.13 and 75.5 MHz for proton and carbon, respectively. Typical ^{1}H-acquisition parameters were as follows: a recycle delay of 1 s, a 7.1 μs pulse width corresponding to a 45 degree flip angle, and an acquisition time of 2 seconds. ^{13}C-acquisition parameters were a 1 s recycle delay, a 7.8 μs pulse width corresponding to a 45° flip angle, and an acquisition time of 1.8 s. All chemical shifts (given as δ in ppm) were referenced either automatically by the software (VNMR 6.1C) or manually using the resonance frequency of the deuterated solvent ($CDCl_3$) with tetramethyl silane as the internal standard.

Table 1 Relative viscosity of common oils

	Viscosity (25°C, @ 3333 s^{-1}) (Pa s)
Soybean oil	0.059
Castor oil	0.673
Vernonia oil	0.132
Epoxidized soybean oil[a]	0.418

[a] Vikoflex® 7170 (Arkema, Inc.)

Gel permeation chromatography (GPC) analysis was performed using a chromatographic system consisting of a Waters 515 HPLC pump, a Waters 2414 refractive index (RI) detector and a Polypore 300 × 7.5 mm column (Polymer Laboratories). Tetrahydrofuran was employed as the mobile phase with toluene as the flow marker (flow rate of 1 mL/min at 40 °C). The RI detector was calibrated using poly(methyl methacrylate) standards (Polymer Laboratories, CA). Viscosity profiles were generated using a BYK-Chemie cone and plate viscometer.

Epoxy content was determined using ASTM D1652 (Test Method B) by titrating the sample against perchloric acid in presence of excess tetraethylammonium bromide. Hydrogen bromide generated in situ by the addition of perchloric acid to the quaternary ammonium halide rapidly opens the oxirane ring. Vernonia oil was determined to have an epoxy content of 10.98% while ESO had an epoxy content of 18.58%.

Synthesis

A 436 g sample (0.48 mols) of vernonia oil and 27 g (0.08 mols) of TBAB were added to the Parr reactor and the reactor was sealed. The system was cooled to 9 °C and pressurized with carbon dioxide to 5.9 MPa. The reactor contents were stirred at 150 rpm and heated to 100 °C while limiting the pressure to <13.8 MPa. The stirring rate was raised to 700 rpm, and the pressure and temperature conditions were maintained for 46 h. At the end of the reaction, the pressure was released slowly to release excess carbon dioxide. Further, the reactor contents were heated to 175 °C for approximately 2 h to decompose the catalyst into its gaseous derivatives and yield carbonated vernonia oil (CVO, 72% yield). ESO was converted into carbonated soybean oil (CSO) using a similar procedure (multiple runs exhibited yields better than 72%). Each carbonated derivative was characterized via FTIR spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy.

Spectroscopic and Physical Data

The FTIR spectra of vernonia oil and CVO are shown in Fig. 2 (FTIR spectra of epoxidized soybean oil and ESO were similar and are not displayed). Characteristic bands of

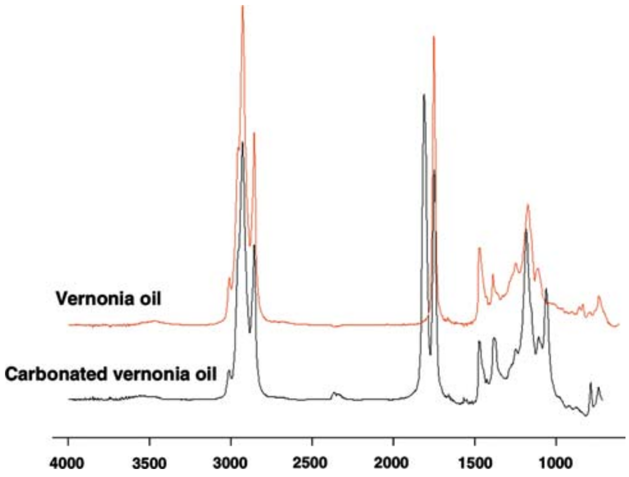


Fig. 2 FTIR spectra of vernonia oil and carbonated vernonia oil

vernonia oil were observed at 3,009, 2,926, 2,855, 1,746, 1,462, 1,164, and 7,23 cm^{-1} resulting from C–H stretching of CH=CH, C–H asymmetric stretching of CH$_2$, C–H symmetric stretching of CH$_2$, C=O stretching of ester (glyceride), CH$_2$ scissoring, O–C–C stretching of ester, and CH$_2$ rocking, respectively. Characteristic epoxide peaks of vernonia oil are noted at 842–822 cm^{-1}. As expected, the FTIR spectrum of CVO lacks these epoxide peaks, but the appearance of an additional spectroscopic peak at 1,793 cm^{-1} (C=O stretch) adjacent to the carbonyl peak associated with the triglyceride ester linkages is attributed to the cyclic carbonate carbonyl, confirming the conversion of epoxide groups to cyclic carbonates. A new peak was also noted at 1,047 cm^{-1} and was attributed to the C–O stretch present in the cyclic carbonate [8].

NMR data for vernonia oil: ^{1}H NMR(CDCl$_3$): 5.05–5.45 (–CH = CH–, –CH–O–CO–), 4.05–4.32 (–CO–O–CH_2–), 2.70–2.87 (epoxide group), 2.20–2.40 (–O–CO–CH_2–), 2.10–2.20 (α –CH_2 of epoxy group), 1.90–2.10 (–CH=CH–CH_2–), 1.40–1.65 (–O–CO–CH$_2$–CH_2–, β –CH_2 of epoxy group), 1.25–1.40 (methylene groups), and 0.75–0.93 (terminal –CH_3).

NMR data for vernonia oil: ^{13}C NMR (CDCl$_3$): 172.53–172.94 (–O–*C*O–CH$_2$–), 154 (cyclic carbonate carbons), 127.03–131.72 (–*C*H=*C*H–), 68.84 (–*C*H–O–CO–, glyceryl), 61.97 (–CO–O–*C*H$_2$–, glyceryl), 33.38–34.05 (–O–CO–*C*H$_2$–), 31.47–31.89 (ω3 –*C*H$_2$–), 28.98–29.71 (–CH=CH–*C*H$_2$–, –CH$_2$–*C*H$_2$–CH$_2$), 27.13 (–CH=CH–*C*H$_2$–CH=CH–), 24.77–25.55 (–O–CO–CH$_2$–*C*H$_2$–), 22.53–22.65 (ω2 –*C*H$_2$–), 14.00–14.20 (ω1 –*C*H$_3$).

NMR data for epoxidized soybean oil: ^{1}H NMR(CDCl$_3$): 5.61 (–CH=CH–), 5.26–5.35 (–CH=CH–, –CH–O–CO–), 4.10–4.40 (–CO–O–CH_2–), 2.85–3.25 (CH of epoxy groups), 2.29–2.34 (–O–CO–CH_2–), 1.70–1.90 (α –CH_2 of epoxy group), 1.55–1.70 (–O–CO–CH$_2$–CH_2–), 1.40–1.55 (β –CH_2 of epoxy group), 1.20–1.40 (methylene groups), 1.00–1.15 (terminal CH_3 of epoxy group at 15–16 carbon) and 0.83–0.95 (–CH$_2$–CH_3).

NMR data for epoxidized soybean oil: ^{13}C NMR (CDCl$_3$): 172.53–172.94 (–O–*C*O–CH$_2$–), 154 (cyclic carbonate carbons), 127.03–131.72 (–*C*H=*C*H–), 68.84 (–*C*H–O–CO–, glyceryl), 61.97 (–CO–O–*C*H$_2$–, glyceryl), 33.38–34.05 (–O–CO–*C*H$_2$–), 31.47–31.89 (ω3 –*C*H$_2$–), 28.98–29.71 (–CH=CH–*C*H$_2$–, –CH$_2$–*C*H$_2$–CH$_2$), 27.13 (–CH=CH–*C*H$_2$–CH=CH–), 24.77–25.55 (–O–CO–CH$_2$–*C*H$_2$–), 22.53–22.65 (ω2 –*C*H$_2$–), 14.00–14.20 (ω1 –*C*H$_3$).

NMR data for carbonated soybean oil:^{1}H NMR (CDCl$_3$): 5.75–5.90 (–CH=CH–), 5.15–5.30 (–CH=CH–, –CH–O–CO–), 4.40–4.95 (cyclic carbonate group), 4.05–4.32 (–CO–O–CH_2–), 2.31–2.65 (α –CH_2 of cyclic carbonate group), 2.20–2.31 (–O–CO–CH_2–), 1.80–2.10 (β –CH_2 of cyclic carbonate group), 1.44–1.75 (–O–CO–CH$_2$–CH_2–), 1.25–1.44 (methylene groups), and 0.75–0.91 (terminal CH_3).

NMR data for carbonated soybean oil: ^{13}C NMR (CDCl$_3$): 172.53–172.94 (–O–*C*O–CH$_2$–), 153.78–154.47 (carbonate carbon), 127.03–131.72 (–*C*H=*C*H–), 79.11–81.88 (methine carbons of cyclic carbonate), 68.84 (–*C*H–O–CO–, glyceryl), 61.97 (–CO–O–*C*H$_2$–, glyceryl), 33.38–34.05 (–O–CO–CH$_2$–), 31.47–31.89 (ω3 –CH$_2$–), 28.98–29.71 (–CH=CH–*C*H$_2$–, –CH$_2$–CH$_2$–CH$_2$), 27.13 (–CH=CH–*C*H$_2$–CH=CH–), 24.77–25.55 (–O–CO–CH$_2$–*C*H$_2$–), 22.53–22.65 (ω2 –*C*H$_2$–), 14.00–14.20 (ω1 –*C*H$_3$).

NMR data for carbonated vernonia oil:^{1}H NMR (CDCl$_3$): 5.40–5.60 (–CH=CH-), 5.20–5.35 (–CH=CH–, –CH–O–CO–), 4.50–4.65 (cyclic carbonate group), 4.0–4.32 (–CO–O–CH_2–), 3.58 (), 2.30–2.75 (α –CH_2 of cyclic carbonate group), 2.15–2.30 (–O–CO–CH_2–), 1.85–2.05 (–CH=CH–CH_2–), 1.40–1.70 (–O–CO–CH$_2$–CH_2–, β –CH_2 of cyclic carbonate group), 1.15–1.40 (methylene groups), and 0.75–0.95 (terminal –CH_3).

NMR data for carbonated vernonia oil: ^{13}C NMR (CDCl$_3$): 172.53–172.94 (–O–*C*O–CH$_2$–), 154.26 (carbonate carbon), 127.03–131.72 (–*C*H=*C*H–), 79.16–80.95 (methine carbons of cyclic carbonate), 68.84 (–*C*H–O–CO–, glyceryl), 61.97 (–CO–O–*C*H$_2$–, glyceryl), 57 (epoxide carbons), 33.38–34.05 (–O–CO–*C*H$_2$–), 31.47–31.89 (ω3 –*C*H$_2$–), 28.98–29.71 (–CH=CH–*C*H$_2$–, –CH$_2$–CH$_2$–CH$_2$), 27.13 (–CH=CH–*C*H$_2$–CH=CH–), 24.77–25.55 (–O–CO–CH$_2$–*C*H$_2$–), 22.53–22.65 (ω2 –*C*H$_2$–), 14.00–14.20 (ω1 –*C*H$_3$).

The ^{1}H-NMR spectra of epoxidized soybean oil and vernonia oil show oxirane hydrogens at δ 2.85 ppm. The new signals at 4.45–4.95 ppm in the ^{1}H-NMR spectra of the carbonated derivatives are attributed to the appearance of the cyclic carbonate group indicating conversion of the epoxide group to cyclic carbonates. The pattern of these signals corresponds to both *cis*- and *trans*-isomers of cyclic

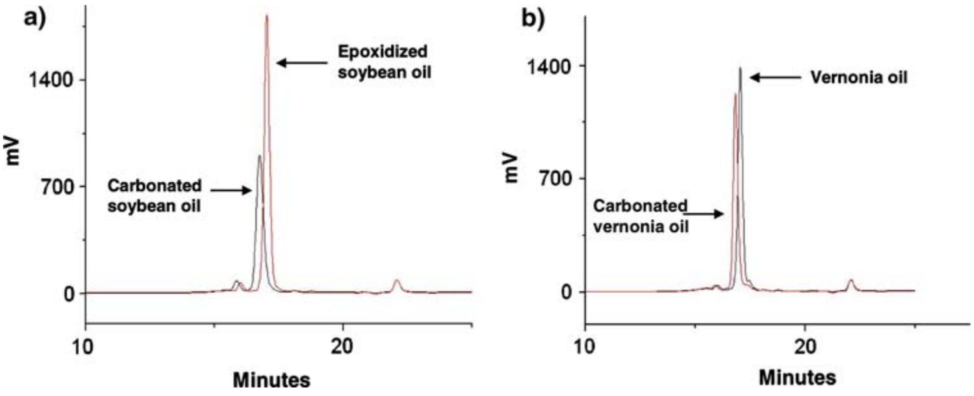


Fig. 3 GPC analysis of **a** epoxidized soybean oil and carbonated soybean oil, and **b** vernonia oil and carbonated vernonia oil

carbonates [12]. No loss of unsaturation was noted in the ^{1}H-NMR spectra. Similarly, the ^{13}C-NMR spectra shows oxirane carbons at δ 57 ppm in epoxidized soybean oil and vernonia oil that are absent in the carbonated derivatives. The signal at δ 154 ppm is representative of cyclic carbonate carbons, further supporting the efficient conversion from epoxide to cyclic carbonate [8].

GPC characterization results are shown in Fig. 3 and confirm little change in molecular weight before and after carbonation for both vernonia oil and epoxidized soybean oil. The viscosity increase upon vernonia oil carbonation is therefore attributed primarily to polar interactions between cyclic carbonates.

Results and Discussion

Wilkes and coworkers [13] reported the synthesis of carbonated soybean oil (CSO) from epoxidized soybean oil (ESO) using carbon dioxide and TBAB with 94% yield after 70 h. In their synthesis, the catalyst was removed by dissolving the reaction mixture in ethyl acetate and washing twice with water. Doll and Erhan improved upon this process by using supercritical carbon dioxide and achieved similar conversion of ESO in 20 h. Moreover, they also reported two simple methods for catalyst removal that eliminated the requirement of organic solvents.

Supercritical carbon dioxide is a non-toxic, non-flammable green solvent with tunable properties such as density, polarity, and solubility parameters as needed for specific reaction conditions using temperature and pressure as controlling variables. The low critical temperature and good solvency of supercritical carbon dioxide enables the extraction of volatile oils and fragrances without degradation or change in odor. The use of supercritical carbon dioxide in dry cleaning to replace perchloroethylene was developed and commercialized by DeSimone [14].

The phase diagram (Fig. 4) illustrates the effects of pressure and temperature on carbon dioxide [15]. The line

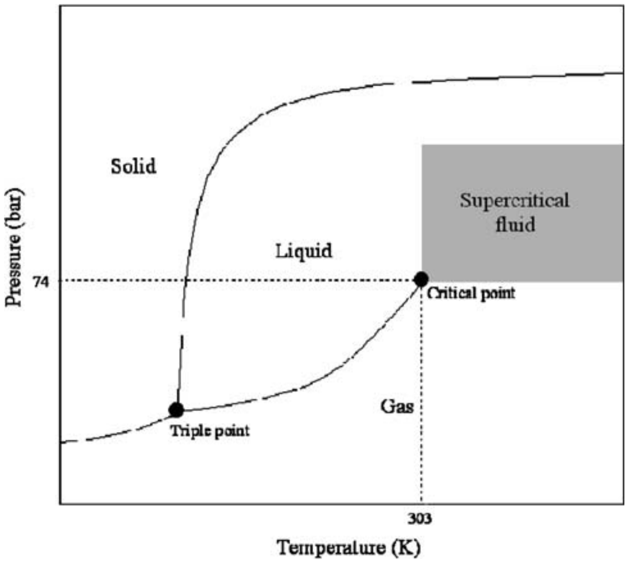
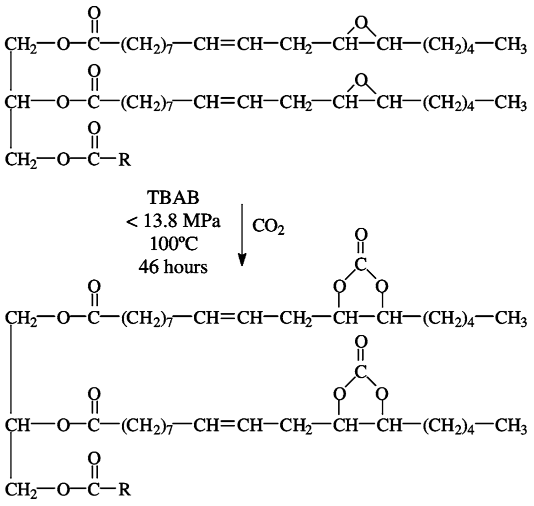


Fig. 4 Carbon dioxide phase diagram [12]



R is derivative of fatty acid RCOOH of varying composition as described in the text

Fig. 5 Carbonation reaction of vernonia oil

Fig. 6 Modified impeller shaft of Parr reactor

separating the liquid and the vapor phase denotes the boiling point of the liquid at the specific pressure, and ends at the critical point. At the critical point, the densities of the liquid phase and the vapor phase become equal, resulting in the formation of a single phase. Thus, carbon dioxide behaves as a supercritical fluid above its critical temperature (31.1 °C) and critical pressure (7.38 MPa). Supercritical fluids possess properties intermediate between that of liquids and gases allowing solubility parameters and solution density to be varied drastically when compared with traditional liquid solvents.

Carbonated vernonia oil (Fig. 5) was synthesized by reacting vernonia oil with supercritical carbon dioxide using the method developed by Doll and Erhan [9, 10]. The synthesis was accomplished in a Parr reactor that was modified for improved agitation by adding a second impeller above the original one (Fig. 6). The dual impeller setup promoted the blending between vegetable oil and carbon dioxide, and enabled greater reactor volume to be utilized (estimated to be 80% by volume). Residual epoxy content was determined to be 0.51% for carbonated vernonia oil and 0.68% for carbonated soybean oil, indicating conversion levels of 95.3% for vernonia oil and 96.3% for epoxidized soybean oil. The low epoxy content suggests that at 175 °C, no significant decarboxylation of cyclic carbonate groups occurred despite the presence of bromide salts.

In model studies involving the reaction of 2,3-epoxypropyl phenyl ether and carbon dioxide, Endo et al. [16] reported that carbonation of epoxides followed the mechanism shown in Fig. 7. The rate determining step was the attack of the catalyst anion on the epoxide ring. The authors also proposed an alternate reaction mechanism for catalysts containing highly nucleophilic anions, especially under high pressure.

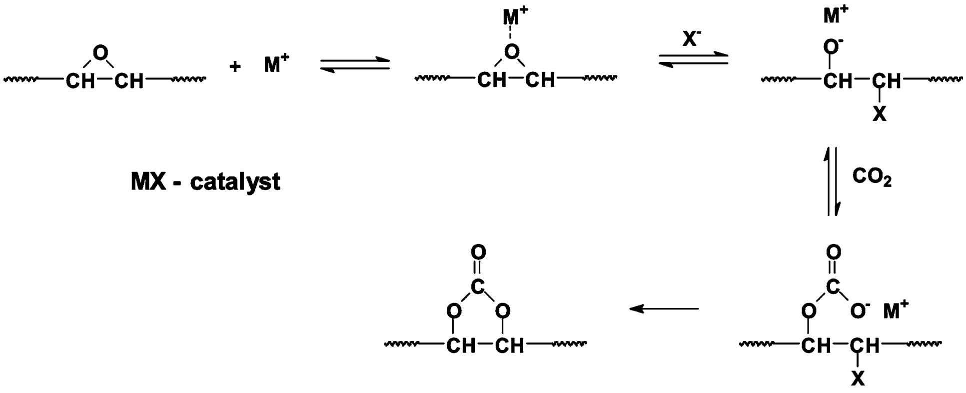
The low viscosity of vernonia oil is also manifested in its carbonated derivative as seen by comparing the viscosities of the different oils on a cone and plate viscometer at 25 °C (Table 2). Carbonation of epoxidized soybean oil increases the viscosity by a factor of 17 while carbonation of vernonia oil exhibits a viscosity increase factor of only 7.6.

With its low viscosity, CVO is a more attractive intermediate for an isocyanate-free route for synthesizing high solids, biobased urethanes than the corresponding derivatives from epoxidized soybean oil. The reaction of CVO with amines and amine alcohols is currently under investigation and will be reported in a subsequent publication.

Table 2 Viscosity profiles

	Viscosity (25 °C, @ 3333 s^{-1}) (Pa s)
Refined vernonia oil	0.13
Carbonated vernonia oil	0.99
Epoxidized soybean oil	0.41
Carbonated soybean oil	7.01

Fig. 7 Proposed reaction mechanism [16]



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