

The Influence of Reaction Parameters on the Epoxidation of Rapeseed Oil with Peracetic Acid

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Abstract The influence of reaction parameters on the epoxidation of rapeseed oil (RO) with peracetic acid obtained in situ from the reaction between 30 wt% hydrogen peroxide and glacial acetic acid (AA) has been studied. The course of the reaction was measured by changes of the iodine number (IN) and epoxy number (EN), used to estimate the degree of rapeseed oil conversion, yield, and the selectivity of transformation to epoxidized rapeseed oil in relation to the total amount of oil undergoing the transformation. The optimal conditions of epoxidation are as follows: temperature 60 °C, molar ratio of hydrogen peroxide to rapeseed oil 9.5:1 mol/mol, molar ratio of acetic acid to rapeseed oil 1.12:1 mol/mol, stirring speed 500 rpm, and reaction time of 4 h. Under these conditions the epoxy number is equal to 0.157 mol/100 g RO and iodine number reaches low values of 0.123 mol/100 g RO. The selectivity of transformation to epoxidized RO calculated from EN and IN is 82.2%, conversion of hydrogen peroxide is 100%, conversion of RO calculated from IN is 60.8%, and yield of RO calculated from EN is 50%.

Keywords Hydrogen peroxide · In situ epoxidation · Peracetic acid · Sulphuric acid · Rapeseed oil

Introduction

Epoxidized vegetable oils have received growing interest in recent years. At the moment, one of the most important epoxidized vegetable oil is soybean oil; its production in 1999 was nearly 200,000 t [1, 2]. Although there are many studies on the epoxidation of soybean oil, there have been few reports concerning the epoxidation of other oils (palm, corn, mahua, etc.) and there have been only a few reports on the epoxidation of rapeseed oil [3].

Epoxidized oils transesterified with low-molecular-weight alcohols are used as plasticizers of polyvinyl chloride [4–6]. Epoxidized oils improve the elasticity of plastics and so are used in the production of packing materials such as wrapping foils [7]. Due to the high reactivity of the oxirane ring in epoxidized oils, they are used as renewable raw materials for manufacturing such intermediate products as alcohols, glycols, alcoxyalcohols, hydroxyesters, *N*-hydroxyalkylamides, mercaptoalcohols, hydroxynitriles, alkanolamines, and carbonyl compounds [1, 2, 8]. Epoxidized vegetable oils are used for both formation of thermosetting composites [9] and coatings obtained by ultraviolet (UV)-initiated cross-linking [9–11]. Epoxidized soybean oil functionalized with diamine is an excellent antioxidant and lubricant, and has been proven as an antifriction agent. Because of its amphiphilic character it is added to base grease oils to improve their application properties [12].

Epoxidation of vegetable oils can be carried out utilizing carboxylic peracids in an acidic environment, with organic hydroperoxides, or with hydrogen peroxide in the presence of metals of variable valence.

The main target of our research is to investigate the reaction parameters of the rapeseed oil epoxidation process.

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Epoxidation with Peracids

A widely used method for epoxidation of vegetable oils relies on the application of carboxylic peracids, either preformed or generated in situ [13, 14]. The content of particular acids in the oil depends on the type and origin of the oil, as well as on its freshness and the refining process to which the oil has been subjected before and after separation from the raw material.

During the epoxidation of unsaturated compound a reversible reaction of carboxylic acid and hydrogen peroxide proceeds with the formation of peracid (Fig. 1) [15]. This peracid is consumed in the epoxidation reaction 2. The acid formed in reaction 2 reacts again with the hydrogen peroxide to reform a peracid. The rate-limiting stage of the process is the generation of peracid.

The generation of peracids is accelerated by strong mineral acids, most often by sulfuric acid [8, 16]. The selection of processing parameters so that the epoxidation will proceed faster than the generation of peracid is an important issue. Otherwise, generated peracid may decompose under the reaction conditions and the yield of epoxidation recalculated based on the consumed hydrogen peroxide will be small [15]. The reaction environment contains water, mineral (catalyst), and organic acids, which may cause the decomposition of the epoxy groups, e.g., due to hydrolysis or acylation (Fig. 2) [13, 14, 17].

Various methods can be used to limit the course of these reactions. For this purpose the sulfuric acid should be neutralized or cation exchangers be used instead, e.g., sulfonated styrene–divinylbenzene copolymer or ion-exchange resin [18].

Epoxidation using in situ generated peracetic acid has the greatest technological importance. This method is the most economical; moreover, the separation of acetic acid from the reaction product is easy due to the difference in solubility of epoxidized rapeseed oil and water. On an industrial scale epoxidation with peracetic acid generated in situ is used for epoxidation of soybean oil [15].

Epoxidation with peracids proceeds under milder reaction conditions in comparison with methods using hydroperoxides. Moreover, epoxidation with peracids does not

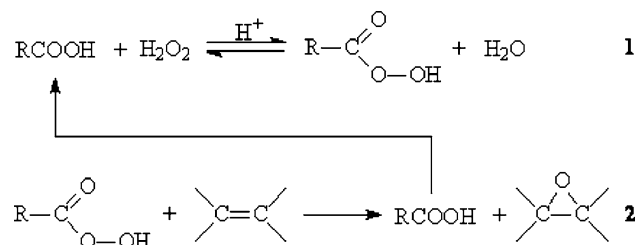


Fig. 1 The main reactions of epoxidation of rapeseed oil with peracids obtained in situ

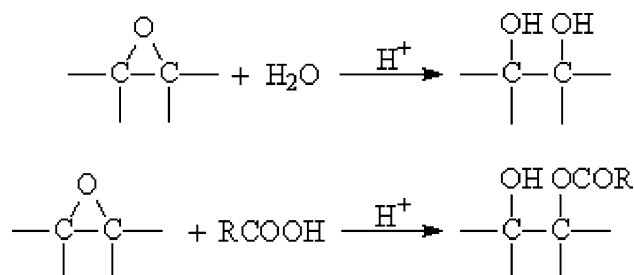


Fig. 2 Side-reactions of the epoxidation process

require the use of a catalyst. Usually, in such reactions, a smaller excess of the unsaturated compound relative to hydrogen peroxide is used for synthesis of the appropriate peracid, and the epoxidation proceeds with higher selectivity.

The advantages of epoxidation with peracids are the low costs of synthesis of the organic peracids, particularly peracetic acid, and the fact that epoxidation with peracids is irreversible (if the acid does not contain admixtures). On the other hand, problems related to this method are associated with the strongly exothermic character of this reaction and the risk of explosion resulting from the necessity of operations with concentrated solutions of peracids. These problems imply the necessity for strict control of temperature and reaction time.

Experimental Procedures

Materials

Rapeseed oil (RO), manufactured by the Fat Industry Co., Warsaw, was used in the studies. The molar mass of oil calculated on the basis of percentage content of carboxylic acids was 882 g/mol, the initial amount of double bonds was $\text{DB} = 0.42$ [$\text{C}=\text{C}/100$ g RO], and the theoretical maximum oxirane oxygen was $\text{OO} = 5.02$ [%/100 g RO]. The following raw materials were used in the syntheses: glacial acetic acid (AA) (99.5 wt%, POCh Gliwice), hydrogen peroxide (30 wt% aqueous solution, POCh Gliwice), and sulfuric acid (Chempur).

Epoxidation Procedure

Epoxidation of the rapeseed oil was carried out with the use of peracetic acid generated in situ as a result of the reaction of 30 wt% solution of hydrogen peroxide and glacial acetic acid. The concentration of hydrogen peroxide was determined before each reaction by iodometric titration. The following parameters were varied during the epoxidation of rapeseed oil: temperature, molar ratio of hydrogen peroxide to rapeseed oil, molar ratio of acetic

acid to rapeseed oil, stirring speed, and reaction time. Rapeseed oil, glacial acetic acid, and concentrated sulfuric acid as a catalyst were placed in a four-neck flask equipped with a thermometer, dropping funnel, stirrer, and reflux. The flask was placed in a water bath whose temperature was controlled by a thermostat and monitored within 0.5 °C. The 30 wt% hydrogen peroxide was added to this solution with a speed enabling a constant reaction temperature to be maintained. In some of the experiments the reaction flask was cooled with water. Depending on the amounts of reagents and other parameters of the process, the introduction of hydrogen peroxide lasted for 10–40 min. After separation of the phases of the reaction mixture, the resulting organic layer was neutralized with 20 wt% sodium hydroxide and washed with distilled water ($5 \times 450 \text{ cm}^3$ water per 0.16 mol RO). Remaining water was removed with anhydrous magnesium sulfate (VI). The conversion of rapeseed oil and the selectivity of transformation to epoxidized oil was calculated on the basis of the determined values of iodine (IN) and epoxy number (EN). The conversion of hydrogen peroxide was calculated after determination of its concentration in the water layer.

The reactions were replicated at least two times.

Analytical Methods

The iodine and epoxy numbers were calculated in accordance with the required standards according to the following equations:

$$\text{IN}_{\text{ae}} = \frac{0.1269(V_1 - V_2)c_{\text{Na}_2\text{S}_2\text{O}_3}}{m_1} \times 100 \times \frac{1}{2A_1}, \quad (1)$$

where IN_{ae} iodine number of RO after epoxidation (mol/100 g RO); 0.1269 mass of iodine correspond to 1 cm^3 of $\text{Na}_2\text{S}_2\text{O}_3$ at $c = 1 \text{ mol/dm}^3$ (g); V_1 volume of $\text{Na}_2\text{S}_2\text{O}_3$ used to titrate blank sample (cm^3); V_2 volume of $\text{Na}_2\text{S}_2\text{O}_3$ used to titrate right sample (cm^3); $c_{\text{Na}_2\text{S}_2\text{O}_3}$ concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution (mol/dm^3); m_1 mass of sample (g); A_1 molecular mass of iodine (g/mol).

$$\text{EN}_{\text{ae}} = \frac{(V_4 - V_3)c_{\text{HClO}_4}100}{1,000m_2} \quad (2)$$

where EN_{ae} epoxy number of RO after epoxidation (mol/100 g RO); V_3 volume of HClO_4 used to titrate blank sample (cm^3); V_4 volume of HClO_4 used to titrate right sample (cm^3); $c_{\text{Na}_2\text{S}_2\text{O}_3}$ concentration of HClO_4 solution (mol/dm^3); m_2 mass of sample (g).

Parameters Characterizing Epoxidation

The conversion of RO, yield of epoxidized RO, and selectivity of transformation to epoxidized RO were

calculated on the basis of the determined values of iodine and the epoxy number, according to the following equations:

$$C_{\text{IN}} = \frac{\text{IN}_{\text{be}} - \text{IN}_{\text{ae}}}{\text{IN}_{\text{be}}} \times 100\%, \quad (3)$$

where C_{IN} conversion of RO calculated from the iodine number; IN_{be} iodine number of RO before epoxidation, 0.314 mol/100 g RO; IN_{ae} iodine number of RO after epoxidation (mol/100 g RO).

$$Y_{\text{EN}} = \frac{\text{EN}_{\text{ae}}}{\text{EN}_{\text{max}}} \times 100\%, \quad (4)$$

where Y_{EN} yield of epoxidized RO calculated from the epoxy number; EN_{ae} epoxy number of RO after epoxidation (mol/100 g RO); EN_{max} epoxy number of RO calculated from the number of unsaturated bonds; $\text{EN}_{\text{max}} = \text{IN}_{\text{be}} = 0.314 \text{ mol/100 g RO}$.

$$S_{\text{EN/IN}} = \frac{\text{EN}_{\text{ae}}}{\text{IN}_{\text{be}} - \text{IN}_{\text{ae}}} \times 100\%, \quad (5)$$

where $S_{\text{EN/IN}}$ selectivity of the transformation to epoxidized RO calculated from the epoxy number and iodine number.

Moreover, the conversion of hydrogen peroxide was calculated in accordance with the required standards (iodometric titration), according to the following equation:

$$C_{\text{H}_2\text{O}_2} = \frac{m_{\text{be}} - m_{\text{ae}}}{m_{\text{be}}} \times 100\%, \quad (6)$$

where $C_{\text{H}_2\text{O}_2}$ conversion of hydrogen peroxide; m_{be} mass of H_2O_2 before epoxidation (g); m_{ae} mass of H_2O_2 after epoxidation (g).

Instrumental Methods

Table 1 presents the fatty-acid composition of the RO that was epoxidized, determined according to the standard procedure for oils and fats [19]. The concentration of methyl esters was determined chromatographically using a Thermoquest GC 8000^{TOP} instrument fitted with a flame ionization detector (FID). All measurements were carried out isothermally at 373 K. A capillary column DB-WAX (J&W) (dimensions: $30 \text{ m} \times 0.32 \text{ mm} \times 0.5 \mu\text{m}$) was used. Helium was used as the carrier gas.

The epoxidized rapeseed oils were analyzed by Fourier-transform infrared (FT-IR) and ^1H nuclear magnetic resonance (NMR) spectroscopy. The FT-IR spectra were obtained by using NICOLET 380 spectrophotometer. Samples were spread as a thin film on KBr plates. A transparent film of the product showed the following FT-IR spectral bands (Fig. 3), $\nu \text{ cm}^{-1}$: 2,954 s (CH_3 asym stretch), 2,925 vs (CH_2 asym stretch), 2,870 s (CH_3 sym stretch), 2,854 vs (CH_2 sym stretch), 1,745 vs ($\text{C}=\text{O}$), 1,465

Table 1 Content of fatty acids in the rapeseed (RO) oil used

A ^a :B ^b	Fatty acid composition of the RO		wt% ^c
14:0	Myristic	CH ₃ (CH ₂) ₁₂ COOH	0.1
16:0	Palmitic	CH ₃ (CH ₂) ₁₄ COOH	4.5
16:1	Oleopalmitic (9 <i>cis</i>)	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOH	0.4
18:0	Stearic	CH ₃ (CH ₂) ₁₆ COOH	2.1
18:1	Oleic (9 <i>cis</i>)	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	64.5
18:2	Linoleic (9 <i>cis</i> , 12 <i>cis</i>)	CH ₃ (CH ₂) ₃ (CH ₂ CH=CH) ₂ (CH ₂) ₇ COOH	18.3
18:3	Linolenic (9 <i>cis</i> , 12 <i>cis</i> , 15 <i>cis</i>)	CH ₃ (CH ₂ CH=CH) ₃ (CH ₂) ₇ COOH	6.8
20:0	Arachidic	CH ₃ (CH ₂) ₁₈ COOH	0.8
20:1	Gadoleic (9 <i>cis</i>)	CH ₃ (CH ₂) ₉ CH=CH(CH ₂) ₇ COOH	1.3
22:0	Behenic	CH ₃ (CH ₂) ₂₀ COOH	0.4
22:1	Erucic (13 <i>cis</i>)	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOH	0.8

Initial amount of double bonds^d, DB = 0.42 [C=C/100 g RO]
 Theoretical maximum oxirane oxygen^e, OO = 5.02 [%/100 g RO]

^a Number of carbon atoms

^b Number of unsaturated bonds

^c International standard PN-EN ISO 5508

^d Calculated as DB = 100y/M, where y is the number of double bonds in the molecule and M is the molar mass of oil (882 g)

^e Calculated as OO = [IN_{be}/(100 + (IN_{be}/A_O))]100A_O, where IN_{be} = 0.314 mol/100 g RO is the iodine number of RO before epoxidation and A_O = 16 g/mol is the molecular mass of oxygen [1, 2]

m-s (–CH₂– deform), 1,376 m (CH₃ deform), 1,240 m-s (O–C=O), 1,162 s (–C–CH–O–), 1,097 (CH₂O stretch), 963 and 901 m (C–O–C epoxide stretch), 723 m (CH₂ wag). In contrast, the initial oil gave FT-IR bands at 3,006 w-m (H–C=C), 2,954 s (CH₃ asym stretch), 2,923 vs (CH₂ asym stretch), 2,870 s (CH₃ sym stretch), 2,854 s-vs (CH₂ sym stretch), 1,745 vs (C=O), 1,654 w (C=C puckering), 1,465 m (–CH₂– deform), 1,376 w-m (CH₃ deform), 1,238 m-s (O–C=O–C–), 1,162 s (–CH–O–C–), 1,118 m-s, 1,097 w (CH₂O stretch), 723 m (CH₂ wag) cm^{–1}. The formation of epoxy groups is reflected by the doublet at 963 and 901 cm^{–1}, the consumption of double bonds is indicated by the decrease of the peaks at 3,006 and 1,654 cm^{–1}.

The ¹H NMR spectrum was obtained using Bruker DPX-400 in CDCl₃ with tetramethylsilane Si(CH₃)₄ (TMS) as internal standard. ¹H NMR (CDCl₃) (Fig. 4) δ: olefinic protons –CH=CH– of the unsaturated fatty acids at δ 5.35 ppm, methine proton of –CH₂CHCH₂– glycerol backbone at δ 5.25 ppm, methylene proton of –CH₂CHCH₂– glycerol backbone at δ 4.12–4.28 ppm, –CH– protons of epoxy ring at δ 3.37 ppm, α–CH₂ to epoxy group at δ 2.85–2.96 ppm, bis-allylic methylene groups –CH₂– of unepoxidized rapeseed oil at δ 2.7–2.8 ppm, α–CH₂ to >C=O at δ 2.29–2.32 ppm, allylic methylene groups –CH₂– of unepoxidized rapeseed oil at δ 2.0–2.1 ppm, β–CH₂ to >C=O at δ 1.6 ppm, β–CH₂ to epoxy group at δ 1.55 ppm, saturated methylene groups at δ 1.25–1.3 ppm, and terminal –CH₃ groups at δ

0.86–0.88 ppm region. In ¹³C NMR spectrum δ: carbonyl carbon >C=O of triacylglycerol at δ 172.84–173.25 ppm, carbons of –CH₂CHCH₂– glycerol backbone at δ 68.87 ppm, carbons of –CH₂CHCH₂– glycerol backbone at δ 62.10 ppm, epoxy methine carbons at δ 57.23 ppm, α–CH₂ to –CHOCH– at δ 34.03 ppm, α–CH₂ to >C=O at δ 31.92 ppm, saturated methylene groups at δ 27.17–29.78 ppm, β–CH₂ to >C=O at δ 24.85 ppm, –CH₂–CH₃ at 22.69, and terminal –CH₃ groups at δ 14.13 ppm. This is accordance with literature data [20].

Results and Discussion

The influence of temperature (30–75 °C), molar ratio of H₂O₂/RO (4.7:1–11.0:1), molar ratio of AA/RO (0.63:1–2.06:1), stirring speed (100–900 rpm), and reaction time (2.5–7 h) were investigated in this study. The course of epoxidation was represented by changes in the iodine and epoxy numbers with the parameters under study.

Influence of Temperature on Epoxidation of Rapeseed Oil

In order to establish the influence of temperature on the course of epoxidation of rapeseed oil, syntheses were carried out at temperatures of 30, 45, 60, and 75 °C. Based on literature data [1, 2, 15] and preliminary investigations, the following initial conditions were used: sulfuric acid

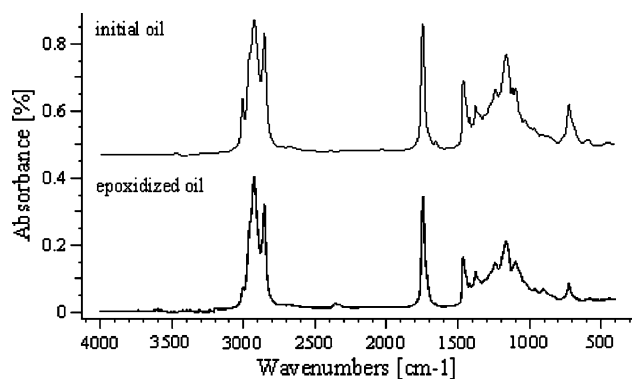


Fig. 3 FT-IR spectra of initial and epoxidized rapeseed oil. Samples were spread as a thin film on KBr plates

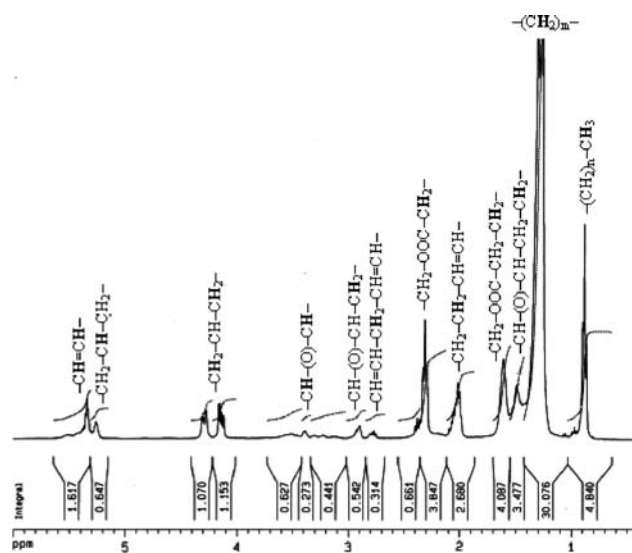


Fig. 4 Proton NMR of epoxidized rapeseed oil with proton area integration. Spectra were obtained in CDCl_3 with TMS as internal standard

catalyst, 2 wt% in relation to the epoxidizing mixture; stirring speed, 700 rpm; reaction time, 4 h; molar ratio of reagents $\text{RO}/\text{H}_2\text{O}_2/\text{AA} = 1:4.7:1.55$. On the basis of obtained results (Fig. 5) it was found that the temperature of 60 °C was the most advantageous for epoxidation of rapeseed oil with peracetic acid generated in situ. The temperature of 60 °C was chosen with regard to obtaining a low iodine number and high epoxy number in comparison with syntheses carried out at other temperatures. Elevation of the temperature from 30 to 60 °C caused a decrease of the iodine number, although the value of the iodine number was constant above 60 °C. Thus, the number of unsaturated bonds in the reaction product does not change. The value of the epoxy number rapidly decreases above 60 °C. The generated epoxy groups undergo both hydrolysis with the formation of glycols and acetylation, resulting in the formation of acetates and diacetates of rapeseed oil.

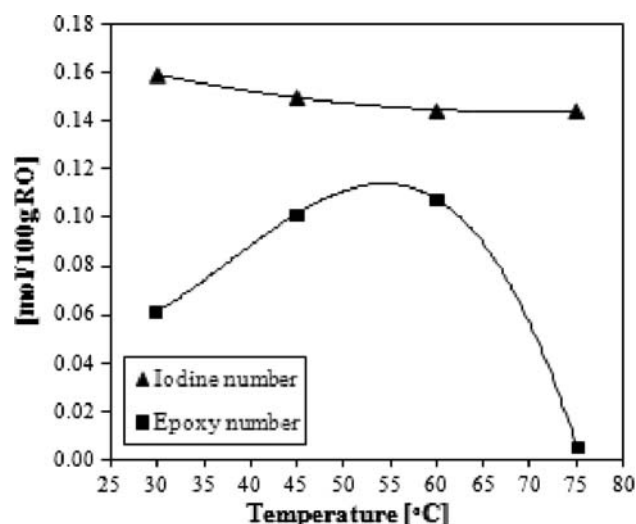


Fig. 5 Influence of temperature on the iodine and epoxy numbers of epoxidized rapeseed oil

Influence of Molar Ratio of Hydrogen Peroxide to Rapeseed Oil

In order to determine the influence of the molar ratio of $\text{H}_2\text{O}_2/\text{RO}$ on the course of the epoxidation process, syntheses were carried out at molar ratios of 4.7:1, 6.3:1, 7.9:1, 9.5:1, and 11.0:1. Temperature of 60 °C and molar ratio of $\text{AA}/\text{RO} = 1.55:1$ were fixed in these studies. The remaining parameters were the same as during the studies on the influence of the temperature. On the basis of changes of the iodine and epoxy number (Fig. 6) it was found that the molar ratio $\text{H}_2\text{O}_2/\text{RO} = 9.5:1$ was the most advantageous. Under these conditions the highest epoxy number and one of the lowest iodine number were achieved.

Influence of Molar Ratio of Acetic Acid to Rapeseed Oil

The influence of the molar ratio of AA/RO was studied for the values 0.63:1, 1.12:1, 1.55:1, and 2.06:1. Temperature of 60 °C and molar ratio $\text{H}_2\text{O}_2/\text{RO} = 9.5:1$ were fixed in these studies. The remaining parameters were the same as in previously performed experiments. On the basis of obtained results (Fig. 7), it was found that the molar ratio of $\text{AA}/\text{RO} = 1.12:1$ was the most advantageous for the preparation of epoxidized rapeseed oil. Under these conditions the selectivity of transformation of the unsaturated bonds in RO to the epoxy groups was the highest.

Influence of Stirring Speed

In order to study this parameter, syntheses were carried out at stirring speeds of 100, 300, 500, 700, and 900 rpm. In

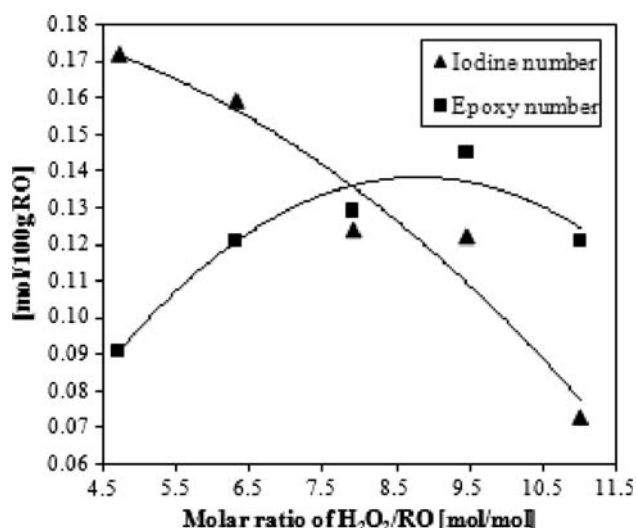


Fig. 6 Influence of H₂O₂/RO on the iodine and epoxy numbers of epoxidized rapeseed oil

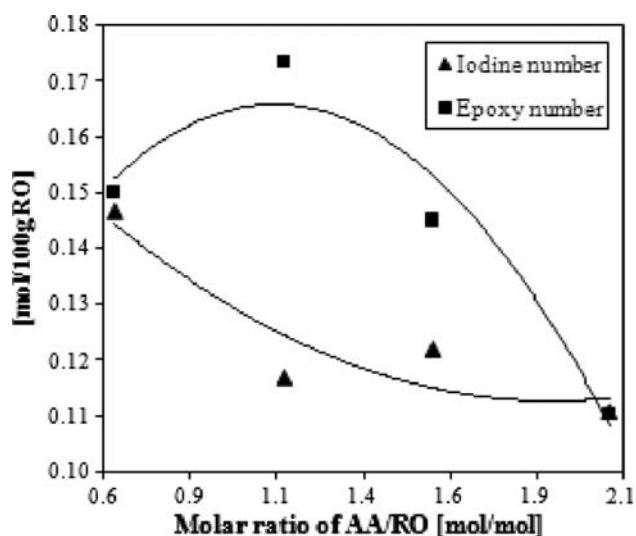


Fig. 7 Influence of AA/RO on the iodine and epoxy numbers of epoxidized rapeseed oil

these studies, the following parameters were fixed: temperature of 60 °C, reaction time of 4 h, and molar ratio of reagents of RO/H₂O₂/AA = 1:9.5:1.12. Similarly, the amount of sulfuric acid used was 2 wt% in relation to the epoxidizing mixture. On the basis of the changes of the iodine and epoxy numbers (Fig. 8), it was found that the highest conversion of rapeseed oil to the epoxy compounds was achieved at stirring speed of 500 rpm. The value of the iodine number underwent insignificant changes when the stirring rate was varied in the range 100–500 rpm. The increase of iodine number after exceeding 500 rpm demonstrates that epoxidation proceeded slowly for those conditions, and a concurrent decrease of epoxy number took place. This is a result of quick-acting hydration,

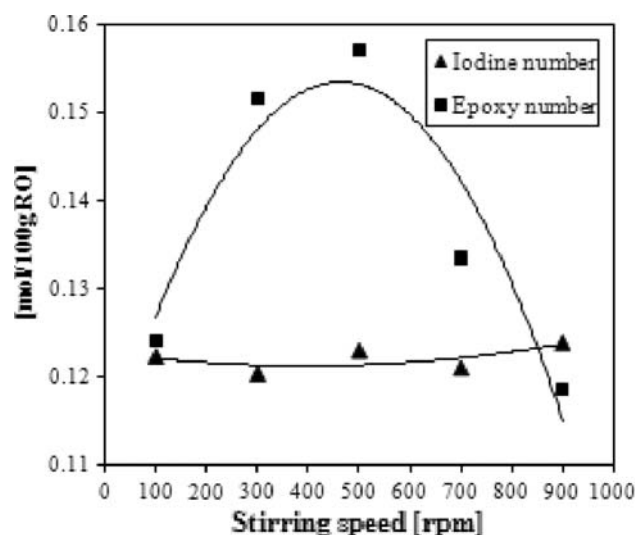


Fig. 8 Influence of stirring speed on the iodine and epoxy numbers of epoxidized rapeseed oil

esterification, and rearrangement of the oxirane groups of the epoxidized oil.

Influence of Reaction Time

In order to investigate the influence of reaction time on the course of epoxidation, syntheses were carried out for 2.5, 4, 5.5, and 7 h. The following parameters were fixed in these studies: temperature of 60 °C, molar ratio of RO/H₂O₂/AA = 1:9.5:1.12, and stirring speed 500 rpm. Sulfuric acid was used as a catalyst in the amount of 2 wt% in relation to the epoxidizing mixture. When the process was carried out under these conditions and the reaction time was changed

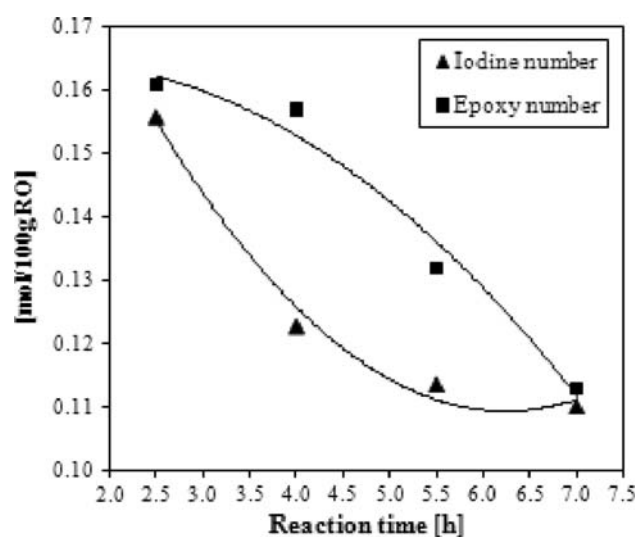


Fig. 9 Influence of reaction time on the iodine and epoxy numbers of epoxidized rapeseed oil

Table 2 Parameters characterizing epoxidation of rapeseed oil under the most advantageous conditions found

Initial amount of RO (g)	141.73
Initial amount of H ₂ O ₂ (g)	51
Initial amount of AA (g)	10.5
Initial amount of catalyst (H ₂ SO ₄) (g)	3.28
Temperature of reaction (°C)	60
Stirring speed (rpm)	500
Time of reaction (h)	4
Iodine number (IN _{ae}), mol/100 g RO (mol/100 g tested product)	0.123
Epoxy number (EN _{ae}), mol/100 g RO (mol/100 g tested product)	0.157
Conversion of RO calculated from IN (C _{IN}) (%)	60.8
Yield of RO calculated from EN (Y _{EN}) (%)	50.0
Selectivity of transformation to epoxidized RO calculated from EN and IN (S _{EN/IN}) (%)	82.2
Conversion of hydrogen peroxide (C _{H₂O₂})(%)	100

(Fig. 9) it could be seen that the highest values of the epoxy number (EN = 0.16 mol/100 g RO) were achieved after 2.5–4 h, whereas the lowest values of the iodine number (IN = 0.114 mol/100 g RO) were obtained after 4.5–5.5 h. Hence, the reaction time of 4 h is the most advantageous for preparation of epoxidized rapeseed oil.

The most advantageous parameters of epoxidation of rapeseed oil with peracetic acid generated in situ were as follows: temperature of 60 °C, molar ratio of reagents RO/H₂O₂/AA = 1:9.5:1.12, stirring speed of 500 rpm, and reaction time of 4 h. Under these conditions, complete conversion of hydrogen peroxide was achieved. The value of the epoxy number is relatively high (EN = 0.157 mol/100 g RO), the iodine number reaches one of its lowest values (IN = 0.123 mol/100 g RO), and the other values characterizing the epoxidation under the most advantageous conditions are satisfactory. These values are presented in Table 2.

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