Synthesis of Epoxidizedcardanol from CNSL (Vietnam) by Glacial Acetic Acid and Hydrogen Peroxide

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ABSTRACT

Cardanol obtained by vacuum distillation of cashew nut shell liquid (CNSL) at 220 – 230 ℃and 2 – 4 mmHg.Epoxidizedcardanol (ECD), derived from cardanol was synthesized at 65℃, 2% catalyst, DB/AA/ H_2O_2 :1/0.5/1, stirring rates are 1800 r/mand characterized by FT – IR, ^{1}H - NMR, ^{13}C – NMR, TGA.

Keywords: Cashew nut shell liquid, cardanol, epoxidizedcardanol

1. Introduction

In industrial applications the use of natural products is increasing due to concerns over environmental issues, waste disposal and depletion of non-renewable resources. Owing to the growing pressure to reduce carbon dioxide emissions by fossil fuels, the need for developing alternate chemical feed stocks from renewable resources is immense. Furthermore, these materials are sometimes cheaper than petrochemicals.

Vietnam is the largest exporter of cashew nuts in the world. However, the cashew nut shell burns only while cashew nut shell oil has great economic potential. Cashew nut shell liquid (CNSL) constitutes nearly one-third of the total nut weight; thus, a large amount of CNSL is formed as a by-product of the mechanical processes used to render the cashew kernel edible and its total production approaches one million tons annually. Thermally treated CNSL, whose main component is cardanol, aphenolderivative mainly having a *meta* substituent of a C15 hydrocarbon chain with one to

Three double bonds, has various potential industrial utilizations, such as resins, friction lining materials, and surface coatings; however, only a small part of the CNSL that is produced is used in the industrialfield.[3]

Cardanol a by product of CNSL has been used to produce phenalkamine low temperature curing agents for the durable epoxy coatings for marine applications[.3]. Frictional materials are made by polymerizing side chain of cardanol, followed by cross polymerization with formaldehyde to yield cardanol formaldehyde resin. Cardanol based polyols have been developed for rigid polyurethane applications. Despite all these uses, only a fraction of the cardanol obtained from cashew nut processing is used in the industrial field. Therefore, there is an overwhelming interest to create new polymer materials with improved performance from cardanol for new applications.

2. Experimental

2.1 Materials

CNSL was purchased from Cat Loi Cashew Oil Production & Export JSC (Vietnam). Cardanol was purified by double-vacuum distillation at 230–240°C under 2–5 mmHg.[2,5] Glacial acetic acid (99– 100%) was obtained from Merck, fomic acid and Hydrogen peroxide (30% V/V) from China. *p*-toluenesulfonic acid from Merck. Solvent ether and toluene (sulfur free) was obtained from China.

2.2 Synthesis of epoxidizedcardanol (ECD)

Epoxidizedcardanol was synthesized by reaction of cardanol with glacial acetic acid anh hydrogen peroxide using p-toluenesulfonic acid as a catalyst, toulen as a solvent. According to a literature procedure adopted for epoxidation of vinyl double bonds.[8]

In a four neck a round bottom flask equipped with a mechanical stirrer, thermometer sensor, and reflux condenser, Cardanol, glacial acetic acid, *p*-toluenesulfonic, and toluene were charged. The mixture was heated to temperature determined and 30% H_2O_2 was added slowly and allowed. After the reaction was complete, the crude product was filtered and washed with a saturated solution of Na_2CO_3 and distilled water, and then dried with anhydrous sodium sulfate. Finally, toluene was removed by distillation under vacuum at 80 °C for 2 h to yield the product.[13,14,15]

3. Results and Discussion

3.1 The effect of temperature on cardanolepoxidation

Cardanol epoxy reactions with reactive temperature from 55 ÷ 70 ° C. After washing and drying, the samples were analyzed for content of epoxy group and iodine index to calculate the efficiency of the reaction. The analysis results are shown in Figure 1.
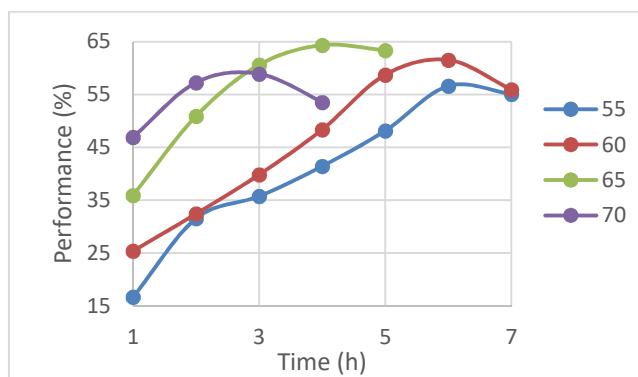

Fig. 1: Effect of temperature on cardanolepoxidation

The results in Figure 3.4 show that the performance of the reaction is lowest at 55°C, highest at 65°C. When raising the temperature, the efficiency of the reaction increases. However, when the temperature rises too high, the reaction efficiency decreases sharply. Because high temperatures, the formed epoxy group is easily broken by temperature. A temperature of 65 ° C is the optimum temperature for cardanol epoxide response to the survey conditions. We choose a temperature of 65 ° C to conduct a survey of the next parameters of the reaction.

3.2 The Effect of catalyst on epoxidation reaction

Examine the effect of catalyst on cardanolepoxidation reaction: 1, 2, 3, 4% over oil at 65 ° C. The analysis results are shown in Figure 2.
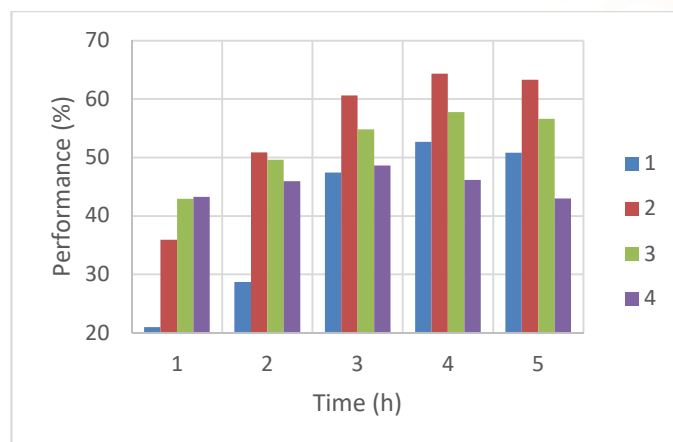

Fig 2: *Effect of catalyst on epoxidation reaction*

The results in Figure 2 show that the performance of the reaction is lowest with catalyst was 4%, the highest with catalyst was 2%. When the catalyst increases the performance of the reaction increases. However, when the catalyst is too high, the reaction efficiency decreases. Because p-toluene suforic is a potent, acidic catalyst, causing the epoxy ring opening reaction. 2% catalyst is the optimal catalyst for cardanolepoxidation with the survey conditions. We chose a 2% catalyst to conduct the next parameter of the reaction

3.3 The Effect of ingredients in the mixture on epoxidation reaction

The ratio of substances is DB / AA / H_2O_2 is 1/0.5/ x with x is 0.5, 1, 1.5, 2 at 65°C, catalyzing 2% of cardanol volume. The results of the experiment are shown in Figure 3
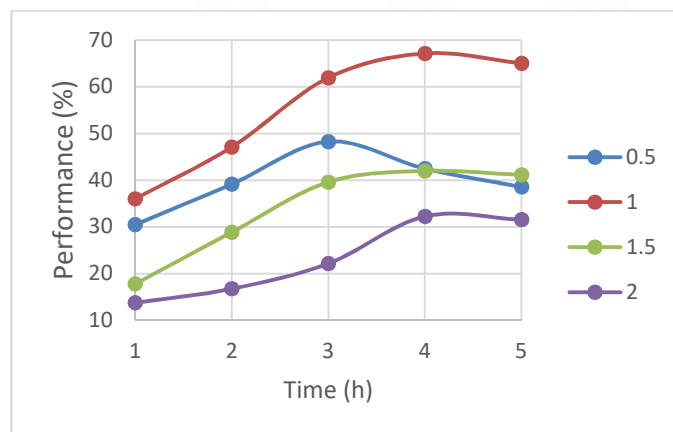

Fig 3: Effect of ingredients in the mixture on epoxidation reaction

The results in Figure 3 show that the performance of the reaction is lowest when the ratio of DB / H_2O_2 is 1/2 and 1/1 is the highest. When H_2O_2 increases the performance of the reaction increases. However, when H_2O_2 increases too high, the reaction efficiency decreases. Because the reaction has reached saturated levels of H_2O_2 or an increase in the amount of H_2O_2 that still increases the formation of the epoxy group while increasing both the epoxy ring-opening reaction.

The ratio of DB/AA/ H_2O_2 to 1/0.5/1 is the optimum ratio for cardanol epoxide response to the survey conditions.

3.4 The Effect of stirring speed on epoxidation reaction

Stirring rates are 1200, 1500, 1800, 2100 r/m at 65°C, catalytic 2% by volume of cardanol and the ratio of DB/AA / H_2O_2 is 1 /0.5/1. The results of the experiment are shown in Figure 4
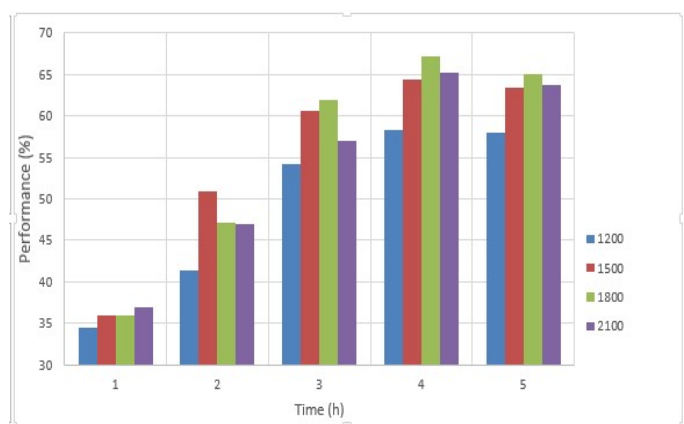

Fig.4: Effect of stirring speed on epoxidation reaction

The performance of the reaction is lowest when the stirring speed 1200 r/m, is highest when the stirring speed is 1800 r/m. When stirring speed increases the performance of the reaction increases. However, when the stirring speed is too high, the reaction efficiency decreases. Because the reaction system is heterologous to cardanol, toluene is hydrophobic, acetic acid and H_2O_2 are hydrophilic, so dispersion of substances in the reaction system is very necessary. The reaction will take place on the surface of the phase separation. Under varying stirring speed, the exposure and phase-difference times result in different reaction results. We chose a stirrer speed of 1800 r/m to conduct a survey of the next parameters of the reaction.

3.5 FTIR spectralanalysis

FT-IR technique was employed first to study the structures of cardanol and ECD. The FI-IR spectra of cardanol and ECD are depicted in Figure 5. In the spectrum of cardanol, there are several typical peaks: the phenolic hydroxyl group (3333 and 1348 cm_{-1}), C-H stretching of the inner unsaturated moiety (3009 cm_{-1}), methyl, methylene and methine groups (2924, 2853 and 1454 cm_{-1}), C=C on aromatic ring (1589 cm_{-1}), symmetric and asymmetric stretching of C=C (1263 cm_{-1}, 1153 cm_{-1}), vibration of the four hydrogen atoms adjacent to the benzene ring (779 cm_{-1}, 692 cm_{-1}).

In the spectrum of ECD, there are alsosome characteristic peaks: the phenolic hydroxyl group (3373 and 1373 cm_{-1}), methyl and methylene (2926 and 2854 cm_{-1}), epoxy group (848 - 918cm_{-1}). And two obvious changes are observed in the spectrum of ECD. First, the peak of C-H in the innerunsaturated moiety at 3009 $cm_{-1}$is absent because of the conversion to epoxide. Second, the characteristic features of the epoxy group are found at 848, 918cm_{-1}. Furthermore, the typical peak of phenolic hydroxyl group still exists. These indicate that cardanol had been converted into ECD.
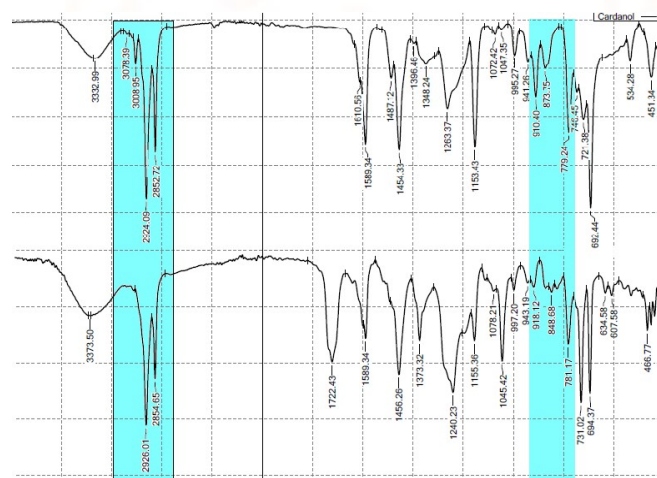

Fig 5: FTIR spectral of cardanol and ECD

3.6 ^1H - NMR and ^{13}C – NMR spectraanalysis

Figure 6 display the ^1H - NMR spectra of cardanol and ECD, respectively. The characteristic peaks at 6.6-7.3 ppm correspond to the protonson the benzene ring. Compared to the spectra of cardanol and ECD, the peaks at 5.4 ppm, corresponding to the proton of -CH=CH- in cardanol, have almost disappeared in ECD. This indicates that the unsaturated double bonds on the alkyl chain have been converted into epoxy groups during the epoxidation. The phenolic hydroxyl group at 5.2 ppm is still observed. Additionally, the

new peaks at 2.9 – 3.2 ppm indicate epoxy groups in ECD. Furthermore, the changed chemical shift of the peaks at 1.3 – 1.8 ppm also supports the formation of epoxidized groups.
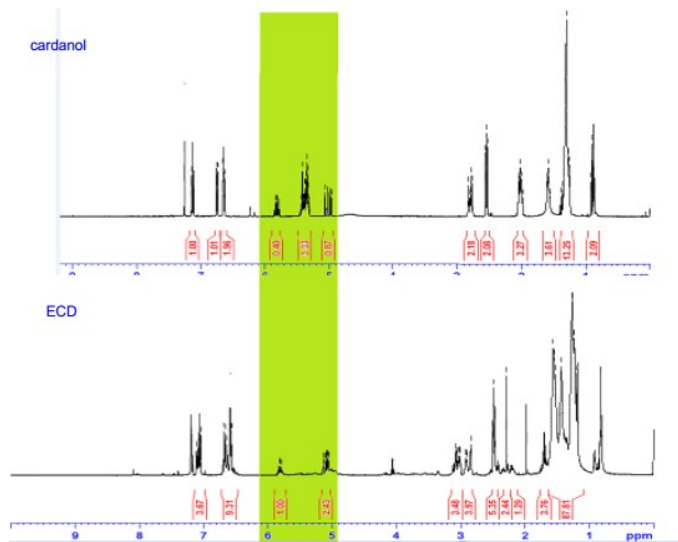

Fig.6. ^{1}H - NMR spectra of cardanol and ECD

Figure 7 display the ^{13}C –NMR spectra of cardanol and ECD.The ^{13}C – NMR peaks at 114.7 – 137.1 ppm are present in Figure 7 assigned to carbons 11, 13 and 14 have dissappeared. The epoxy groups distinguish between cardanol and ECD with the new cacbons in the epoxy.
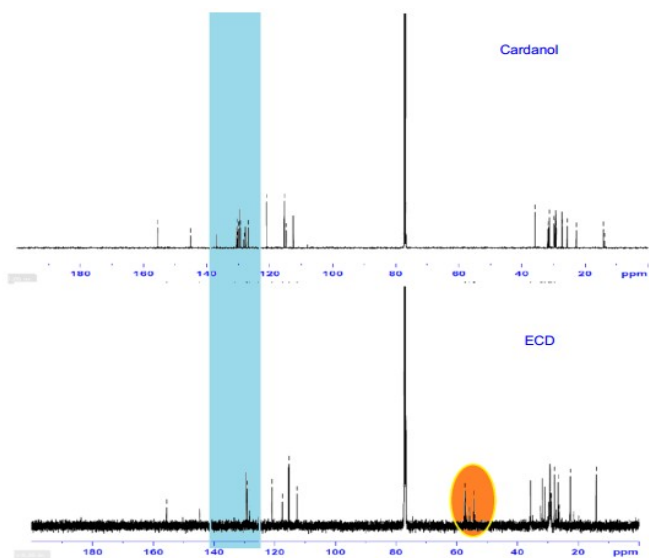

Fig.7. ^{13}C - NMR spectra of cardanol and ECD.

3.7. Thermal stability of ECD

Figure 8 shows the TGA curves of cardanol and ECD

heated in nitrogen at the rate of 10°C/min. It can be obserced that 10% weight loss (T_{10}) and 50% weight

loss (T_{50}) of cardanol happened at 285 and 409°C and the temperature is 200 and 393°C for the ECD
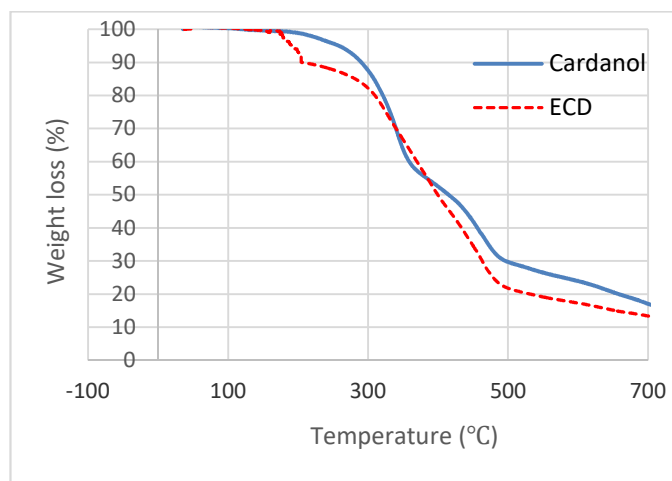

Fig.8. TGA curves of cardanol and ECD samples

The decomposition rate of ECD is faster than that of cardanol. So, the thermal stability of ECD is lower than that of cardanol. These results indicate the ECD is suitable for application at medium temperature.

Experimental results showed that 60°C was the most suitable temperature for cardanol epoxide oxidation with 91%.

4. Conclusion

In the study, Cardanol – derived ECD was synthesized at 65°C, 2% catalyst, DB/AA/ H$_2$O$_2$: 1/0.5/1, stirring rates are 1800 r/m and characterizedby FT – IR, ^{1}H - NMR, ^{13}C – NMR.

However, the effect of the reaction is not high (70%) due to the high temperature, which is more likely to occur when the epoxy ring is opened.

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