The Effect of Formic Acid, Hydrogen Peroxyde and Other Conditions on Epoxidized Reaction of Cardanol Extracted from Cashew Nut Shell Liquid of Vietnam

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ABSTRACT

Epoxidized vegetable oil have drawn much attention in recent yearrs, especially in the polymer industry as they are economical, available, environmentally friendly, non-noxious and renewable. Cashew nut shell liquid (CNSL), an agricultural by-product abundantly available in tropical countries such as Vietnam, India, is one of the major and economical resources of naturally occurring phenols. Cardanol a byproduct of CNSL could be epoxidized by reacting carbon-carbon double bonds of long unsaturated chain with peracids via the Prileshajev-epoxidation process or the conventional process. This paper deals with the epoxidized reaction of cardanol take place in formic acid and hydrogen peroxide. The results shown that the conversion efficiency of the epoxidized reaction reacheres 80% at 60^0C, stirring rates 1800 rpm, 2% p-toluenesulfonic acid catalyst and rate of double bonds (DB)/HCOOH (AF)/H_2O_2 = 1.0/0.5/1.5. The product of epoxidized cardanol is also characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR.

KEYWORDS: *epoxidized reaction, cashew nut shell liquid, cardanol, formic acid, hydrogen peroxyde, conversion efficiency*

INTRODUCTION

The global use of vegetable oils was basically classified into two main categories: food industry and industrial application [1]. The largest propotion of vegetable oils, approximately 80%, was utilized for food, while the share was taken up by the industrial sectors [2]. In general, advances in oleochemistry technology today make posible for researchers to chemically modify and transform the triglyceride of vegetable oils into polymerizable monomer via epoxidation metathesis of double bonds acrylation of epoxies, reaction with maleic anhydride or transesterification [3,4]. Among those reactions, epoxidation is a commercially importance reaction in organic synthesis since the high reactivity of oxirane rings makes them to be readily transformed into desired functionality [5-7].

Cashew nut shell liquid (CNSL) is one of the natural polyphenols that non-food renewable biomass resource and inexpensive organic natural resource extracted from cashew nuts. CNSL is a mixture of cardanol, cardol, anacardic acid and 2-methylcardol. All these posses a characteristic long alkyl chain in the meta position of the phenolic ring that confers attractive properties such as good prosessability and hidh solubility in organic solvens; but also influence many chemical transformation introducing novel functionalitis [8-10]. CNSL has already been extensively commercialized in industrial coatings, resins and compounds with formaldehyde, metal catalyst and volatile organic compounds [11,12].

Cardanol obtained via vacuum distillation of CNSL is nowadays considered very attractive precursor to develop new materials to be used in eco-friendly processes. The cardanol has been the centre of attraction for many researchers for the production of phenolic resins, epoxy resins, vinyl ester resins,

phenalkamines, polyols, etc. in the past [13-16]. In this study, we report synthesis of epoxidizedcardanol extracted from CSNL of Vietnam with formic acid and hydrogen peroxyde catalyzed by p-toluenesulfonic acid.

Experimental
Materials
CNSL was purchsed from Cat Loi Cashew Oil Production & Export JSC (Vietnam). Formic acid was obtained from Merck (Germany) with content $\geq$ 99,8%; water $\leq$ 0,2%; Hydrogen peroxyde (content 50%) from Xilong (China); p-toluensulfonic acid was obtained from Merck (Germany).Solvent ether and toluene from Xilong (China). Cardanol was obtained by vacuum distillation of CNSL at 245^0C under 2-5 mmHg.

Methods
Synthesis of epoxidizedcardanol
Epoxidizedcardanol was synthesized by reaction of cardanol with formic acide and hydrogen peroxyde using p-toluensulfonic acid as a catalyst, toluene as a solvent. The process is carried out according to the reference [15]. The scheme of the epoxidation reaction of cardanol are shown in Figure 1.
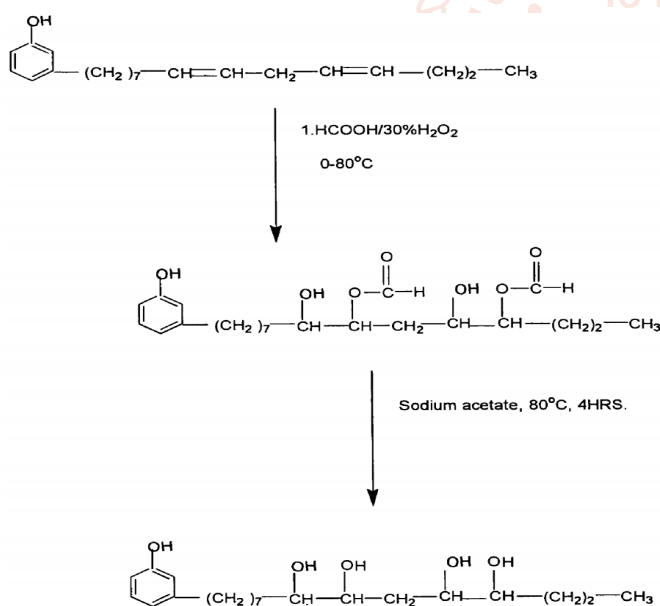

Fig.1: Scheme of the epoxidation reaction of cardanol

Characterization of compounds
The viscosity of cardanol was determined at room temperature with a Brookfield RVT viscometer. The density was determined by Erichsen Pycnometer Model 290 accoding to the standard ISO 2611. The iodine index was determined according to the standard ASTM D5768-02 (Wijs method).The hydroxyl value of compounds was determined according to the standard ASTM D1957-86.

Fourier transform infrared (FT-IR) spectroscopy was performed on a FT/IR Affinity-1S (Shimadzu-Japan) spectometer using NaCl plate at 23^0C $\pm$ 1^0C. The samples was scanned from 4000 to 400 cm^{-1}.

Proton and carbon NMR (^{1}H-NMR and ^{13}C-NMR) spectra of the compounds in deuterated chloroform (CDCl$_3$) were recorded with a Bruker 400 MHz spectrmeter (Bruker, Rheinstetten, Germany) at room temperature.

Results and discussion
Characteristics of cardanol
Cadanols extracted from CNSL Vietnam have the following properties: Viscosity 38 Cps; density 0.933; hydroxyl number 219 mg KOH/g; Iodine index 215g/100g. The FT-IR spectra of cardanol are shown in Figure 2.In the spectrum of cardanol, there are several typical peaks: the phenolic hydroxyl group (3332 and 1348 cm^{-1}), C-H stretching of the inner unsaturated moiety (3008 cm^{-1}), methyl, methylene and methine groups (2924, 2852 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}).
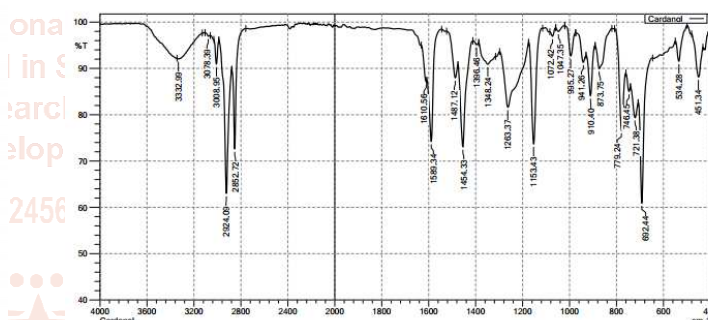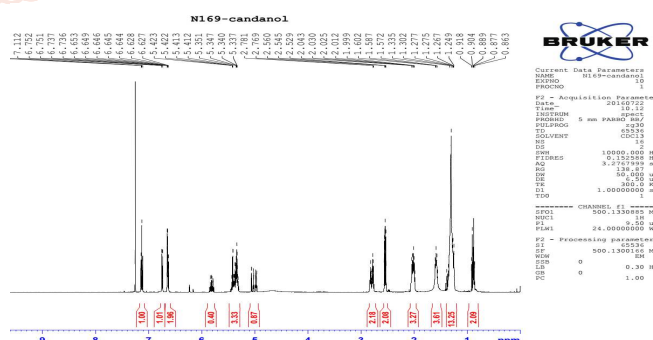

Fig.2:FT-IR spectra of cardanol

Fig.3: ^{1}H NMR spectra of cardanol

Figure 3 display the ^{1}H NMR spectra of cardanol. In the ^{1}H NMR spectra of cardanol, the characteristic peaks at 6.6-7.3 ppm correspond to the protons on the benzene ring and the phenolic hydroxyl group at 5.2 ppm. The peaks at 5.4 ppm correspond to the proton of –CH=CH- on the alkyl chain of cardanol.

Synthesis of the epoxidizedcardanol

The effect of temperature on cardanol epoxidation reaction

The cadanol epoxidation reaction was carried out over a temperature range of 50^0C to 65^0C with a step change of 5^0C. Molar ratio of the components: double bond (DB)/HCOOH/H_2O_2 = 1.0/0.5/1.5. Catalyst is p-toluensulfonic acid with content 2% w/w. The stiring rates 1800 rpm and time of the reaction is from 1h to 7h. The conversion efficiency of cardanol epoxjdation reaction is calculated based on the amount of epoxy group formed in the raction. The results are shown in Figure 4.
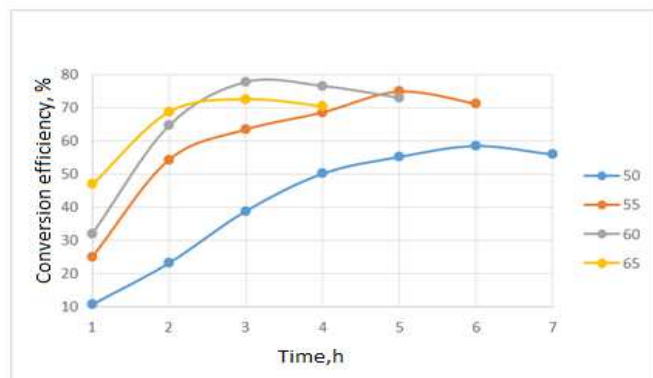

Fig.4: Effect of temperature on cardanol epoxidation reaction

The results in Fig. 4 show that the conversion efficiency (CE) of the cardanol epoxidation reaction is lowest at 50^0C and highest at 60^0C. When raising the temperature from 50^0C to 60^0C, the CE of the reaction increases, but when the temperature increases to 65^0C the CE deareases. This can happen because when the temperature is high, the epoxy group formed from the reaction is unstable and easy to decompose. Therefore, 60^0C is the suitable temperature chosen for the epoxidation of cadanols in the medium of formic acid and hydrogen peroxide.

The effect of the initial component ratio on cardanol epoxidation reaction

The molar ratio of the initial components to the cardanol epoxidationreaction is changed as follows:DB/HCOOH/H_2O_2 = 1.0/0.5/1.0; 1.0/0.5/1.5; 1.0/0.5/2.0; and 1.0/0.5/2.5. The temperature of the reaction is 60^0C. Other conditions same as at (3.2.1). The analysis results are shown in Figure 5.
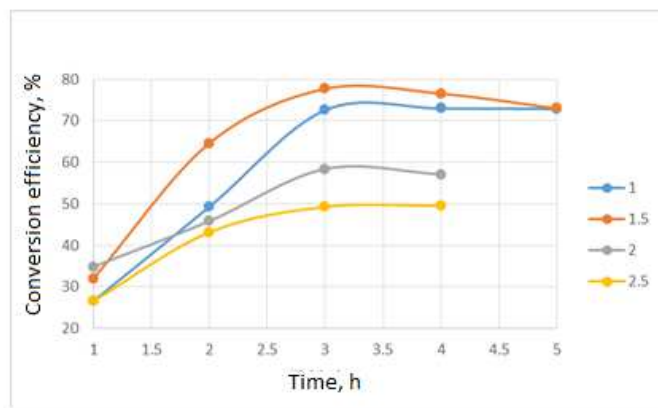

Fig.5: Effect of initial component ratio on cardanol epoxidation reaction

The results in Fig. 5 show that the CE of the cardanol epoxidation reaction is lowest at molar ratio DB/H_2O_2 = 1.0/2.5 and highest at DB/H_2O_2 = 1.0/1.5. When H_2O_2 increases too high, the CE of the reaction decreases sharply. This may be because the reaction has reached saturation to H_2O_2, or increasing the amount of H_2O_2 still increases the formation of the epoxy group and also increases the epoxy ring-opening reaction. Thus, the ratio of DB/HCOOH/H_2O_2 is 1.0/0.5/1.5 which is the optimal ratio for the epoxidation of cardanol with the investigated conditions.

The effect of the stirrng rate on cardanol epoxidation reaction
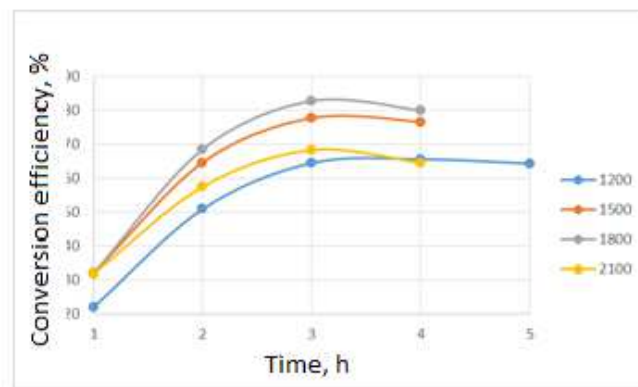

Fig.6: Effect of stirring rate on cardanol epoxidation reaction

The stirring rate in the cardanol epoxidationreaction is changed as follows: 1200 rpm; 1500 rpm; 1800 rpm and 2100 rpm. The ratio of DB/HCOOH/H_2O_2 = 1.0/0.5/1.5. The temperature of the reaction is 60^0C and catalyst of 2% p-toluenesulfonic acid. The analysis results are shown in Figure 6.

The results in Figure 6 indicate that the CE off reaction is lowest when the stirring speed is 1200 rpm, the highest when the stirring speed is 1800 rpm. As the stirring rate increases, the CE increases. However, when the stirring rate was increased too high, the CE decreased. This can be easily explained because the reaction system here is heterogeneous with cardanol, toluene is hydrophobic, formic acid and H_2O_2 are hydrophilic, so uniform dispersion of the substances in the reaction system is essential, necessary because the reaction will take place on the phase division surface. Under different stirring rate, different contact capacity and phase contact time lead to different reaction results. Thus, the stirring rate of 1800 rpm is the optimal stirring speed for the cardanol epoxidation reaction with the investigated conditions.

The effect of the time on cardanol epoxidation reaction

The time in the cardanol epoxidationreaction is changed as follows: 1h; 2h; 3h; 4h and 5h. The ratio of $DB/HCOOH/H_2O_2 = 1.0/0.5/1.5$. The temperature of the reaction is 60^0C and catalyst of 2% p-toluenesulfonic acid. The stirring rate of the reaction iss 188 rpm. The results are shown in Figure 7.
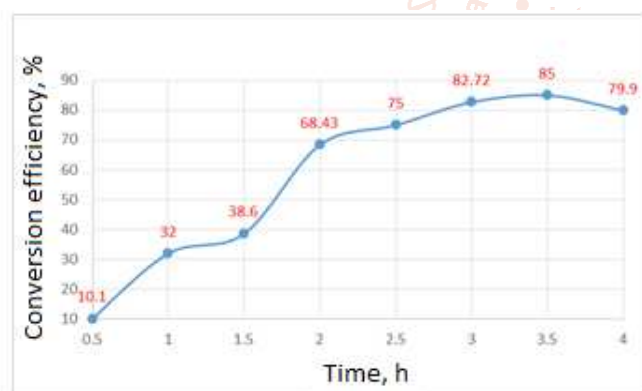

Fig.7: Effect of time on cardanol epoxidation reaction

The above results show that the CE of the reaction increases gradually over time. Highest CE when reaction time is 3.5h. Continuing the reaction, the CE of the reaction decreases. This may be because when conducting the reaction for a long time, epoxy ring-opening side reactions will occur. When the ring formation rate is less than the ring opening rate, the conversion efficiency will decrease. Thus, the reaction time of 3.5h is the optimal time for the cardanol epoxidation reaction with the investigated conditions.

The characterization of epoxidized carrdanol (ECD)

FT-IR technique was employed first to study the structure of cardanol and ECD. The spectra of cardanol and ECD are depicted in Figure 8.
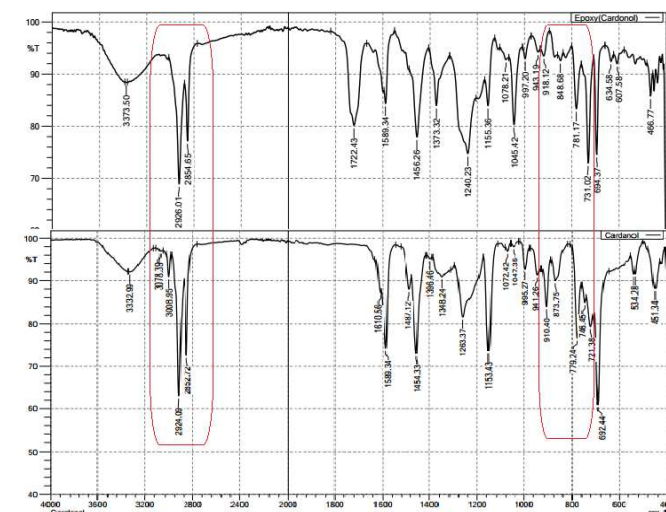

Fig.8: FT-IR spectra of cardanol and ECD

Two obvious changes are observed in the spectrum of ECD. First, the peak of C-H in the inner unsaturated moiety at 3008 cm^{-1} is absent because of the conversion to epoxide. Second, the characteristic features of the spoxy group are found at 848 cm^{-1} and 918 cm^{-1}. Furthermore, the typical peak of phenolic hydroxyl group still exists. These indicate that cardanol had been converted into ECD.

Figure 9 and Figure 10 display ^{1}H NMR and ^{13}C-NMR spectra of cardanol and ECD, respectively. The characteristic peaks at 6.6-7.3 ppm correspond to the protons on the benzene ring. When compare the spectra of cardanol and ECD it is found that the peaks at 5.4 ppm, corresponding to the proton of –CH=CH- of 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 changed chemical shift of the peaks at 1.3-1.8 ppm also supports the formation of epoxidized groups. The ^{13}C-NMR peaks at 114.8-137.2 ppm assigned to carbon 11, 13, 14 in cardanol have disappeared in ECD. Likewise, the epoxy groups distinguish between cardanol and ECD with the new peaks at 54.6-54.7 ppm corresponding to the carbons in the epoxy group.
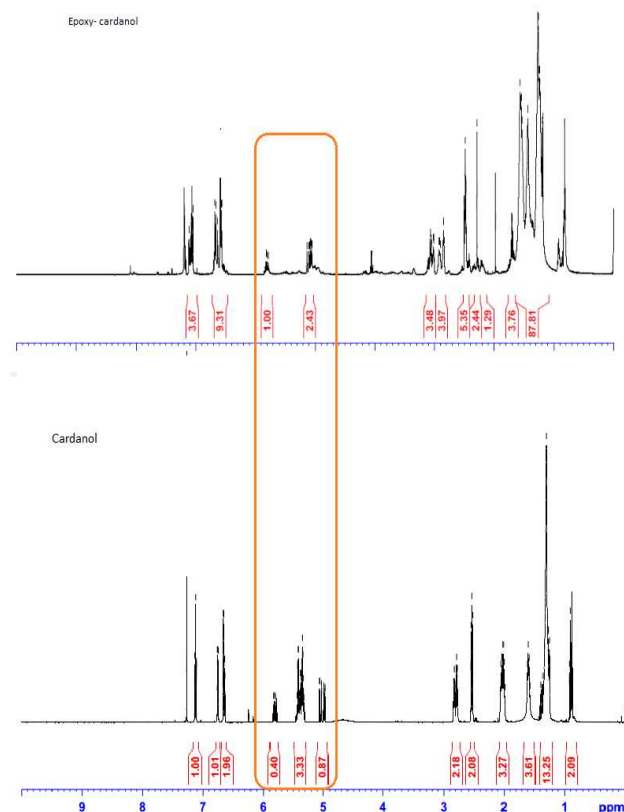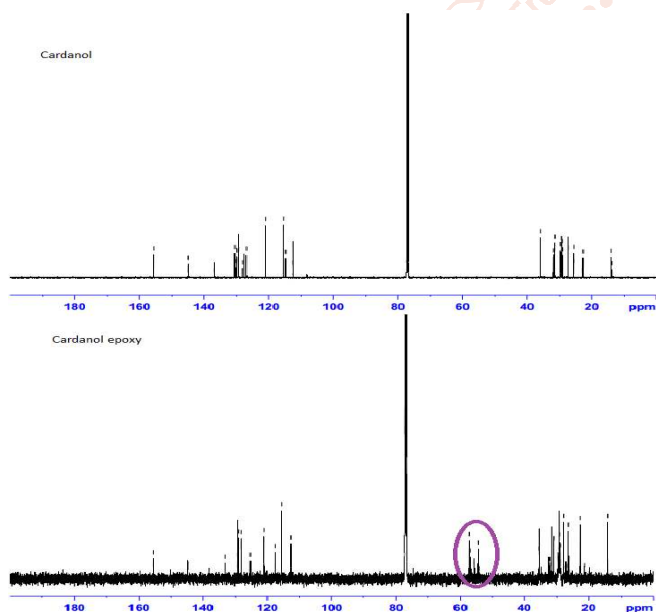
Fig. 9: ^{1}H NMR spectra of cardanol and ECD

Fig. 10: ^{13}C-NMR spectra of cardanol and ECD

Conclusion
In this study, cardanol was obtained by vacuum distillation of CNSL Vietnam at 245^0C under 2-5 mmHg. The epoxidizedcardanol was synthesized at the temperature 60^0C; molar ratio DB/HCOOH/H$_2$O$_2$ = 1.0/0.5/1.5; stirring rate 1800 rpm and 2% catalyst p-toluenesulfonic acid. The analysis of FT-IR, ^{1}H NMR and ^{13}C-NMR of cardanol and ECD showed that the unsaturated double bonds on the alkyl chain in cardanol have been converted into epoxy groups in ECD.

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