

Epoxidation of Soybean Oil and its Blend with Waste Cooking Oil Using H₂SO₄ as Homogeneous Catalyst

Hong Phuong Phan*, Trung Dang-Bao, Hoa-Hung Lam

Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, Ho Chi Minh City, Vietnam

phphuongdk@hcmut.edu.vn

Epoxidation of soybean oil is carried out at different conditions such as the feed ratio of C=C/CH₃COOH/H₂O₂ (1:1:1, 1:1:2, 1:2:1, 1:2:2, 1:2:4), reaction temperature (50 °C, 65 °C) and reaction time (3–7 h). Physicochemical properties of the reagent and product such as viscosity at 40 °C and 100 °C, viscosity index, iodine index as well as FT-IR spectral analysis are studied to find out suitable epoxidation reaction conditions. The experiment results showed that conversion of C=C in soybean oil through epoxidation could reach high value (96.0 %) at 65 °C for 5 h of reaction with the C=C/CH₃COOH/H₂O₂ molar ratio of 1:2:4 and viscosity index of epoxidised product was 156. IR results of the epoxidised oil obtained also exhibits that the peaks characteristic for the C=C bond disappear and the peaks characterising for epoxy rings are observed in the product, supporting evidence for epoxidation.

Epoxidation of soybean oil blended with waste cooking oil (90:10) is performed at the above suitable condition. The obtained results exhibited that C=C conversion of blended oil could still reach above 98 % and viscosity index of epoxidised oil is 151. The FT-IR spectral analysis of the epoxidised oil also clearly shows the appearance of peaks characterizing the epoxy ring.

1. Introduction

Nowadays, the source of base oil used in manufacturing of lubricants is mainly from mineral oil (Salimon et al., 2012). The decline in crude oil reservoirs as well as increasing environmental pollution lead to growing interest in renewable and biodegradable fuels or lubricants. In these terms, vegetable oils have been more popular in various applications, including lubricant base oil.

Compared to mineral base oil, vegetable oils have higher flash point, higher viscosity index, higher lubricity and lower evaporation loss. The large amount of C=C bonds in the fatty acid chains of vegetable oils (e.g. soybean, flax, sunflower, safflower, etc.) being responsible for poor oxidation stability and restricted viscosity range limiting their use as lubricants (Rani et al., 2015). Changing the chemical structure of vegetable oil has generated an important direction for building efficient and environmentally friendly reaction processes for creating new products or new applications for existing chemical compounds (Moser et al., 2018). Chemical transformation of C=C double bonds in fatty acids by reactions such as epoxidation (Figure 1) has been becoming increasingly important in the industry to improve oxidation stability and achieve proper characteristics for coatings, plasticizers or composites (Thomas et al., 2023).

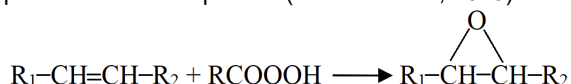


Figure 1: Schematic representation of epoxidation reaction (Tayder et al., 2011)

Blending of vegetable oils can provide many benefits such as improvement of viscosity index, acid value, saponification and iodine value (Marotrao, 2012). The iodine value is notably high and needs to be reduced. Epoxidation could be achieved using homogeneous, heterogeneous catalyst or metal catalyst (Marriam et al., 2023). While using heterogeneous catalyst provides an easy way to separate the product, homogeneous catalysts such as inorganic acids could speed up reaction and produce a high content of epoxy rings in the final product.

Riccardo et al. (2022) reported that ability to convert the double bonds through the epoxidation depends on the unsaturation degree of the feed. The epoxidation of safflower oil using H_2SO_4 as catalyst could reach 99.8 % at specific conditions. Dinda et al. (2008) has used inorganic acid catalyst to produce performic/peracetic acid that initiates epoxidation of cottonseed oil. Optimal conditions were found out but the viscosity and viscosity index of the product were not evaluated. H_2SO_4 was found to be the most effective catalyst. Since it is a strong acid, it leads to side reactions such as oxirane-ring opening to form diols, hydroxyesters, estolides and dimers (Lathi et al., 2006). While the formation rate of oxirane ring is high with formic acid, acetic acid is more efficient in promoting the transport of oxygen from the aqueous phase to the oil phase (Campanella et al., 2005). Epoxidation of palm oil-fatty acid with molar ratio of oil: H_2O_2 :formic acid of 1:1:1 within 2 h reached the best performance (Raofuddin et al., 2023). H_2O_2 :C=C molar ratio of 1.5:1 and 75 °C were found as the best condition for epoxidation of chia seed oil (Dominguez-Candela et al., 2022). Palm oil, soybean oil, rapeseed oil, and sunflower oil have been reported as the most important vegetable oils in the world accounting for over 80 % of the market (Frank et al., 2009). Among these vegetable oils, linseed oil and soybean oil have been attracting the most interest of scientists in investigation of their epoxidation due to their availability and price (Clayton et al., 1988). Compared to linseed oil, soybean oil has much lower iodine value (120–141 vs 170–204 $\text{gI}_2/100\text{g}$ oil) and higher kinematic viscosity at 38 °C (32.6 vs 27.2 mm^2/s) (Kapur et al., 1982). Waste cooking oils (WCO) from household, including vegetable oils as well as animal fats have been discarded into the environment with large amount every year (Cosetta et al., 2022). The use of vegetable oil in epoxidation could raise a competition between food and fuel, so blending vegetable oil with a portion of waste cooking oil would reduce this conflict. Epoxidation of oleic acid in the mixture of palm oil and waste palm cooking oil could reach the maximum conversion to oxirane of 65 % at 75 °C (Kadir, 2023). From the literature review, there is no paper reporting about epoxidation of blended WCO and vegetable oil. In this study, some properties of soybean oil and blended soybean oil with WCO including viscosity at different temperature, viscosity index, iodine value of soybean oils and blended soybean oil with WCO were analysed. The epoxidation of soybean oil was carried out with varying chemical reagents ratio (C=C/ $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$), time and temperature of reaction to find out a set of proper reaction parameter. Soybean oil blended with WCO was epoxidised at proper conditions above.

2. Experiment

2.1 Epoxidation reaction

In the first stage, epoxidation of soybean oil was performed using a mixture of CH_3COOH and H_2O_2 in a two-necked flask. The reaction parameters would be changed to find out suitable conditions for epoxidation. Molar ratio of C=C (oil)/ $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ is 1:1:1, 1:1:2, 1:2:1, 1:2:2, 1:2:4. The reaction temperature was 50 °C and 65 °C while epoxidation duration was 3 h, 5 h, 7 h. The reaction mixture was then neutralized by water and diethyl ether to enhance the separation of epoxidised oil. In the second stage, epoxidation of blended soybean oil and waste cooking oil with mass ratio of 90:10 was carried out at suitable condition found in the first stage. Experiments were repeated at least three times until similar results were obtained. The data were reported as a mean value of the three replicates.

2.2 Viscosity measurement and viscosity index determination

Kinematic viscosity was determined using a Redwood viscometer. A fixed volume of sample (7 mL) would flow through a glass capillary tube of definite diameter kept at a certain temperature (40 °C and 100 °C). The kinematic viscosity value (in cSt) was obtained from the flow time t (s) and the viscometer constant C (depending on the viscometer used) according to Eq(1):

$$v = C.t \quad (1)$$

The viscosity index is determined using viscosity at 40 °C, 100 °C according to ASTM D2270. Viscosity of the soybean oil blended SO with WCO and samples of epoxidised products were measured repeatedly. The value reported for each sample was a median of the three replicates.

2.3 Determination of Iodine index

The iodine index of feed and epoxidised oil were determined by titration according to ASTM D5768. Soybean oil, blended SO with WCO and samples of epoxidised products were subjected to the analysis of iodine index. The results were shown as a median value of three replicates.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The analysis of the chemical structure of the soybean oil and epoxidised product is accomplished using Fourier Transform Infrared Spectroscopy (FTIR), measured on a Tensor 27 Bruker instrument (Germany) in the wavenumber range of 4000–400 cm^{-1} , using the KBr pellet preparation method.

3. Result and discussion

3.1 Effect of reaction condition on C=C conversion of soybean oil

The C=C/ CH₃COOH/ H₂O₂ molar ratio of feed in epoxidation of soybean oil was changing at different values (1:1:1, 1:1:2, 1:2:1, 1:2:2, 1:2:4) to investigate the ratio at which a high conversion of C=C in soybean oil could be reached. All reagents were mixed at 50 °C within 3 h under 600 rpm. The iodine value of fresh soybean oil and different epoxidised products were presented in Table 1 and Figure 3.

Table 1: Iodine index and C=C conversion through epoxidation changing C=C/ CH₃COOH/ H₂O₂ molar ratio; viscosity at 40 °C and 100 °C, viscosity index of epoxidised oil

C=C/ CH ₃ COOH/ H ₂ O ₂ molar ratio	Iodine index	C=C conversion, %	Viscosity at 40 °C, cSt	Viscosity at 100 °C, cSt	Viscosity index
Soybean oil	126		30.72	7.53	228
1:1:1	107	15.12	41.11	8.18	178
1:1:2	106	15.93	39.77	8.13	184
1:2:1	97.1	22.98	51.52	9.99	185
1:2:2	94.5	25.00	49.45	9.93	193
1:2:4	90.2	28.43	48.25	9.84	195

Table 1 exhibited that when C=C/ CH₃COOH/ H₂O₂ molar is 1:1:1, the iodine value of epoxidised oil obtained was 107, presenting a C=C conversion of soybean oil was about 15.12 %. This could be explained by the role of CH₃COOH and H₂O₂ in epoxidation. These two reagents would produce peracetic acid that proceed epoxidation of C=C in the oil. While the concentration of H₂O₂ in feed was higher (with feed ratio of 1:1:2), iodine value of epoxidised oil did not change significantly. An excess of H₂O₂ could not produce more peracetic acid, being attributed to this result. With original molar ratio of feed (1:1:1), CH₃COOH might be the limiting reagent while H₂O₂ is in excess. If concentration of CH₃COOH in feed was raised (with corresponding feed molar ratio of 1:2:1), the iodine value of the obtained product dropped to 97.1 with a C=C conversion of 22.98 %. While amount of CH₃COOH was double (with C=C/CH₃COOH molar ratio changes from 1:1 to 1:2), an increase in H₂O₂ amount (with CH₃COOH/H₂O₂ molar ratio in the feed of 2:1, 2:2 and 2:4) resulted in a decrease of iodine index and an improvement of C=C conversion as shown in Figure 2. More H₂O₂ in this situation could shift equilibrium of peracetic acid formation to the right, producing more peracetic acid to combine with C=C in the feed oil.

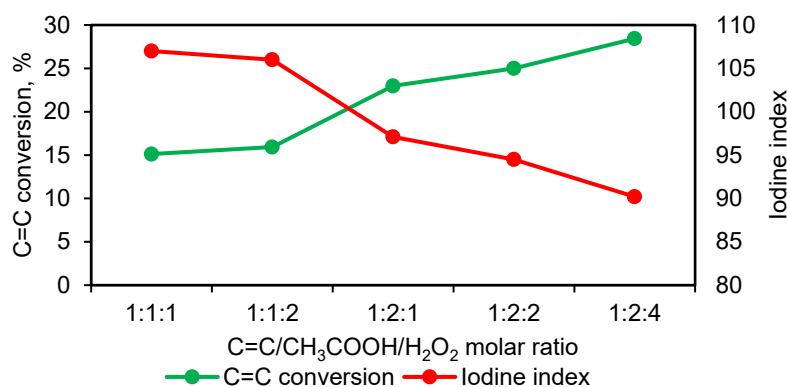


Figure 2: C=C conversion and Iodine index of epoxidised product obtained by changing C=C/ CH₃COOH/ H₂O₂ molar ratio

Viscosity at 40 °C, 100 °C and viscosity index results exerted a fact that epoxidation with variable molar ratio of feed could increase viscosity of epoxidised oil compared to the fresh oil as feed. Viscosity index of obtained oil reduced indicating a higher sensitivity of epoxidised oil raising temperature. Among the molar ratio of feed investigated, C=C/CH₃COOH/H₂O₂ ratio of 1:2:4 produced epoxidised oil having both high viscosity and high viscosity index. With a fixed C=C/ CH₃COOH/ H₂O₂ molar ratio of 1:2:4 in the feed, the reaction temperature of epoxidation at 50 °C and 65 °C would be investigated. All data about iodine index, C=C conversion in epoxidation, viscosity and viscosity index of epoxidised oil were presented in Table 2.

Table 2: Iodine index and C=C conversion through epoxidation changing reaction temperature; viscosity at 40 °C and 100 °C, viscosity index of epoxidised oil

Reaction temperature	Iodine index	C=C conversion	Viscosity at 40 °C, cSt	Viscosity at 100 °C, cSt	Viscosity index
50 °C	90.2	28.48	48.25	9.84	195
65 °C	35.3	71.97	88.56	13.17	149

It could be seen from Table 2 that iodine index of epoxidised oil decreased dramatically from 90.2 to 35.3 when epoxidation temperature was raised from 50 to 65 °C. C=C conversion of soybean oil through epoxidation increased from 28.48 to 71.97 %. The reaction temperature could not exceed 70 °C because side reactions such as polymerization and oxirane-ring opening by H₂O and/or acetic acid were favoured. H₂SO₄ could play the role as a strong oxidant which boosted the polymer reaction. 65 °C was chosen as suitable temperature for this epoxidation. Table 2 showed that viscosity at both 40 °C and 100 °C of epoxidised oil also increased with epoxidation temperature. This could be explained by the fact that less C=C in epoxidised oil (lower degree of unsaturation) caused higher viscosity. The viscosity index of epoxidised oil decreased from 195 to 149 when epoxidation temperature changed from 50 to 65 °C.

With fixed C=C/ CH₃COOH/ H₂O₂ molar ratio in the feed of 1:2:4, reaction temperature of 65 °C, reaction duration was changed in the range of 3–7 h to investigate its effect on epoxidised product.

The results of iodine index and C=C conversion through epoxidation at different reaction duration as well as viscosity at 40 °C and 100 °C, viscosity index of epoxidised oil were presented in the Table 3 and Figure 3.

Table 3: Iodine index and C=C conversion through epoxidation changing reaction duration; viscosity at 40 °C and 100 °C, viscosity index of epoxidised oil

Reaction temperature	Iodine index	C=C conversion	Viscosity at 40 °C, cSt	Viscosity at 100 °C, cSt	Viscosity index
3 h	35.3	71.97	88.56	13.17	149
5 h	5.03	96.00	117.97	16.87	156
7 h	1.41	98.88	147.72	20.31	160

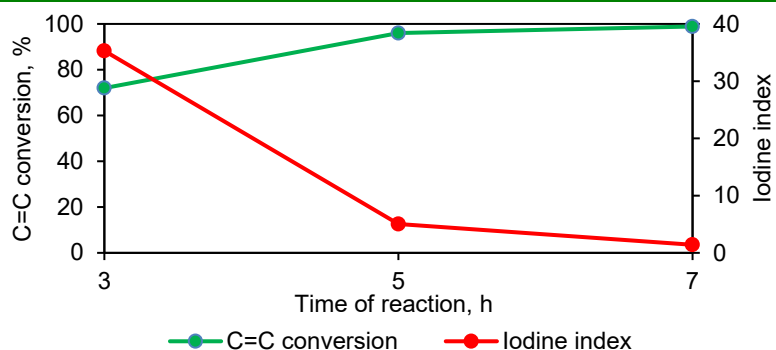


Figure 3: C=C conversion and Iodine index of epoxidised product obtained by changing time of epoxidation

It could be asserted from Table 3 and Figure 3 that reaction duration significantly increased C=C conversion into an oxirane ring. Iodine index of epoxidised product dropped from 35.3 to 5.03 and C=C conversion is enhanced from 71.97 to 96.00 % when reaction duration was raised from 3 h to 5 h. As more C=C bond was converted into oxirane ring, epoxidised product was more viscous. Both viscosity at 40 °C and 100 °C were improved remarkably when the duration of epoxidation was extended. Prolonging the reaction duration up to 7 h did not affect considerably iodine index and C=C conversion. Viscosity at both 40 °C and 100 °C of epoxidised product increased noticeably. This could be explained by the fact that lengthening the reaction from 5 h to 7 h mainly caused side reaction as oxirane-ring opening than main reaction as epoxidation. 5 h was chosen as a suitable duration for epoxidation in this study.

3.2 Epoxidation of blended soybean oil with waste cooking oil

In the above experiments, soybean oil was used as feed for epoxidation. The suitable conditions for reaction were found and listed as follows: C=C/ CH₃COOH/ H₂O₂ molar ratio of 1:2:4, reaction temperature of 65 °C and reaction duration of 5 h. Epoxidation of soybean oil blended with waste cooking oil with volume ratio of 90:10

was investigated at these conditions (C=C/ CH₃COOH/ H₂O₂ molar ratio of 1:2:4, 65 °C within 5 h). The results showed that iodine index of the product obtained was as low as 7.12 with corresponding a C=C conversion of 94.33 %. The viscosity of epoxidised oil at 40 °C and 100 °C were 108.22 and 15.07. Viscosity index of epoxidised oil was 147. Adding small amount of waste cooking oil to fresh oil did not affect considerably on suitable conditions for epoxidation.

3.3 FT-IR spectra of samples

Characteristic functional groups in soybean oil, epoxidised product of blended soybean and waste cooking oil were analysed to evaluate the performance of epoxidation using FTIR spectra. The Figure 4 below showed the FTIR spectra of soybean oil, epoxidised product obtained at two different reaction conditions.

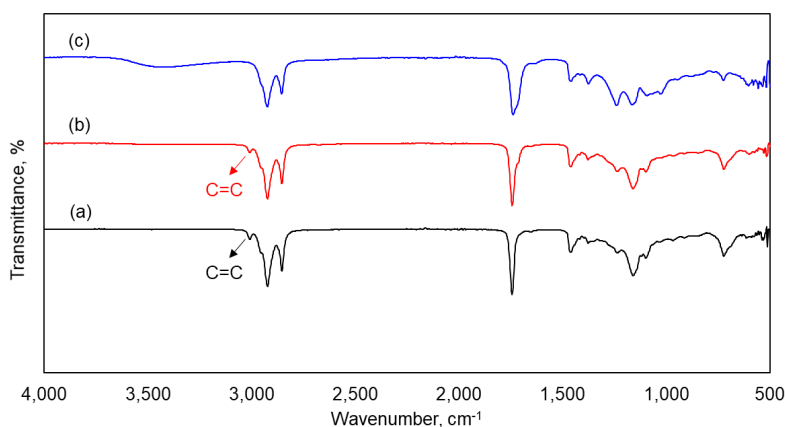


Figure 4: FTIR spectra of (a) soybean oil, (b) epoxidised product [C=C/CH₃COOH/H₂O₂ 1:1:1, 50 °C, 3 h], (c) epoxidised product [C=C/CH₃COOH/H₂O₂ 1:2:4, 65 °C, 7 h]

The presence of CH₃, CH₂, CH groups in all the samples was confirmed by absorption peak at 1376 cm⁻¹, 1461 cm⁻¹ and 2854–2924 cm⁻¹. The C–O and C=O bonds attributed to the ester linkage (O–C=O) were observed in the spectra of both initial and epoxidised oils, with absorption peaks at 722 and 1743 cm⁻¹. Sharma et al. (2015) indicated that absorption peak at 3007 cm⁻¹ in the FT-IR spectrum of canola oil showed the presence of C=C double bond. In the FT-IR spectra of epoxidised oil, no peak characteristic for the C=C double bond was found, and instead, the appearance of a peak at 831 cm⁻¹ indicated the presence of epoxy rings in epoxy canola oil structure. In this study, soybean oil and epoxidised product [C=C/CH₃COOH/H₂O₂ 1:1:1, 50 °C, 3 h] had the peak of C=C at 3008 cm⁻¹ (Figure 4a and 4b) while epoxidised product [C=C/CH₃COOH/H₂O₂ 1:2:4, 65 °C, 7 h] did not have this peak (Figure 4c). This fact confirmed that epoxidation with C=C/CH₃COOH/H₂O₂ ratio of 1:2:4, reaction temperature of 65 °C and duration of 7 h could convert almost C=C, being consistent with conversion of 98.88 % as listed in Table 3.

A broad band of adsorption appeared in the range of 3260–3570 cm⁻¹ in the FT-IR spectra of epoxidised product [C=C/CH₃COOH/H₂O₂ 1:2:4, 65 °C, 7 h] (Figure 4c), characterising O–H bond. This fact showed that some oxirane ring in the epoxidised oil had been opened in the side reaction – oxirane ring opening.

FT-IR spectrum of product obtained by epoxidation of soybean oil at C=C/H₂O₂/CH₃COOH of 1:1:1 within 3 h at 50 °C was shown in Figure 4b. As could be seen, epoxy band was noted to appear at around 849 cm⁻¹ confirming conversion of C=C in soybean oil into epoxide. Figure 4c exhibited the FT-IR spectrum of sample resulted through epoxidation of soybean oil at C=C/H₂O₂/CH₃COOH of 1:2:4 within 7 h at 65 °C. An additional band was observed at 3426 cm⁻¹ due to bending and stretching of O–H bond. This could be explained by the fact that some oxirane rings had been opened as epoxidation duration was longer and the reaction was carried out at higher temperature.

4. Conclusions

In this study, the suitable condition for epoxidation of soybean oil have been found out. The C=C/CH₃COOH/H₂O₂ molar ratio of 1:2:4 produces epoxidised oil having both high viscosity and high viscosity index. Although the viscosity index of epoxidised oil decreases from 195 to 149 when epoxidation temperature was raised from 50 °C to 65 °C at proper reaction condition, 65 °C is chosen as more suitable temperature due to improvement of C=C conversion and higher viscosity at both 40 °C and 100 °C of the obtained product. 5 h was

more suitable reaction time in this study because extending epoxidation duration could raise probability of oxirane-ring opening. As it has been concluded, the FT-IR spectrum confirms oxirane-ring opening reaction if epoxidation time was 7 h through appearance of O–H bond in the epoxidised product. Epoxidation of soybean oil blended with waste cooking oil with mass ratio of 90:10 carried out at C=C/CH₃COOH/H₂O₂ molar ratio of 1:2:4, reaction temperature of 65 °C and duration of 5 h could reach C=C conversion as high as 94.33 %. Viscosity of this epoxidised oil at 40 °C and 100 °C were 108.22 and 15.07 while its viscosity index was 147.

Acknowledgments

We acknowledge Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for supporting this study.

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