

EVALUATION OF AN ACID CATALYZED HETEROGENOUS REACTION CONDITION TO SYNTHESIZE POLYEPOXY CARDANOL

Kyla Snyder,* Jason McCaslin,* Marlene Jantes* and Maha L. Shrestha†

Department of Chemistry & Physics, West Texas A&M University, Canyon, TX 79016

Abstract

A heterogenous reaction condition using acetic acid along with an ion exchange resin is evaluated in obtaining polyepoxidized cardanol derived from cashew nut shell liquid (CNSL). Standard analytical techniques combined with spectroscopic analysis, Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) and Matrix-Assisted Laser Desorption/Ionization-Time of Flight/ Mass Spectrometry (MALDI-TOF/MS) suggest the formation of products with varying degrees of epoxy functional groups. The resulting products were also compared with those produced through a 24-hour reaction catalyzed by formic acid, which is more acidic. More importantly, this study reveals that a similar outcome can be achieved in a much shorter time using the method that involves the heterogenous reaction condition.

†Corresponding author: mshrestha@wtamu.edu

*Undergraduate researchers sand co-authors

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Introduction

Cashew nut shells are non-edible, inexpensive, easily accessible, and one of the best alternatives to nonrenewable fossil resources. Decarboxylation of cashew nut shell liquid (CNSL), also known as cardanol, is a complex mixture of natural phenols.¹ The *meta*-phenolic ring with 3 non-conjugated C=C double bonds on a hydrocarbon chain containing 15 carbons, is predominantly found despite the fact that the chemical composition of cardanol depends on the origin of the cashew nuts.^{1, 2} Other prominent chemical structures include the *meta*-phenolic ring with mono or difunctional C=C double bonds on its hydrocarbon chain.

Cardanol is of significant interest to researchers due to its aromatic ring possessing higher cohesive force, unlike many other agricultural or vegetable-based resources such as soybean oil and castor oil with aliphatic chains. Hence, cardanol provides unique characteristics that can enhance overall physio-mechanical properties of the resulting products. Cardanol and its derivatives are often utilized in preparation of polymeric materials such as surfactants, plasticizers in PVC, epoxy resins, and diluents. The unsaturated side chain of cardanol is versatile in developing various bio-based building blocks. One of the variants in obtaining such building blocks is the transformation of unsaturated C=C double bonds to epoxy or oxirane functional groups.

Several studies have investigated the epoxidation of the side chain of cardanol and its derivatives using different oxidants, catalysts, and reaction conditions. For instance, the C=C double bonds of the side chain were epoxidized by adding hydrogen peroxide dropwise to a heated solution in toluene with formic acid and *p*-toluenesulfonic acid.³ Similar procedures were followed in the epoxidation of cardanol glycidyl ether using formic acid.⁴ Epoxidation of the side chain of internal C=C double bonds of the cardanol derivatives was also performed successfully using meta-chloroperoxybenzoic acid (m-CPBA).⁵⁻⁷ Nevertheless, the major drawback of using strong acids is the side reactions opening the oxirane ring/s reducing the epoxy contents of the resulting products.⁵ To minimize the effect of strong acids, the reaction was also carried out with enzymes such as lipase along with acetic acid and hydrogen peroxide in toluene.⁸ Various organic acids were also evaluated under enzymatic reaction conditions.⁹ Similar to

the epoxidation of cardanol and its derivatives, several reports on epoxidation of other natural oils such as soybean oil, castor oil, etc. using acidic catalysts were also published.¹⁰⁻¹⁸ These studies also involved heterogenous reaction condition using acetic acid and ion exchange resins that provided the desired products with minimal side reactions. Acetic acid being the weaker acid compared to other organic acids such as formic acid and peroxy acids,^{19, 20} ion exchange resins are usually added with acetic acid for the synergistic effects. Despite the fact that many successful epoxidation reactions on C=C double bonds of agriculturally based natural oils such as castor oil, soybean oil, etc. were reported using heterogenous reaction condition with the ion exchange resin and acetic acid,^{10, 13-18} this reaction condition has not yet been explored extensively for the epoxidation of the side chain of cardanol and its derivatives.^{21, 22} Therefore, our current work focuses on acetic acid catalyzed heterogenous reaction condition to obtain polyepoxy cardanol derivatives. The resulting products were evaluated by standard analytical methods combined with Fourier Transform Infrared (FTIR) spectroscopy, Matrix-Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometry (MALDI-TOF/MS), ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectroscopies. Moreover, the results were compared directly with the products obtained from the more acidic formic acid catalyzed reaction.

Experimental

Materials:

Cardanol glycidyl ether (CGE), NC-513 was kindly provided by Cardolite Corporation. Acetic acid and toluene were received from Fisher Chemical. Ethyl acetate, hydrogen peroxide, and anhydrous sodium sulfate were purchased from VWR Chemicals, and Amberlite ICR 120H was obtained from Supelco.

Synthesis

Method 1: The epoxidation was conducted by heating a mixture of 35.655 g (0.2 eq. wt.) cardanol glycidyl ether (CGE), 6 g (5.7 mL, 0.1 mol) acetic acid, 8.913 g Amberlite (25 % w/w Amberlite to cardanol) and 17.84 g (20.58 mL toluene, 50 % w/w toluene to cardanol) at 60 °C, in a 3-neck R. B. flask equipped with a thermometer, an addition funnel and a magnetic stir bar. 33.92 g, (30.54 mL, 0.3 mol) of 30 % hydrogen peroxide was added to the reaction mixture slowly over the course of about an hour.

After the complete addition of hydrogen peroxide, the temperature was increased to 70 °C and continued the reaction for 5 hours. The reaction mixture was cooled to room temperature, and the ion exchange resin was filtered off, followed by extraction while neutralizing the solution to pH ~7. The solvent was removed using the rotary evaporator prior to analysis.

Method 2: Following the literature procedure,^{3,4} 17.83 g (0.1 eq) cardanol glycidyl ether (CGE), 4.025 g (3.29 mL, 0.1 mol) formic acid and 23.03 g (19.94 mL) toluene were added to a 3-neck R. B. flask equipped with a thermometer and an addition funnel. 34 g (30.63 mL, 1 mol) hydrogen peroxide was added slowly to a stirring solution of the reaction mixture at room temperature. After that, the reaction mixture was heated to 40 °C and continued the reaction for about 24 hours. Once the reaction was complete, the product solution was neutralized to pH 7 by using sodium bicarbonate solution followed by deionized water. The solvent was removed using a rotary evaporator.

Analysis

Viscosities of the cardanol glycidyl ether (CGE) and polyepoxy cardanol glycidyl ether (PECGE) were determined by HAAKE Viscometer iQ (Thermo Scientific) at 25° C. Iodine values and oxirane % were calculated using the titrations the Hanus method and ASTM D1652 method respectively. The Attenuated Total Reflection Fourier Transform Infrared (ATR/FT-IR) spectrometer from

Thermo Scientific was utilized to analyze the functional groups. ¹H and ¹³C NMR spectra were obtained from a 600 MHz Bruker's Nuclear Magnetic Resonance (NMR) spectrometer using deuterated chloroform as a solvent. MALDI-TOF analysis were performed from an Electrospray Ionization / Mass Spectrometry (ESI/MS) with an Orbitrap Fusion Mass Spectrometer (Bruker UltraflexX-treme MALDI-TOF/MS). The samples were diluted to approximately 10 µM in methanol prior to conducting MALDI-TOF/MS experiments.

Results and Discussion

Acetic acid catalyzed heterogenous reaction condition was used to epoxidize the C=C double bonds on the side chain of cardanol glycidyl ether (CGE), NC 513 that delivered orange-yellow colored liquid after the 5-hour long reaction.

The viscosity of the resulting product, polyepoxy glycidyl ether (PECGE) was higher, i.e. 25.7 mPa s compared to the starting material 11.84 mPa s. The epoxy equivalent weight of the CGE obtained from titration is 555 which is in the range of 425-575 that the manufacturer, Cardolite Corporation provided. Oxirane contents of the products PECGE obtained from titration suggest the epoxidation occurred as the epoxy equivalent of the products decreased; however, the iodine values of the products were rather too high (Table 1) to determine the conversion of the reactions. Therefore, ¹H NMR spectroscopy was used for accurate estimation

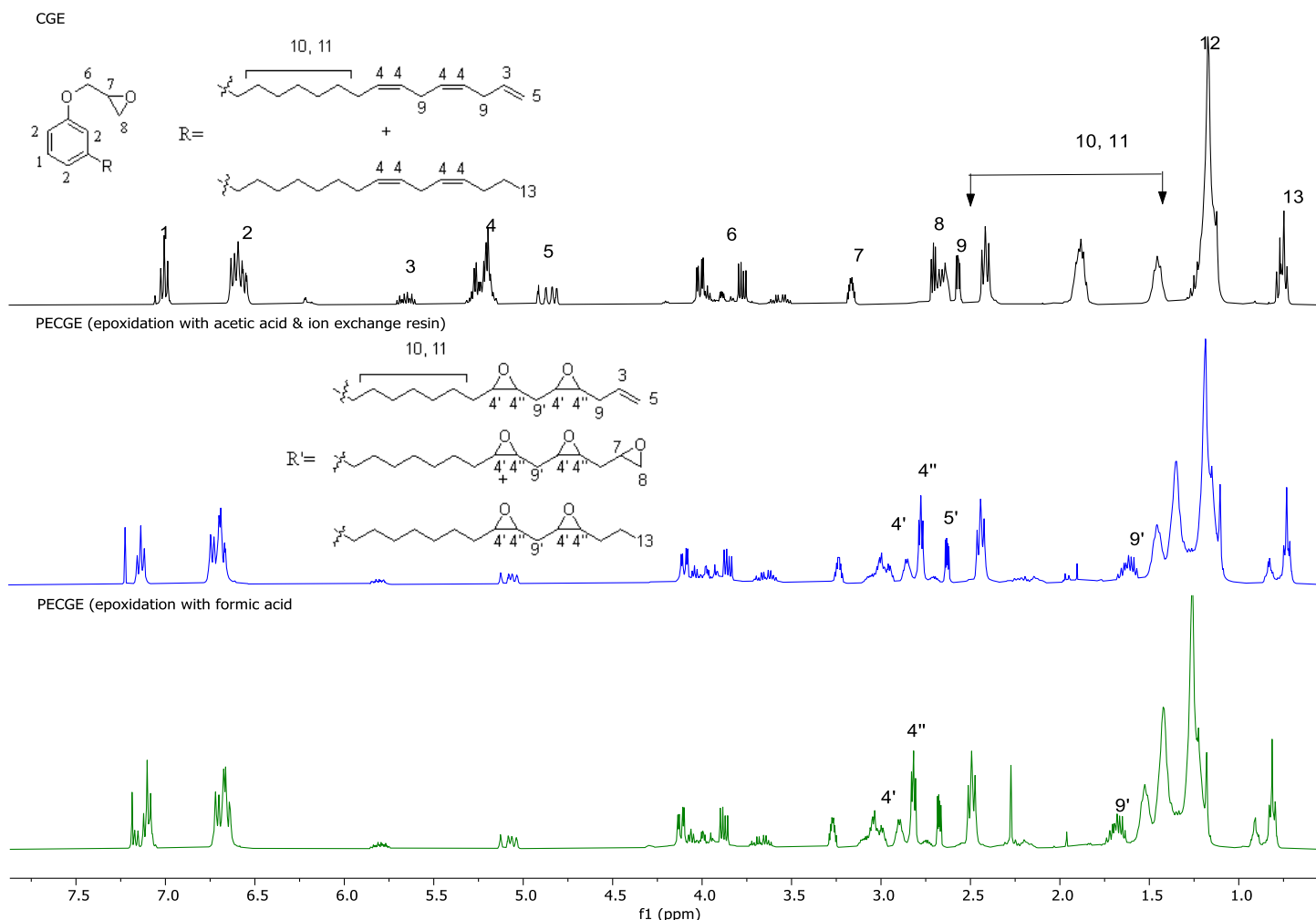
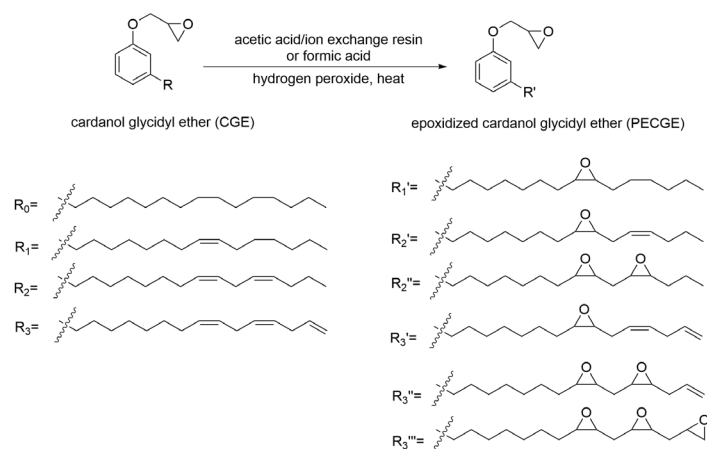


Fig. 1: ¹H NMR spectra of the CGE and the PECGE obtained after acid catalyzed epoxidation reactions



Scheme 1: Acid catalyzed epoxidation of cardanol glycidyl ether (CGE), NC 513

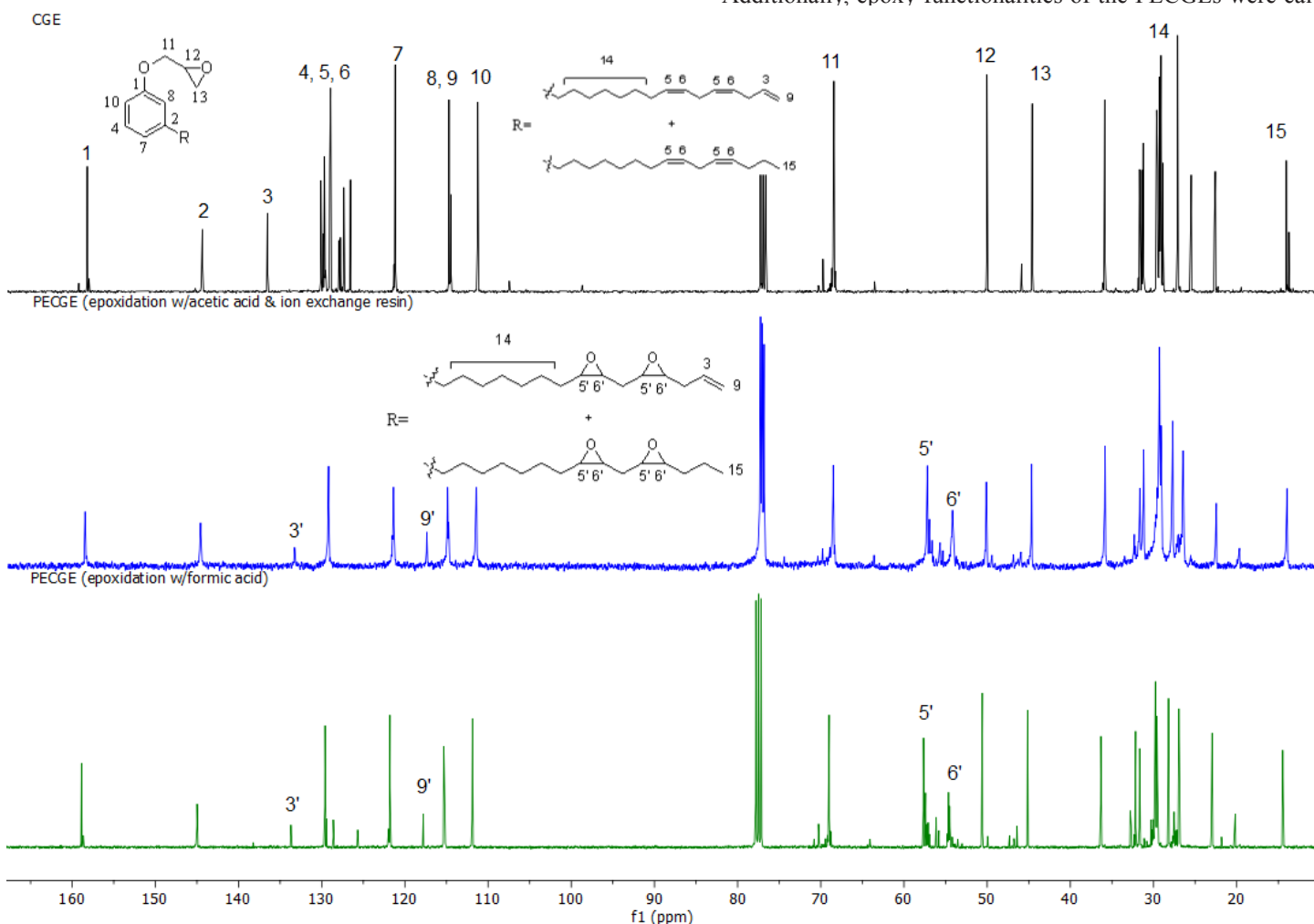
Table 1: Characteristics of the CGE and the PECGE after acid catalyzed epoxidation reactions

	CGE	PECGE (w/acetic acid)	PECGE (w/formic acid)
Iodine value (g/100 g)	135±0.52	26.05±0.5	26.00±0.48
Epoxy content (%)	2.88±0.12	7.41±0.04	7.37±0.04
Epoxy equivalent (g/eq)	555	216	217

of the epoxy values including the conversion.

¹H NMR analysis of cardanol glycidyl ether (CGE) suggests the presence of methine and methylene peaks of the glycidyl ether at 3.31 ppm and 2.71 ppm respectively (Fig. 1). A multiplet centered at 5.33 ppm was assigned for internal C=C double bonds. Although the chemical structure of the CGE, NC 513 provided by the manufacturer indicated only the internal C=C double bonds between C8-C9 and C11-C12 of the side chain, the multiplets centered at 5.80 ppm and 5.05 ppm show the terminal double bond also present. The ¹H NMR spectrum of the products PECGE obtained after epoxidation using the heterogenous reaction conditions demonstrate that the multiplet corresponding to internal double bonds at around 5.33 ppm disappeared with the evolution of new peaks in between 2.93 ppm and 3.20 ppm. These results were consistent with the ¹H NMR spectrum of the PECGE obtained using formic acid catalyzed 24 hours long reaction. The aromatic protons at the range 6.65 ppm and 7.20 ppm were used as a reference to determine the conversion of the reactions.¹⁶ The calculations suggest that the internal double bonds reacted predominantly, whereas the terminal double bond reacted only partially. The study also shows the similarity in conversion of the terminal double bond between the 5-hour long acetic acid catalyzed heterogenous reaction condition (35 %) and the formic acid catalyzed 24-hour long reaction (32 %).

Additionally, epoxy functionalities of the PECGEs were cal-

Fig. 2: ¹³C NMR spectra of the CGE and the PECGE obtained after acid catalyzed epoxidation reactions

culated using the technique described in published work^{4, 23} that suggests 2.95 epoxies/molecule (2.01 internal epoxies+ 0.94 terminal and primary epoxies) for the products obtained by using the heterogenous acidic reaction condition. These results resemble the epoxy values 2.93 (2.06 internal epoxies +0.87 terminal and primary epoxies) of the products obtained from the formic acid catalyzed reaction. However, the internal epoxy value resulted from the acetic acid catalyzed heterogenous reaction condition was slightly lower compared to the formic acid catalyzed reaction. The higher temperature used to perform the reaction that involved heterogenous condition may have caused the lower epoxy values as the oxirane ring opening reaction is more prone at higher temperature.²⁴ Nevertheless, the heterogenous reaction condition provided relatively higher epoxy values in a much shorter reaction time.

Likewise, ¹³C NMR analysis of the CGE shows the peaks at 44.77 ppm and 50.23 ppm corresponding to methylene and methine carbons of the oxirane ring (Fig. 2). The peaks at 129.33 ppm, 144.70 ppm and 158.50 ppm were assigned for the aromatic ring. Peaks at the range 126.85-130.14 ppm refers to the internal C=C double bonds, whereas the peaks at 136.84 and 114.75 the terminal C=C double bond which still existed after epoxidation performed under the heterogenous reaction condition, indicating the terminal C=C double bonds did not react completely. Evolution of new peaks at 57.28 ppm and 54.11 ppm on the ¹³C NMR spectrum of the PECGE corresponds to new epoxy rings. Similar results were observed in the PECGE synthesized from the formic acid catalyzed reaction as well.

Furthermore, FTIR spectrum of the starting material and the products obtained after the epoxidation reactions were evaluated. The spectrum of the CGE contains peaks at 2925 cm⁻¹ and 2852 cm⁻¹ which are due to -CH stretch of alkyl groups, and a peak at 3008 cm⁻¹ because of the C=C double bonds (Fig. 3). A broad peak at around 3400 cm⁻¹ in the IR spectrum of the PECGE corresponds to hydroxyl groups which suggests the presence of hydroxyl group/s due to a side reaction, opening the oxirane ring. Nevertheless, the resulting product lacks the characteristic C=C double

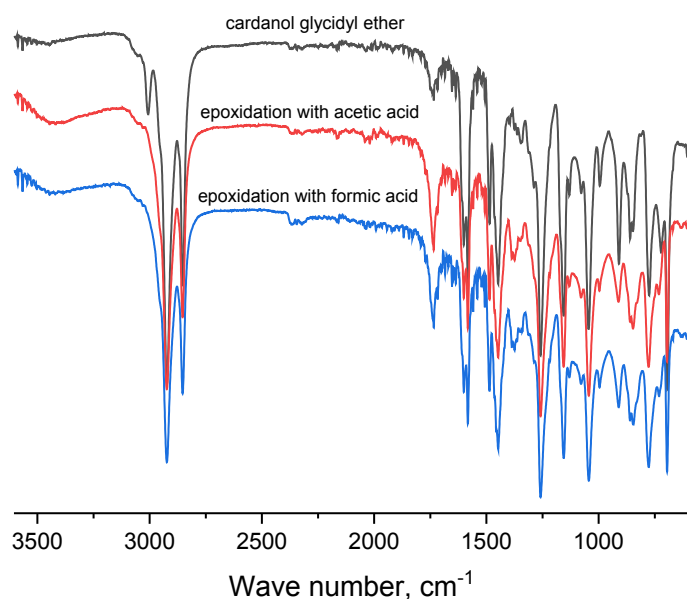


Fig. 3: Overlay of the FT-IR spectra of the CGE, and the PECGE obtained after acid catalyzed epoxidation reactions

bond peak at 3008 cm⁻¹ confirming that the double bonds reacted.²¹ Additionally, the new peaks at 776 cm⁻¹, 847 cm⁻¹ and 910 cm⁻¹ infers the formation of oxirane (epoxy) rings suggesting successful epoxidation using acetic acid with ion exchange resin.⁵ Similar results were observed when compared with the PECGE obtained from formic acid catalyzed reaction.

MALDI-TOF/ MS results of the starting material, CGE also show a complex mixture that contains varying degree of unsaturation on its side chain, ranging from 0 to 3 double bonds (Fig. 4 and Table 2). Additionally, an oxirane ring on its side chain with no double bond, 1 double bond and 2 double bonds were also observed at 397.28, 395.25 and 393.24. A fragment at 399.29 was also found which may be assigned for CGE containing a saturated side chain and a hydroxyl group in the aromatic ring.

As the starting material provided for our work contains a complex mixture, the MALDI-TOF of the products, PECGE obtained after epoxidation under the heterogenous reaction conditions with acetic acid and ion-exchange resin also shows the mixture of the epoxidized derivatives (Fig. 5). The side chain of the resulting products comprises no to 1 or 2 sets of double bonds (Table 2).

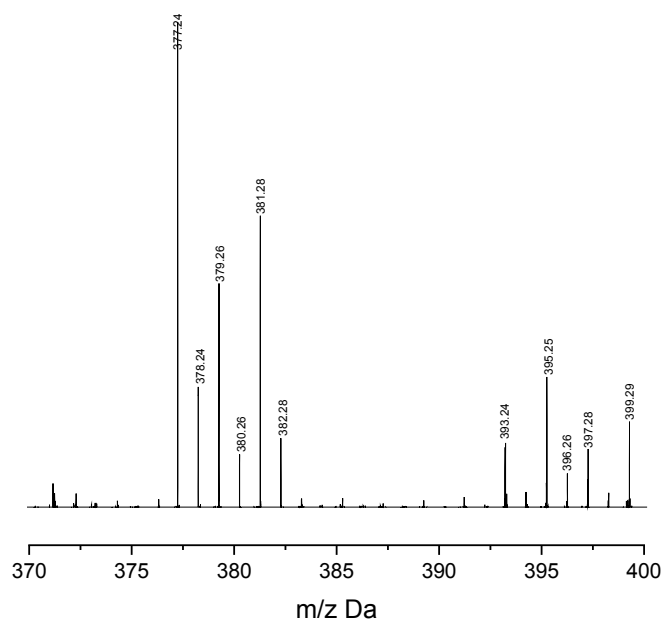


Fig. 4: MALDI-TOF / MS of the starting material CGE, NC 513

Table 2: Maldi-TOF / MS analysis of the CGE, and the PECGE obtained after acid catalyzed epoxidation reactions (ro = ring opening)

[M] ⁺ /before epoxidation	CGE	[M] ⁺ /after epoxidation	PECGE (w/acetic acid)	PECGE (w/formic acid)
[R ₃ +Na] ⁺	377.24	[R ₁ ' +Na] ⁺	397.27	397.27
[R ₃ +Na+H] ⁺	378.25	[R ₁ ' +Na+H] ⁺	398.27	398.27
[R ₂ +Na] ⁺	379.26	[R ₃ ' +Na] ⁺	409.23	409.23
[R ₂ +Na+H] ⁺	380.26	[R ₃ ' +Na+H] ⁺	410.23	410.24
[R ₁ +Na] ⁺	381.28	[R ₂ ' +Na] ⁺	411.25	411.25
[R ₁ +Na+H] ⁺	382.28	[R ₂ ' +Na+H] ⁺	412.25	412.25
[R ₃ ' +Na] ⁺	393.24	[R ₂ ' +Na] ⁺ (ro)	415.28	415.25
[R ₂ ' +Na] ⁺	395.25	[R ₃ ' +Na] ⁺	425.23	425.23
[R ₁ ' +Na] ⁺	397.28	[R ₃ ' +Na+H] ⁺	426.24	426.24
[R ₀ +Na+OH] ⁺	399.29	[R ₃ ' +Na] ⁺ (ro)	427.24	427.24
		[R ₃ ' +Na] ⁺ (ro)	429.26	429.26
		[R ₀ +74] ⁺	434.34	434.34
		[R ₃ ' +Na+OH] ⁺	441.20	441.20
		[R ₂ ' +74] ⁺	446.30	446.30
		[R ₁ ' +74] ⁺	448.31	448.31
		[R ₂ ' +74] ⁺	462.29	462.29

A fragment at 415.28 may have resulted due to ring opening of diepoxy rings located on its side chain. Likewise, 427.24 suggests the side reaction involving terminal epoxy ring opening and 429.26 could be the result of an internal and terminal ring opening reactions. Other fragments $[M+Na+H]^+$, $[M+Na+O]^+$ and $[M+74]^+$ were also seen which is possibly due to a charge driven process occurred during the ionization phenomena.²⁵ Similar results were obtained when the epoxidation reaction was performed with formic acid (Fig. 6 and Table 2).

In conclusion, all the above-described analysis suggests that the epoxidation reaction using the heterogenous reaction condition with acetic acid was successful. The higher reaction temperature may have stimulated epoxy ring opening resulting in slightly lower secondary epoxy values compared to formic acid reaction conditions. Nevertheless, the results obtained in a much shorter

reaction time, 5 hours, were consistent with that of the formic acid catalyzed 24-hour long reaction.

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References

1. Tyman, J. H. P.; Wilczynski, D.; Kashani, M. A. *Journal of the American Oil Chemists' Society* **1978**, 55 (9), 663-668. DOI: 10.1007/BF02682455.
2. Elijah, A. T. Cashew Nut Shell Oil — A Renewable and Reliable Petrochemical Feedstock. In *Advances in Petrochemicals*, Vivek, P. Ed.; IntechOpen, 2015; p Ch. 1.
3. Liu, Z.; Chen, J.; Knothe, G.; Nie, X.; Jiang, J. *ACS Sustainable Chemistry & Engineering* **2016**, 4 (3), 901-906. DOI: 10.1021/acssuschemeng.5b00991.
4. Kinaci, E.; Can, E.; Scala, J. J. L.; Palmese, G. R. *Polymers* **2020**, 12 (9), 1956.
5. Chen, J.; Nie, X.; Liu, Z.; Mi, Z.; Zhou, Y. *ACS Sustainable Chemistry & Engineering* **2015**, 3 (6), 1164-1171. DOI: 10.1021/acssuschemeng.5b00095.
6. Jaillet, F.; Darroman, E.; Boutevin, B.; Caillol, S. *Oil-seeds and fats crops and lipids* **2016**, 23 (5), 511-518. DOI: 10.1051/ocl/2016022 Cnrs Ensc-montpellier Icg Inc-cnrs Chimie Univ-montpellier Um-2015-2021 Test2-halcnrs.
7. Greco, A.; Brunetti, D.; Renna, G.; Mele, G.; Maffezzoli, *Polymer Degradation and Stability* **2010**, 95 (11), 2169-2174. DOI: <https://doi.org/10.1016/j.polymdegradstab.2010.06.001>.
8. Kim, Y. H.; An, E. S.; Park, S. Y.; Song, B. K. *Journal of Molecular Catalysis B: Enzymatic* **2007**, 45 (1), 39-44. DOI: <https://doi.org/10.1016/j.molcatb.2006.11.004>.
9. Yang, Z.; Zhang, Y.; Chu, L.; Bao, N.; Shen, L. *Industrial & Engineering Chemistry Research* **2023**, 62 (50), 21644-21653. DOI: 10.1021/acs.iecr.3c03583.
10. Petrović, Z. S.; Zlatanić, A.; Lava, C. C.; Sinadinović-Fišer, S. *European Journal of Lipid Science and Technology* **2002**, 104 (5), 293-299. DOI: [https://doi.org/10.1002/1438-9312\(200205\)104:5<293::AID-EJLT293>3.0.CO;2-W](https://doi.org/10.1002/1438-9312(200205)104:5<293::AID-EJLT293>3.0.CO;2-W) (accessed 2026/04/03).
11. Campanella, A.; Fontanini, C.; Baltanás, M. A. *Chemical Engineering Journal* **2008**, 144 (3), 466-475. DOI: <https://doi.org/10.1016/j.cej.2008.07.016>.
12. Olivieri, G. V.; de Quadros, J. V., Jr.; Giudici, R. *Industrial & Engineering Chemistry Research* **2020**, 59 (42), 18808-18823. DOI: 10.1021/acs.iecr.0c03847.
13. Meadows, S.; Hosur, M.; Celikbag, Y.; Jeelani, S. *Polymers and Polymer Composites* **2018**, 26 (4), 289-298. DOI: 10.1177/096739111802600403.

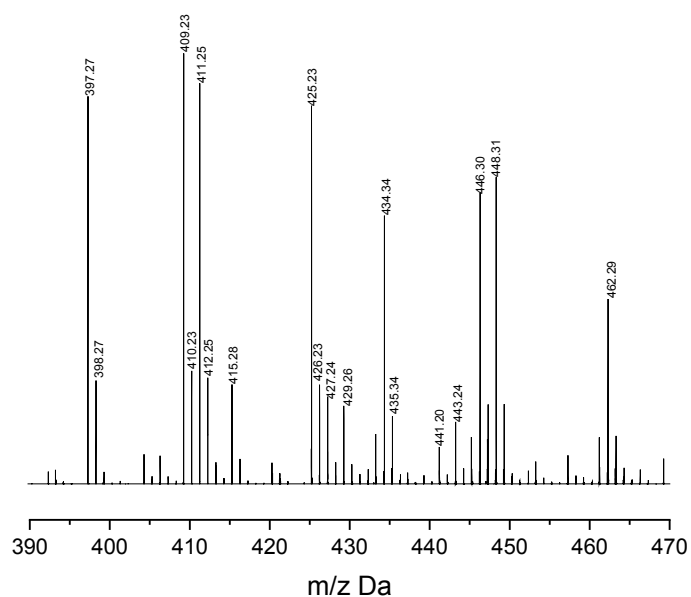


Fig. 5: Maldi-TOF / MS analysis of the PECGE obtained from acetic acid catalyzed heterogenous reaction condition

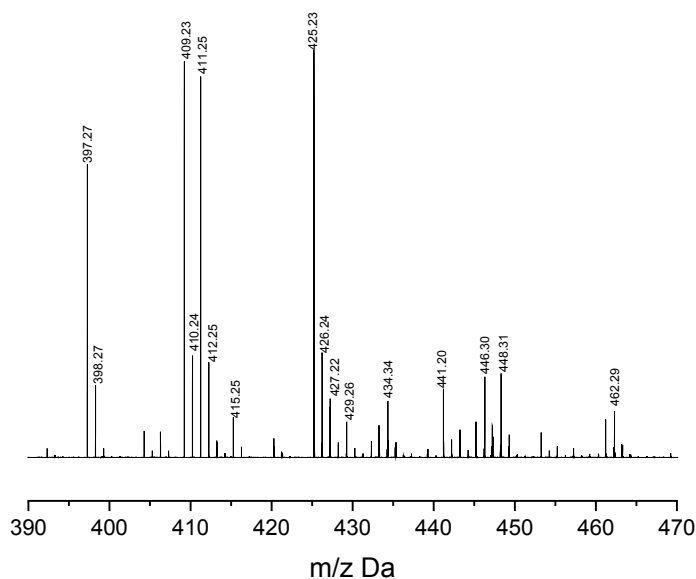


Fig. 6: Maldi-TOF / MS analysis of the PECGE obtained from formic acid catalyzed reaction condition

14. Borugadda, V. B.; Goud, V. V. *Energy Procedia* **2014**, *54*, 75-84. DOI: <https://doi.org/10.1016/j.egypro.2014.07.249>.
15. Montenegro, J. A. S.; Ries, A.; Silva, I. D. S.; Luna, C. B. B.; Souza, A. L.; Wellen, R. M. R. *Polymers* **2023**, *15* (11), 2477.
16. Juan F. Nieto, E. V. S., Susana Hernández López. *Advances in Analytical Chemistry* **2021**, *11* (1), 1-8. DOI: 10.5923/j.aac.20211101.01.
17. Sinadinović-Fišer, S.; Janković, M.; Petrović, Z. S. *Journal of the American Oil Chemists' Society* **2001**, *78* (7), 725-731. DOI: <https://doi.org/10.1007/s11746-001-0333-9> (accessed 2026/06/30).
18. Park, S.-J.; Jin, F.-L.; Lee, J.-R. *Macromolecular Chemistry and Physics* **2004**, *205* (15), 2048-2054. DOI: <https://doi.org/10.1002/macp.200400214> (accessed 2026/06/30).
19. Kim, H.; Gao, J.; Burgess, D. J. *International Journal of Pharmaceutics* **2009**, *377* (1), 105-111. DOI: <https://doi.org/10.1016/j.ijpharm.2009.05.018>.
20. Santacesaria, E.; Turco, R.; Russo, V.; Tesser, R.; Di Serio, M. *Processes* **2020**, *8* (9), 1134.
21. Rao, B. S.; Palanisamy, A. *European Polymer Journal* **2013**, *49* (8), 2365-2376. DOI: <https://doi.org/10.1016/j.eurpolymj.2013.05.029>.
22. Noè, C.; Malburet, S.; Milani, E.; Bouvet-Marchand, A.; Graillot, A.; Sangermano, M. *Polymer International* **2020**, *69* (8), 668-674. DOI: <https://doi.org/10.1002/pi.6031> (accessed 2026/07/21).
23. Kinaci, E.; Can, E.; Scala, J. J. L.; Palmese, G. R. *Polymers* **2020**, *12* (9), 2104.
24. Wang, Z.; Cui, Y.-T.; Xu, Z.-B.; Qu, J. *The Journal of Organic Chemistry* **2008**, *73* (6), 2270-2274. DOI: 10.1021/jo702401t.
25. Cheng, C.; Gross, M. L.; Pittenauer, E. *Analytical Chemistry* **1998**, *70* (20), 4417-4426. DOI: 10.1021/ac9805192.