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KINETICS OF SOYBEAN OIL EPOXIDATION WITH PERACETIC ACID FORMED *IN SITU* IN THE PRESENCE OF AN ION EXCHANGE RESIN: PSEUDO-HOMOGENEOUS MODEL

Article Highlights

- *In situ* epoxidation of soybean oil in the presence of an ion exchange resin is studied
- Occurrence of the reactions during the incremental addition of the reactant is considered
- Pseudo-homogeneous kinetic model is applied
- Temperature dependency of kinetic parameters was determined
- The kinetic model fits well the experimental data

Abstract

A kinetic model was proposed for the epoxidation of vegetable oils with peracetic acid formed *in situ* from acetic acid and hydrogen peroxide in the presence of an acidic ion exchange resin as a catalyst. The model is pseudo-homogeneous with respect to the catalyst. Besides the main reactions of peracetic acid and epoxy ring formation, the model takes into account the side reaction of epoxy ring opening with acetic acid. The partitioning of acetic acid and peracetic acid between the aqueous and organic phases and the change in the phases' volumes during the process were considered. The temperature dependency of the apparent reaction rate coefficients is described by a reparameterized Arrhenius equation. The constants in the proposed model were estimated by fitting the experimental data obtained for the epoxidations of soybean oil conducted under defined reaction conditions. The highest epoxy yield of 87.73% was obtained at 338 K when the mole ratio of oil unsaturation:acetic acid:hydrogen peroxide was 1:0.5:1.35 and when the amount of the catalyst Amberlite IR-120H was 4.04 wt.% of oil. Compared to the other reported pseudo-homogeneous models, the model proposed in this study better correlates the change of double bond and epoxy group contents during the epoxidation process.

Keywords: soybean oil, epoxidation, peracetic acid, ion exchange resin, kinetics.

The epoxidation of soybean oil is commercially important since the obtained epoxide is used as polymer stabilizer and plasticizer, paint and coating component, and lubricant. It is also an intermediate for the production of glycols, alkanolamines, polyols and polymers [1,2]. Besides performic acid, peracetic acid is a common oxidizing agent for the epoxidation of vegetable oils [3,4]. Because of instability and safety

issues, peracetic acid is usually produced *in situ* through the acid-catalyzed peroxidation of acetic acid with hydrogen peroxide in an aqueous solution [5]. The epoxidation of vegetable oil double bonds with *in situ* generated peracetic acid also involves an uncatalyzed reaction of epoxy ring formation in the organic phase, and a few side reactions of acid-catalyzed epoxy ring opening. Some soluble mineral acids, like sulphuric acid [1,5-8], and acidic ion exchange resins can be applied as catalysts for this process [3,9-20]. The stability of epoxy ring and, thus, the selectivity of the process, are higher when an ion exchange resin is used as the catalyst compared to the mineral acid [21]. Among the sulphonated ion

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exchange resins investigated, the highest conversion and selectivity, which were almost constant for five reuses, were obtained with Amberlite IR-120H [20]. The volume of this resin increases about 43% in water and about 8% in glacial acetic acid [22]. The swelling occurs because of the absorption and adsorption of solvent molecules on the sulphonated groups inside the catalyst pores [23,24].

Since the epoxidation of vegetable oils is significantly influenced by the reaction conditions, such as molar ratio of reactants, type of the catalyst, catalyst concentration, temperature, stirring speed, and presence of the solvent, it is necessary to establish an appropriate kinetic model for its optimization. In some studies, the effect of reaction conditions on the *in situ* epoxidation of vegetable oils has been investigated [9,10,18,19], whereas in other studies, the process kinetics was also considered [1,3-6,11-17,25-33].

When the ion exchange resin is used as the catalyst for *in situ* generation of peracetic acid, the reaction system for the epoxidation of vegetable oils is three-phase liquid-liquid-solid (organic-aqueous-solid). For rigorous mathematical modeling of such a system, the intrinsic kinetics, the mass diffusion, and the partitioning of the components between the phases have to be considered. Up to the present, this reaction system has been described with the pseudo-homogeneous [3,16,17] or pseudo-two-phase (liquid-solid) [11-15,33] models. Both types of models took into consideration the main reactions of peracetic acid and epoxy compound formation, as well as some of the side reactions of epoxy ring opening that may occur during the process. The proposed pseudo-homogeneous models were developed by assuming that the ion exchange resin is dissolved in the reaction mixture. The pseudo-two-phase models were established by applying Eley-Rideal and Langmuir-Hinshelwood-Hougen-Watson approaches to the reaction of peracetic acid formation. Although a few authors investigated the partitioning of acetic acid between the aqueous and organic phases separately from the epoxidation process [34-36], this phenomenon was not considered in the reported kinetic models.

Because of the aforementioned, the objective of this study was to develop a kinetic model for the epoxidation of vegetable oils with peracetic acid formed *in situ* in the presence of an acidic ion exchange resin which takes into consideration the partitioning of acetic acid and peracetic acid between the organic and aqueous phases, as well as the change in the volume of these two phases. The pseudo-homogeneity of the catalyst with respect to

the aqueous phase is assumed. Besides the main reactions, the model describes the epoxy ring opening reaction with acetic acid. The model parameters were determined by fitting the experimental data obtained for the epoxidation of soybean oil. The proposed model was compared with the pseudo-homogeneous model reported in the literature.

EXPERIMENTAL

Materials

Soybean oil was kindly provided by Dijamant (Zrenjanin, R. Serbia). The acid form of sulphonated polystyrene-type ion exchange resin Amberlite IR-120H from Rohm&Hass Co. (Philadelphia, PA, USA) was used as the catalyst. Glacial acetic acid, 30% aqueous hydrogen peroxide solution and hydrobromic acid were purchased from J.T. Baker (Deventer, Netherlands). Alfapanon (Novi Sad, Serbia) was a supplier of the aqueous solutions of sodium hydroxide (0.1 N) and sodium thiosulfate (0.1 N). Iodine (p.a.) and bromine (p.a.) were purchased from Centrohem (Stara Pazova, R. Serbia). Potassium iodide (extra pure), chloroform (min 98.5%), benzene (min 99.8%), potassium hydrogen phthalate (min 99.0%) were bought from LachNer (Neratovice, Czech Republic). Hydrogen bromide solution (33.0%) in acetic acid and crystal violet were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Epoxidation procedure

The epoxidation of soybean oil in bulk was carried out with peracetic acid formed *in situ* according to the method reported in the literature [15]. Soybean oil with an initial iodine number (I_N) of 128.62, which corresponds to 0.5067 mol of double bond per 100 g of oil, was used for the syntheses. The molar ratio of soybean oil unsaturation:acetic acid:hydrogen peroxide was approximately 1:0.5:1.35 for all runs. The oil (approximately 150 g) was mixed with an appropriate mass of glacial acetic acid before being poured into a 1000 mL three-neck glass reactor equipped with a magnetic stirrer, a thermometer, a reflux condenser and an addition funnel. The reactor was placed in a water bath. Amberlite IR-120H ion exchange resin was introduced to the reactor before the reactants. The amount of catalyst was 1.98–7.86 wt.% of oil. Subsequently, the 30% aqueous hydrogen peroxide solution was added drop-wise to the reaction mixture at a constant rate within 40 to 65 min. During the addition, the temperature of the mixture was maintained at 323 or 338 K with fluctuation of less than ± 1 K. Further, where applicable, the tem-

perature was increased at a uniform rate to the desired level and maintained at 323, 338, 348 or 353 K within ± 1 K. The temperature of the reaction mixture was controlled by changing the water bath temperature. The fine dispersion of oil in the reaction mixture was achieved with the uniform agitation using a PTFE-coated cylindrical stirring bar (35 mm \times 6 mm) under constant stirring speeds of 900, 1000 or 1100 rpm. The beginning of the addition of hydrogen peroxide solution was considered to be the “zero time” of the process. The progress of epoxidation was followed by withdrawing 8 mL samples of the reaction mixture at defined time intervals. The first sample was taken immediately after the completion of the hydrogen peroxide addition, whereas the second immediately after raising the reaction temperature, where applicable. The others were collected at about 30, 60 or 120 min intervals. After cooling and centrifugation of the sample, the separated organic phase was washed with water (323 K) until pH 7. Water was evaporated from the sample at 333 K under the vacuum. The evaporation lasted a minimum of 1 h. The samples were then analyzed to determine the iodine number (*IN*) and epoxy oxygen content (*EO*). The infrared analysis of the samples was also provided.

Analyses

The iodine number and epoxy oxygen content were measured in triplicate according to the Hanus method and the standard HBr-acetic acid method, respectively [37]. Using attenuated total reflectance (ATR) FT-IR spectroscopy, the spectra were recorded by Thermo Finnigan's Nicolet 5700 FTIR spectro-

meter in the range of 4000–400 cm^{-1} by accumulating 32 scans at a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Soybean oil epoxidation

Nine epoxidation runs were conducted using soybean oil and peracetic acid formed *in situ* from acetic acid and 30% hydrogen peroxide aqueous solution in the presence of Amberlite IR-120H. The mole ratio of soybean oil unsaturation:acetic acid:hydrogen peroxide was approximately 1:0.5:1.35 for all runs. The reaction conditions and some of the results are summarized in Table 1. Residual iodine number (*IN*), conversion of double bond (*X*), relative epoxy yield (*REY*) and selectivity (*SE*) are presented only for the content of epoxy oxygen (*EO_t*) reached in each run after defined period of time (*t*).

The disappearance of double bonds and formation of epoxy groups during the runs were monitored on the basis of the FT-IR spectrum of the samples, as illustrated in Figure 1. The changes in the intensities of epoxy group doublet band (with maxima at 823 and 845 cm^{-1}) and double bond band (at 3007 cm^{-1}) were qualitatively analyzed.

The progress of the epoxidation was quantified by determining the iodine number (*IN*) and epoxy oxygen content (*EO*) for all samples withdrawn during the run. The values are presented as points in Figures 2–4.

There are detailed discussions in our previous studies [15,16] and in other studies [3,9–14,17] on the

Table 1. Reaction conditions and the residual iodine number (*IN*), conversion of double bond (*X*), relative epoxy yield (*REY*) and selectivity (*SE*) for content of epoxy oxygen (*EO_t*) reached after reaction time (*t*) in each run of the epoxidation of soybean oil (*SO*)^(a) in bulk with peracetic acid formed *in situ* from 30% hydrogen peroxide aqueous solution (aqHP) and acetic acid (*A*) in the presence of Amberlite IR-120H as the catalyst when the molar ratio of soybean oil unsaturation:acetic acid:hydrogen peroxide was approximately 1:0.5:1.35; initial iodine number $IN_0 = 128.62$ corresponds to theoretical epoxy oxygen content (EO_{th}) of 7.50% where $EO_{th} = 100\{(IN_0/2A_0)/[100+(IN_0/2A_0)A_0]\}A_0$

Run	Measured mass, g			Amberlite ^a wt. %	Stirring speed rpm	Temperature, K		<i>t</i> min	<i>EO_t</i> %	<i>IN</i> ^b	<i>X</i> ^c %	<i>REY</i> ^d %	<i>SE</i> ^e
	SO	A	aqHP			H ₂ O ₂ addition	Reaction						
1	150.00	22.82	116.83	3.92 [4.21]	1000	323	323	630	4.65	44.2	65.64	62.00	0.94
2	150.00	22.82	116.83	3.92 [4.21]	1000	323	338	645	6.25	7.45	94.21	83.33	0.88
3	150.00	22.82	116.83	3.92 [4.21]	1000	323	348	635	6.22	1.73	98.65	82.93	0.84
4	150.00	22.82	116.83	3.92 [4.21]	1000	323	353	470	6.08	4.45	96.54	81.06	0.84
5	145.44	21.66	115.90	4.04 [4.27]	1100	338	338	625	6.58	1.99	98.45	87.73	0.89
6	150.23	22.81	109.46	3.91 [4.45]	1000	338	338	480	6.45	7.22	94.39	86.00	0.91
7	145.50	21.91	117.02	4.04 [4.23]	900	338	338	615	6.40	2.71	97.89	85.33	0.87
8	148.32	21.84	112.56	1.98 [2.19]	1100	323	353	590	6.37	2.87	97.77	84.93	0.87
9	149.82	21.57	114.53	7.86 [8.65]	1100	323	323	630	5.51	22.63	82.41	73.46	0.89

^aCatalyst concentration is expressed in percentage of soybean oil weight; value given in square brackets is percentage of catalyst in respect to acetic acid and 30% hydrogen peroxide weight; ^bresidual iodine number, *IN*; ^cdouble bond conversion, $X = 100(IN_0 - IN)/IN_0$; ^drelative epoxy yield, $REY = 100EO_t/EO_{th}$; ^eselectivity, $SE = EO_t/IN_0/[EO_{th}(IN_0 - IN)]$

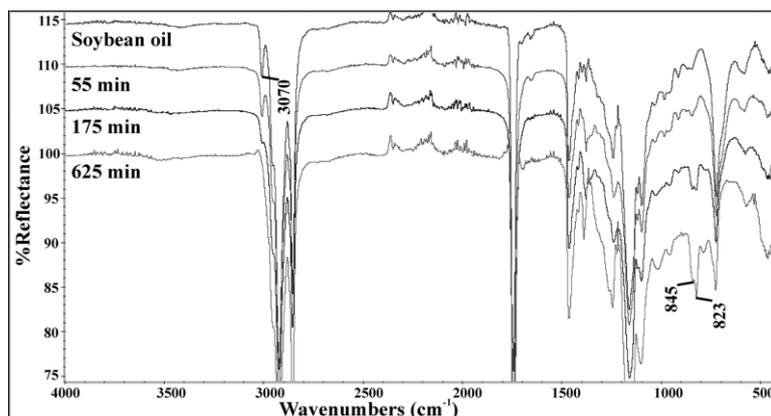


Figure 1. FT-IR spectra of soybean oil and samples taken after 55, 175 and 625 min of soybean oil epoxidation in bulk with peracetic acid formed in situ from acetic acid and hydrogen peroxide in the presence of amberlite IR-120H in the amount of 4.04 wt. % of oil at 338 K and 1100 rpm, when the mole ratio of double bond in oil:acetic acid:hydrogen peroxide was approximately 1:0.5:1.35.

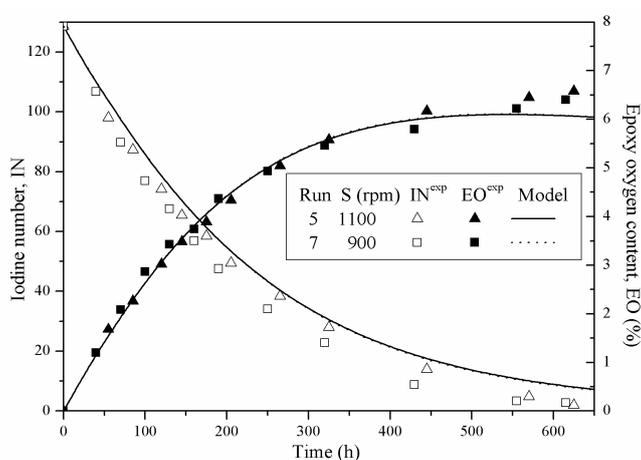


Figure 2. Time dependency of experimentally determined (points) and calculated (curves) iodine number (IN) and epoxy oxygen content (EO) for the epoxidation of soybean oil in bulk with peracetic acid generated in situ in the presence of Amberlite IR-120H in the amount of approximately 4.0 wt. % of oil at 338 K, when the stirring speeds (S) were 900 and 1100 rpm and when the mole ratio of double bond in oil:acetic acid:30 wt. % hydrogen peroxide was approximately 1:0.5:1.35.

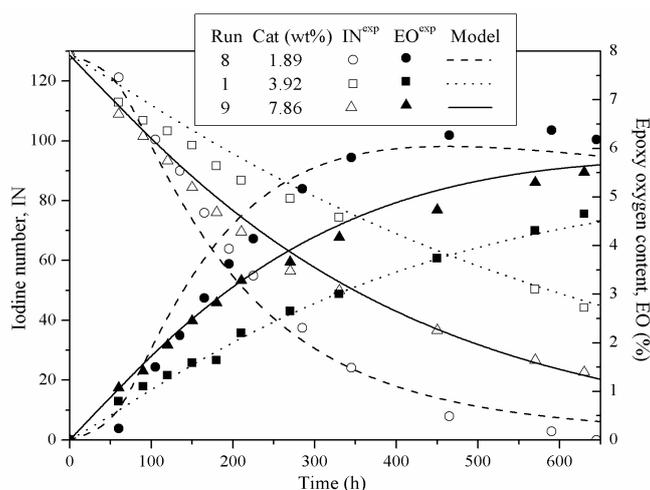


Figure 3. Time dependency of experimentally determined (points) and calculated (curves) iodine number (IN) and epoxy oxygen content (EO) for the epoxidation of soybean oil in bulk with peracetic acid generated in situ in the presence of Amberlite IR-120H in the amount of 1.98, 3.92 and 7.86 wt. % of oil at 323 (Runs 1 and 9) or 353 K (Run 8), when the mole ratio of double bond in oil:acetic acid:30 wt. % hydrogen peroxide was approximately 1:0.5:1.35.

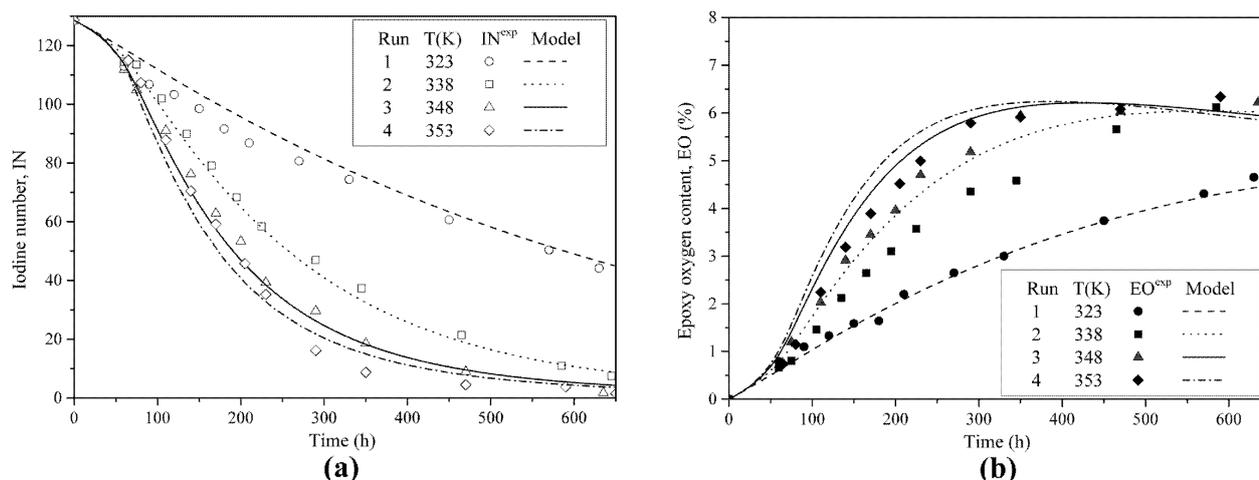


Figure 4. Time dependency of experimentally determined (points) and calculated (curves): a) iodine number (IN) and b) epoxy oxygen content (EO), for the epoxidation of soybean oil in bulk with peracetic acid generated in situ in the presence of Amberlite IR-120H in the amount of 3.92 wt.% of oil at 323, 338, 348 and 353 K and 1000 rpm, when the mole ratio of double bond in oil:acetic acid:30 wt.% hydrogen peroxide was approximately 1:0.5:1.35.

influence of the reaction conditions on the conversion of double bond, relative epoxy yield, and selectivity for the *in situ* epoxidation of vegetable oils with peracetic acid in the presence of the ion exchange resin. This study discusses the results obtained for the *in situ* epoxidation of soybean oil.

The stoichiometric ratio of hydrogen peroxide to vegetable oil unsaturation is 1:1. However, this oxygen agent is usually applied in excess for the epoxidation of vegetable oils [3,9-18]. The mole ratio of hydrogen peroxide to double bond was studied in the range from 0.8 to 3 for various oils [3,9-18]. The significant increase in the rate of epoxy ring formation was observed with an increase in molar ratio from 0.8 to 1.5 [9,12-14] or 2 [10,11]. With a further increase in molar ratio, there was no appreciable decrease of the residual iodine number or change of the epoxy oxygen content [9-14]. Also, when a mole ratio higher than 1.5 was applied, a higher rate of the epoxy ring opening reactions was observed [3,9,10]. Additionally, the excess of hydrogen peroxide solution in the reaction system decreases the concentration of acetic acid as the other reactant in the reaction of peracetic acid formation. Hence, a hydrogen peroxide to vegetable oil unsaturation molar ratio of about 1.35 was chosen for this study.

The stirring speed influences the external mass transfer in the multiphase reaction systems. To reduce the mass transfer resistance, adequate mixing has to be achieved. Under a particular stirring speed, the intensity of mixing also depends upon the type and design of a stirrer [18]. At higher stirring speeds, the mass transfer resistance is lower. Consequently, the rate of the epoxidation should be higher. How-

ever, no significant influence on the double bond conversion and relative epoxy yield was observed when the stirring speed changed from 900 to 1100 rpm under the conditions applied in this study (Figure 2).

The reported amounts of catalyst for the epoxidation of vegetable oils vary from 1.28 to 25 wt.% of oil [3,9-18]. The quantity of Amberlite IR-120H used in this study was 1.98-7.86 wt.% of oil. To ensure good mixing of the reaction mixture, such low amounts of the catalyst were chosen. As concluded in most papers, when a higher amount of the catalyst was used, an increase in the double bond conversion and epoxy yield was observed. At the same time, the selectivity of the process was reduced with an increase in the catalyst load (Table 1, runs 1 and 9). This was the consequence of the promotion of acid-catalyzed epoxy ring opening reactions. Figure 3 shows the change in iodine number and epoxy oxygen content over time for the epoxidations of soybean oil performed under different catalyst concentrations. It should be noted that the reaction temperature of the run with the lowest catalyst loading was higher than the temperature for the other two runs.

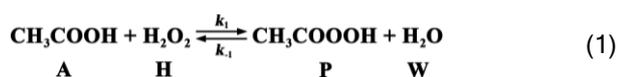
The temperature of the process should be adjusted to increase the rate of the peracetic acid formation and epoxidation reaction, but not to compromise the stability of the epoxy ring. For the epoxidations of different vegetable oils, the temperatures varied from 303 to 363 K [3,9-17]. In order to determine the dependency of the Arrhenius type model parameters from temperature, the epoxidations of soybean oil were carried out at 323, 338, 348 and 353 K in this study. The reaction temperatures were the same or higher than the temperature at which the

hydrogen peroxide solution was added into the reaction mixture. The addition was performed gradually to avoid an increase in temperature due to the exothermic effect of the reaction of peracetic acid formation. An increase in the reaction rates with an increase in the reaction temperature was observed (Figure 4a and b). Consequently, the reaction time for achieving the same epoxy yield was shortened.

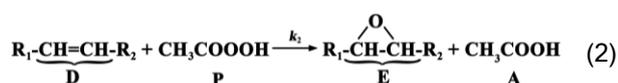
The highest yield of epoxide of 87.73% with almost complete conversion of double bonds of 98.45% was achieved after 625 min, when the temperature of the hydrogen peroxide solution addition was the same as desired reaction temperature of 338 K. The amount of the catalyst was only 4.04 wt.% of oil. The selectivity of double bond conversion to epoxide of 0.89 and the residual unsaturation of epoxidized soybean oil of 1.99 imply good quality of the obtained product (Table 1).

Kinetic model

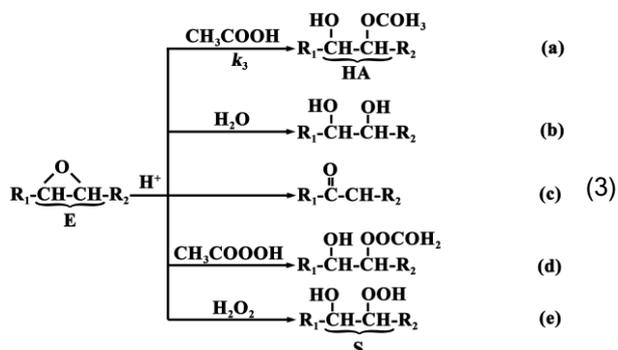
The epoxidation of soybean oil involves an acid-catalyzed reaction of the peracetic acid (P) and water (W) formation from acetic acid (A) and hydrogen peroxide (H):



followed by an un-catalyzed reaction of the double bond (D) conversion into the epoxy ring (E):



Among a few acid-catalyzed side reactions of epoxy ring cleavage (Eqs. (3a)-(3e)), the most likely is the reaction with acetic acid that leads to the formation of hydroxy acetate (HA), Eq. (3a) [38]:



In this three-phase organic-aqueous-solid reaction system, the catalyst Amberlite IR-120H swells due to its sorption affinity towards the polar components. It can be assumed that the swelling of the resin is completed already at the beginning and that the swelling

degree is constant during the epoxidation. Because of the preferential sorption of some components over the others, the concentrations of the components differ in the aqueous bulk phase and inside the catalyst pores [23,24]. The proceeding of the reactions causes the mass transfer phenomena across the organic-aqueous interface, across the aqueous-solid interface, and through the resin pores. In Figure 5a, the system phases with the possible reactions and mass transfer of the components across the reaction system are schematically presented.

Acetic acid and hydrogen peroxide diffuse from the aqueous bulk phase to the catalyst external surface and further into the catalyst pores, in both cases, to reach the active sites where they react. The products of the reaction, peracetic acid and water, migrate to the aqueous phase. As a consequence of the reaction, a concentration gradient of the components exists inside the catalyst pores. From the aqueous phase, the peracetic acid diffuses into the organic bulk phase where it epoxidizes the triglyceride double bond. In the epoxidation reaction, regenerated acetic acid diffuses to the aqueous phase. A fraction of the acid reacts with the epoxy ring, however. The epoxidized triglycerides diffuse from the organic phase to the aqueous phase to reach the catalyst. Due to steric hindrance, the epoxidized triglycerides cannot enter the catalyst pores. However, they react with acetic acid or hydrogen peroxide at acidic active sites available at the external surface of the catalyst [39]. Triglycerides with opened epoxy rings diffuse into the aqueous and further to the organic phase. The epoxy ring opening reaction also occurs at the organic-aqueous interface according to some authors [25,29].

Since a mathematical description of the three-phase reaction system for the epoxidation of vegetable oils is complex, the kinetic models developed in other studies are based on a simplified reaction scheme, a reduced number of phases, and/or neglected transport phenomena [11-17,26,33]. The model proposed in this study is established by assuming that only reactions (1), (2) and (3a) occur during the epoxidation. Some authors reported that the effect of internal mass transfer is negligible in the reaction system for the epoxidation of vegetable oils with peracetic acid formed *in situ* [11-14]. The same was concluded for the peracetic acid formation investigated apart from the epoxidation process [30]. Therefore, the preferential sorption and internal mass transfer inside the resin pores were neglected in this study. This enabled using a pseudo-homogeneous model to describe the kinetics of the reaction of peracetic acid formation.

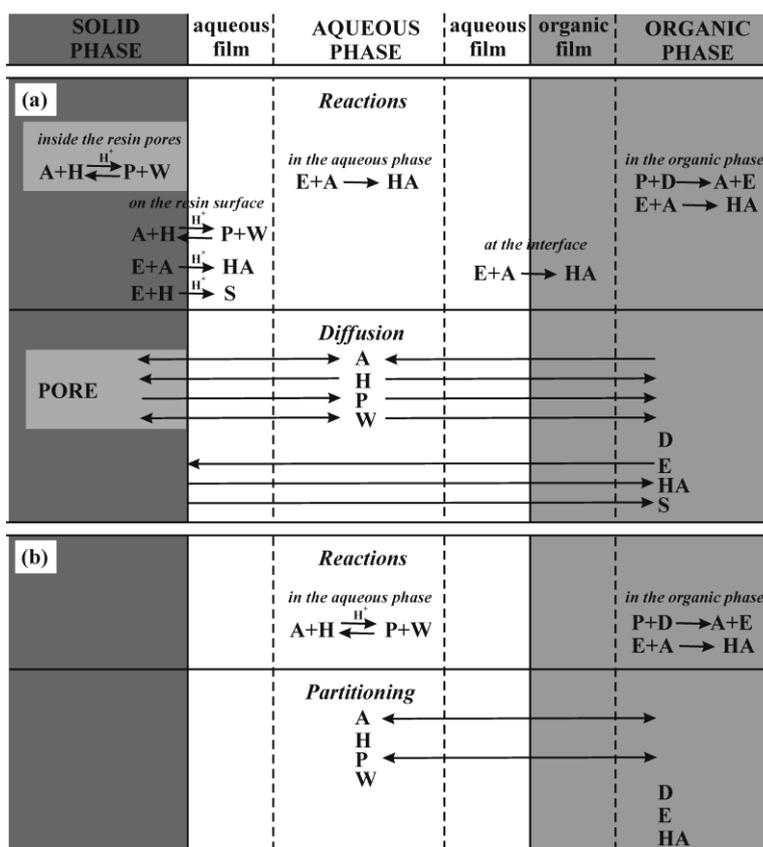


Figure 5. The reaction system for the epoxidation of soybean oil with peracetic acid formed in situ from acetic acid and hydrogen peroxide in the presence of Amberlite IR-120H: a) reactions and mass diffusion and b) in this work considered reactions and partitioning of the components.

To develop the mathematical model for the epoxidation of vegetable oils, the material balances for components in the reaction system were derived from the equation for semi-batch, *i.e.*, feed-batch reactor [40]:

$$\frac{dN_j}{dt} = F_j + V \sum_{i=1}^{NR} \alpha_{j,i} r_i \quad (4)$$

where N_j (mol) is the number of moles of component j ; t (min) indicates the reaction time; F_j (mol/min) is the molar flow of component j ; V (L) indicates the volume; NR is the total number of reactions; $\alpha_{j,i}$ is the stoichiometric coefficient of component j in the reaction i ; and r_i is the rate of reaction i .

It is known from the literature that the solubility of hydrogen peroxide in the organic phase of the epoxidation reaction system can be neglected [39]. The amount of water in the organic phase of the epoxidized soybean oil-acetic acid-water system ranges from 1.62 to 3.04 wt.% at 323-353 K [36], whereas it is not present in the organic phase of the soybean oil-acetic acid-water system [34,35]. However, for the sake of simplicity, it was assumed that

the water is present only in the aqueous phase, whereas the triglycerides are present only in the organic phase of the investigated reaction system. Thus, the number of moles of the components is: $N_H^{aq} = N_H$, $N_W^{aq} = N_W$, $N_D^o = N_D$, $N_E^o = N_E$ and $N_{HA}^o = N_{HA}$. Since acetic acid and peracetic acid are partitioned between the organic and aqueous phases, the mass transfer and concentrations of these components in the particular phase should be taken into consideration [5]:

$$\frac{dN_A^{aq}}{dt} = V^{aq} \sum_{i=1}^{NR^{aq}} \alpha_{A,i}^{aq} r_i^{aq} + k_{L,A} a (C_A^o - K_A C_A^{aq}) V^o \quad (5)$$

$$\frac{dN_A^o}{dt} = V^o \sum_{i=1}^{NR^o} \alpha_{A,i}^o r_i^o - k_{L,A} a (C_A^o - K_A C_A^{aq}) V^o \quad (6)$$

$$\frac{dN_P^{aq}}{dt} = V^{aq} \sum_{i=1}^{NR^{aq}} \alpha_{P,i}^{aq} r_i^{aq} - k_{L,P} a (K_P C_P^{aq} - C_P^o) V^o \quad (7)$$

$$\frac{dN_P^o}{dt} = V^o \sum_{i=1}^{NR^o} \alpha_{P,i}^o r_i^o + k_{L,P} a (K_P C_P^{aq} - C_P^o) V^o \quad (8)$$

where superscripts *aq* and *o* denote the aqueous and organic phases, respectively; $k_{L,A}$ and $k_{L,P}$ (m/min) are

the mass transfer coefficients for acetic acid and peracetic acid, respectively; a (m^2/m^3) indicates the interface area; C_A^o , C_A^{aq} and C_P^o , C_P^{aq} (mol/L) are the concentrations of acetic acid and peracetic acid in a particular phase, respectively; and K_A and K_P indicate the partition coefficients for acetic acid and peracetic acid, respectively.

The partition coefficients of acetic acid and peracetic acid are defined as follows:

$$K_A = \frac{C_A^o}{C_A^{aq}} = \frac{N_A^o / V^o}{N_A^{aq} / V^{aq}} \quad (9)$$

$$K_P = \frac{C_P^o}{C_P^{aq}} = \frac{N_P^o / V^o}{N_P^{aq} / V^{aq}} \quad (10)$$

When the number of moles of acetic acid in the organic phase is expressed from Eq. (9) and substituted in the material balance equation for acetic acid:

$$N_A = N_A^{aq} + N_A^o \quad (11)$$

the following equation is derived:

$$N_A = N_A^{aq} + \frac{K_A N_A^{aq} V^o}{V^{aq}} \quad (12)$$

From Eq. (12), the number of moles of acetic acid in the aqueous phase may be expressed as a function of the total number of moles of acetic acid in the system:

$$N_A^{aq} = \frac{V^{aq} N_A}{V^{aq} + K_A V^o} \quad (13)$$

Therefore, the concentration of acetic acid in the aqueous phase is:

$$C_A^{aq} = \frac{N_A}{V^{aq} + K_A V^o} \quad (14)$$

Likewise, the number of moles and concentration of acetic acid in the organic phase are as follows:

$$N_A^o = \frac{K_A V^o N_A}{V^{aq} + K_A V^o} \quad (15)$$

$$C_A^o = \frac{K_A N_A}{V^{aq} + K_A V^o} \quad (16)$$

Analogously, the concentrations of peracetic acid in the aqueous and organic phases can be derived and expressed as follows:

$$C_P^{aq} = \frac{N_P}{V^{aq} + K_P V^o} \quad (17)$$

$$C_P^o = \frac{K_P N_P}{V^{aq} + K_P V^o} \quad (18)$$

To reduce the external mass transfer resistance between the organic and aqueous phases, as well as between the aqueous and solid phases, effective mixing was ensured by vigorous stirring in this study. By investigating the influence of the stirring speed on the kinetics of the epoxidation process, it was found that the mass transfer is faster than the reaction kinetics. Thus, the mass transfer resistance can be neglected and the terms related to the mass transfer can be omitted from the kinetic model [4]. The material balance equation for acetic acid, on the basis of the Eqs. (5), (6) and (11), becomes:

$$\begin{aligned} \frac{dN_A}{dt} &= \frac{dN_A^{aq}}{dt} + \frac{dN_A^o}{dt} = \\ &= V^{aq} \sum_{i=1}^{NR^{aq}} \alpha_{A,i}^{aq} r_i^{aq} + V^o \sum_{i=1}^{NR^o} \alpha_{A,i}^o r_i^o \end{aligned} \quad (19)$$

and, likewise, the material balance equation for peracetic acid is as follows:

$$\begin{aligned} \frac{dN_P}{dt} &= \frac{dN_P^{aq}}{dt} + \frac{dN_P^o}{dt} = \\ &= V^{aq} \sum_{i=1}^{NR^{aq}} \alpha_{P,i}^{aq} r_i^{aq} + V^o \sum_{i=1}^{NR^o} \alpha_{P,i}^o r_i^o \end{aligned} \quad (20)$$

Now, the mathematical model that describes the reaction system for the epoxidation of vegetable oils is derived as:

$$\left(\frac{dN_H^{aq}}{dt} \right)_1 = -k_1 C_{H_3O^+}^{aq} \left(C_A^{aq} C_H^{aq} - \frac{C_P^{aq} C_W^{aq}}{K_1} \right) V^{aq} \quad (21)$$

$$\frac{dN_H^{aq}}{dt} = \left(\frac{dN_H^{aq}}{dt} \right)_1 + F_H \quad (22)$$

$$\frac{dN_A}{dt} = \left(\frac{dN_H^{aq}}{dt} \right)_1 + k_2 C_P^o C_D^o V^o - k_3 C_E^o (C_A^o)^n V^o \quad (23)$$

$$\frac{dN_P}{dt} = - \left(\frac{dN_H^{aq}}{dt} \right)_1 - k_2 C_P^o C_D^o V^o \quad (24)$$

$$\frac{dN_W^{aq}}{dt} = - \left(\frac{dN_H^{aq}}{dt} \right)_1 + F_W \quad (25)$$

$$\frac{dN_D^o}{dt} = -k_2 C_P^o C_D^o V^o \quad (26)$$

$$\frac{dN_E^o}{dt} = k_2 C_P^o C_D^o V^o - k_3 C_E^o (C_A^o)^n V^o \quad (27)$$

$$\frac{dN_{HA}^o}{dt} = k_3 C_E^o (C_A^o)^n V^o \quad (28)$$

where k_1 ($\text{mol}^2\text{min}^{-1}$), k_2 ($\text{mol}^{-1}\text{min}^{-1}$) and k_3 ($\text{mol}^{-n}\text{min}^{-1}$) are the rate coefficients for the reactions (1), (2) and (3a); and n is the order of epoxy ring opening reaction with respect to acetic acid which was assumed to be the first or the second. The reactions and the partitioning of the components considered in the model proposed in this study are shown in Figure 5b.

Since the model is pseudo-homogeneous with respect to the aqueous phase, the concentration of hydronium ions ($C_{H_3O^+}$) corresponds to the complete dissociation of resin sulphonated groups in the aqueous phase and it is expressed as:

$$C_{H_3O^+}^{aq} = \frac{mC_s}{V^{aq}} \quad (29)$$

where m (g) is the mass of the catalyst; and C_s (mol/g catalyst) indicates the concentration of active catalyst sites (sulphonated groups).

After substituting the expressions (29), (14) and (16)-(18) in the model Eqs. (21)-(28) and expressing the concentrations of components as the ratio of the number of moles and the phase volume, the model equations become functions of the total number of moles of the components:

$$\left(\frac{dN_H}{dt}\right)_1 = -\frac{mC_s k_1}{V^{aq}} \left(\frac{N_A N_H}{V^{aq} + K_A V^o} - \frac{N_P N_W}{K_1(V^{aq} + K_P V^o)} \right) \quad (30)$$

$$\frac{dN_H}{dt} = \left(\frac{dN_H}{dt}\right)_1 + F_H \quad (31)$$

$$\frac{dN_A}{dt} = \left(\frac{dN_A}{dt}\right)_1 + k_2 \frac{K_P N_P N_D}{V^{aq} + K_P V^o} - k_3 N_E \left(\frac{K_A N_A}{V^{aq} + K_A V^o} \right)^n \quad (32)$$

$$\frac{dN_P}{dt} = -\left(\frac{dN_P}{dt}\right)_1 - k_2 \frac{K_P N_P N_D}{V^{aq} + K_P V^o} \quad (33)$$

$$\frac{dN_W}{dt} = -\left(\frac{dN_W}{dt}\right)_1 + F_W \quad (34)$$

$$\frac{dN_D}{dt} = -k_2 \frac{K_P N_P N_D}{V^{aq} + K_P V^o} \quad (35)$$

$$\frac{dN_E}{dt} = k_2 \frac{K_P N_P N_D}{V^{aq} + K_P V^o} - k_3 N_E \left(\frac{K_A N_A}{V^{aq} + K_A V^o} \right)^n \quad (36)$$

$$\frac{dN_{HA}}{dt} = k_3 N_E \left(\frac{K_A N_A}{V^{aq} + K_A V^o} \right)^n \quad (37)$$

Instead of using the number of moles of component j (N_j) in the model Eqs. (30)-(37), the amount of component j in the reaction system can be expressed as the number of moles of component j per 100 g of oil ($[j]$).

For the regression of the experimental data by the proposed model, some approximations were applied as follows.

The volumes of the organic and aqueous phases were accepted as the sums of the components' volumes. For this purpose, the influence of temperature on the densities of both phases was neglected. The volume of the aqueous phase may be expressed per 100 g of oil as:

$$V^{aq} = V_W^{aq} + V_H^{aq} + V_A^{aq} + V_P^{aq} \quad (38)$$

The volume of each component in the aqueous phase per 100 g of oil was expressed as the ratio of mass and density of the component. Further, the mass was defined *via* the component's molecular mass and its amount, or its concentration in the aqueous phase:

$$V^{aq} = \frac{[W]M_W}{\rho_W} + \frac{[H]M_H}{\rho_H} + \frac{C_A^{aq} V^{aq} M_A}{\rho_A} + \frac{C_P^{aq} V^{aq} M_P}{\rho_P} \quad (39)$$

where ρ_W, ρ_H, ρ_A and ρ_P (g/L) are densities of water, hydrogen peroxide, acetic acid and peracetic acid, respectively. By substituting the concentrations of acetic acid and peracetic acid, expressed from Eqs. (14) and (17), into Eq. (39), the volume of the aqueous phase becomes:

The volume of the organic phase per 100 g of oil is calculated from the material balance of the initial double bonds, which undergo epoxidation and further the acetylation, as follows:

$$V^{aq} = \frac{[W]M_W}{\rho_W} + \frac{[H]M_H}{\rho_H} + \frac{[A]V^{aq}M_A}{\rho_A(K_A V^o + V^{aq})} + \frac{[P]V^{aq}M_P}{\rho_P(K_P V^o + V^{aq})} \quad (40)$$

$$V^o = \frac{C_A^o V^o M_A}{\rho_A} + \frac{C_P^o V^o M_P}{\rho_P} + \frac{100[D] + (100 + 76.054[D]_0)[HA] + (100 + 16[D]_0)[E]}{\rho_0^o [D]_0} \quad (41)$$

where $[D]_0$ (mol/100 g of oil) is the initial amount of double bond in the oil; and ρ_o^o (g/L) is the density of the oil in the organic phase. Further, density of the oil in the organic phase was calculated by the linear interpolation of densities of soybean oil (ρ_{SO}) and epoxidized soybean oil (ρ_{ESO}) for the particular double bond and epoxy group concentrations in the oil:

$$\rho_o^o = \rho_{SO} + \frac{EO}{EO_{ESO}}(\rho_{ESO} - \rho_{SO}) \quad (42)$$

where EO_{ESO} (wt.%) is the epoxy oxygen content in epoxidized soybean oil. By substituting the concentrations of acetic acid and peracetic acid in the organic phase, expressed on the basis of Eqs. (16) and (18), into the Eq. (41), the volume of the organic phase becomes:

$$v^o = \frac{[A]v^oM_A}{\rho_A \left(v^o + \frac{v^{aq}}{K_A} \right)} + \frac{[P]v^oM_P}{\rho_P \left(v^o + \frac{v^{aq}}{K_P} \right)} + \frac{100[D] + (100 + 76.054[D]_0)[HA] + (100 + 16[D]_0)[E]}{\rho_o^o[D]_0} \quad (43)$$

The system of two nonlinear Eqs. (40) and (43), with two unknowns, v^{aq} and v^o , may be solved by some of numerical methods, such as the Newtonian method of simultaneous solving the system of nonlinear equations. However, in this case, the sequential determination of the unknowns' values with a two loops algorithm was applied to simplify the calculation. The value of v^o was determined in the outer loop, whereas the value of v^{aq} was determined in the inner loop for the current value of v^o . In both loops, the modified Newtonian method for nonlinear equations was applied. The calculation of the phases' volume must be run at each step of integration of the differential Eqs. (30)-(37).

The amounts of acetic acid and peracetic acid in one phase were calculated on the basis of the partition coefficients and known amounts of components in the other phase. The partition coefficient for acetic acid at temperature T was approximated by double linear interpolation of the values of the partition coefficient for acetic acid for the soybean oil-acetic acid-water and epoxidized soybean oil-acetic acid-water systems:

$$K_{A,SO} = K_{A,SO,\rho} + \frac{K_{A,SO,\rho+1} - K_{A,SO,\rho}}{T_{\rho+1} - T_{\rho}}(T - T_{\rho}) \quad (44)$$

$$K_{A,ESO} = K_{A,ESO,\rho} + \frac{K_{A,ESO,\rho+1} - K_{A,ESO,\rho}}{T_{\rho+1} - T_{\rho}}(T - T_{\rho}) \quad (45)$$

$$K_A = \frac{K_{A,SO}[D] + K_{A,ESO}[E]}{[D] + [E]} \quad (46)$$

where $K_{A,SO}$, $K_{A,SO,\rho}$ and $K_{A,SO,\rho+1}$ are the partition coefficients for acetic acid between the soybean oil and water at the temperatures T , T_{ρ} and $T_{\rho+1}$, respectively; $K_{A,ESO}$, $K_{A,ESO,\rho}$ and $K_{A,ESO,\rho+1}$ are the partition coefficients for acetic acid between the epoxidized soybean oil and water at the temperatures T , T_{ρ} and $T_{\rho+1}$, respectively; and T_{ρ} and $T_{\rho+1}$ are the temperatures given in Table 2 with the closest values to the T . The values of the partition coefficients for these three-component systems were calculated on the basis of the experimental data given in the literature [34,36]. Further, it was assumed that the value of the partition coefficient for peracetic acid is always 2.5 times higher than the value of the partition coefficient for acetic acid [5].

Table 2. Values of the partition coefficient for acetic acid in the systems soybean oil-acetic acid-water (SO-A-W) and epoxidized soybean oil-acetic acid-water (ESO-A-W) calculated on the basis of experimental data reported the literature [34,36]

T / K	Partition coefficient for acetic acid	
	SO-A-W	ESO-A-W
323	0.04255	0.1647
338	0.04568	0.1620
353	0.04867	0.1860

For the temperature dependency of the chemical equilibrium constant for peracetic acid formation from acetic acid and hydrogen peroxide in an aqueous solution (K_1), the expression reported in the literature was applied [41]:

$$K_1 = \exp(12.2324 \ln T - 0.0229913T + 9.70452 \times 10^{-6}T^2 + 3045.76/T - 72.8758) \quad (47)$$

where T (K) is the temperature.

A drop-wise addition of the hydrogen peroxide solution to the reaction mixture is approximated with continuous flows of hydrogen peroxide (F_H) and water (F_W), both in (mol/(min·100 g oil)):

$$F_H = \begin{cases} m_{HS} w_H M_H^{-1} t_{HS}^{-1} & t \leq t_{HS} \\ 0 & t > t_{HS} \end{cases} \quad (48)$$

$$F_W = \begin{cases} m_{HS}(1-w_H)M_W^{-1} t_{HS}^{-1} & t \leq t_{HS} \\ 0 & t > t_{HS} \end{cases} \quad (49)$$

where m_{HS} (g) is the mass of the hydrogen peroxide aqueous solution; w_{H} is the mass fraction of hydrogen peroxide in the solution; M_{H} and M_{W} (g/mol) are molecular masses of hydrogen peroxide and water; and t_{HS} (min) is the duration of hydrogen peroxide solution addition.

The temperature dependency of the rate coefficient k_i for the reaction i is expressed with reparameterized form of the Arrhenius equation [42]:

$$k_i = \exp \left[k_{i,0} - \frac{k_{i,E_a}}{R} \left(\frac{1}{T} - \frac{1}{T_a} \right) \right] \quad (50)$$

where $k_{i,0}$ and k_{i,E_a} are the modified Arrhenius equation constants related to the frequency coefficient and the activation energy, respectively; R (8.3143 J/(mol K)) is the universal gas constant; and T_a (K) indicates an average temperature of experiments.

Kinetic parameters

Prior to fitting the experimental data with the proposed model, it is necessary to define the time dependency of the reaction temperature. In this study, the hydrogen peroxide aqueous solution addition to the reaction mixture was isothermal. The increase in temperature to the desired reaction temperature was approximated as linear with reaction time. Further, the epoxidation was run isothermally. These temperature changes are described mathematically as follows:

$$T = \begin{cases} T_{\text{HS}} & t \leq t_{\text{HS}} \\ T_{\text{HS}} + (T_r - T_{\text{HS}})(t_{\text{HS}} + t_{\text{T1}} - t) / t_{\text{T1}} & t_{\text{HS},k} < t \leq (t_{\text{HS}} + t_{\text{T1}}) \\ T_r & (t_{\text{HS}} + t_{\text{T1}}) < t \end{cases} \quad (51)$$

where T_{HS} (K) is the temperature of the hydrogen peroxide solution addition; T_r (K) is the temperature of the reaction; and t_{T1} (min) is the period of the temperature increase.

The constants of the reparameterized Arrhenius equation, $k_{i,0}$ and k_{i,E_a} , were determined by fitting the values of double bond [D] and epoxy group [E] amount changes with reaction time (t) for the soybean oil epoxidations run under different reaction conditions. The Marquardt method was used to fit the data [43]. The following objective function (F) was minimized:

$$F = \sum_{k=1}^{\text{NRN}} \sum_{j=1}^{\text{NS}_k} \left[\left([D]_{k,j}^{\text{calc}} - [D]_{k,j}^{\text{exp}} \right)^2 + \left([E]_{k,j}^{\text{calc}} - [E]_{k,j}^{\text{exp}} \right)^2 \right] \quad (52)$$

where NRN indicates the number of runs and NS_k is the number of samples in run k ; [D] and [E] are determined as $[D] = IM/2A_I$ and $[E] = EO/[100A_O]$,

where A_I is the atomic mass of iodine and A_O is the atomic mass of oxygen; and superscripts calc and exp indicate the calculated and experimentally determined value, respectively.

The model's system of differential Eqs. (30)-(37) was integrated by applying a fourth order Runge-Kutta method.

The model parameters, *i.e.*, the rate coefficients k_i for the investigated reactions were calculated when the average temperature of the experiments (T_a) was accepted as 338 K and assuming the first and the second order of the epoxy ring opening reaction with respect to acetic acid. The results are presented in Table 3 together with the values of the least sum of squares (objective function F) and average absolute deviations for amounts of double bond ($AAD_{[D]}$) and epoxy group ($AAD_{[E]}$).

The least sum of squares is lower (0.06519) when the order of the side reaction was assumed as the first. The temperature dependencies of the kinetic parameters for such assumption are determined as follows:

$$k_1 C_s = \exp \left[-10.15365 - \frac{83959.13}{R} \left(\frac{1}{T} - \frac{1}{T_a} \right) \right] \quad (53)$$

$$k_2 = \exp \left[-2.564719 - \frac{1425.418}{R} \left(\frac{1}{T} - \frac{1}{T_a} \right) \right] \quad (54)$$

$$k_3 = \exp \left[-6.143859 - \frac{6873.391}{R} \left(\frac{1}{T} - \frac{1}{T_a} \right) \right] \quad (55)$$

Note that the rate coefficients are not intrinsic but apparent, since the effect of the mass transfer resistance on the kinetics was not taken into consideration. Also, the rate coefficient for peracetic acid formation is expressed in combination with the concentration of the active catalyst sites (C_s). An increase of all rate coefficients with an increase in temperature was obtained. Since all calculated reactant and product amounts have positive values, the viability of the developed kinetic model is confirmed. Due to lower average absolute deviation of 0.01258 than 0.01530, it can be concluded that the model fits the time variation of double bond amount slightly better than epoxy group amount, respectively (Table 3). On the basis of double bond and epoxy group amounts

Table 3. Statistical values of the model parameters determination when the models proposed in this study and in the literature [16] were applied for the *in situ* epoxidation of soybean oil. The order of the epoxy ring opening reaction with respect to acetic acid was 1 or 2. The constants of the reparameterized Arrhenius equation for compared models are given

Parameter	This study		Reference [16]	
	Order of the epoxy ring opening reaction, <i>n</i>			
	1	2	1	2
	Error			
<i>F</i>	0.06519	0.06764	0.12250	0.11800
<i>AAD</i> _[D] ^a	0.01258	0.01275	0.01999	0.01953
<i>AAD</i> _[E] ^b	0.01530	0.01556	0.01937	0.01879
	Constants of the reparameterized Arrhenius equation			
$(k_1C_s)_0$	-10.15365	-10.20897	-5.171507	-5.172997
$(k_1C_s)_{Ea}$	83959.13	82829.17	79854.73	79039.30
<i>k</i> _{2,0}	-2.564719	-2.501162	-1.332284	-1.282917
<i>k</i> _{2,Ea}	1425.418	-1040.259	-11635.34	-13083.98
<i>k</i> _{3,0}	-6.143859	-4.765239	-5.737784	-4.010654
<i>k</i> _{3,Ea}	6873.391	300.7545	-3704.474	-3174.165

$$^a \text{Average absolute deviation for double bond amount: } AAD_{[D]} = \frac{1}{\sum_{k=1}^{NRN} NS_k} \sum_{k=1}^{NRN} \sum_{l=1}^{NS_k} \left| [D]_{k,l}^{\text{calc}} - [D]_{k,l}^{\text{exp}} \right|$$

$$^b \text{average absolute deviation for epoxy group amount: } AAD_{[E]} = \frac{1}{\sum_{k=1}^{NRN} NS_k} \sum_{k=1}^{NRN} \sum_{l=1}^{NS_k} \left| [E]_{k,l}^{\text{calc}} - [E]_{k,l}^{\text{exp}} \right|$$

estimated with developed model, the iodine number and epoxy oxygen content, respectively, were calculated. In Figures 2-4 are shown changes of the iodine number and epoxy oxygen content over time for the epoxidations of soybean oil with peracetic acid generated *in situ* in the presence of Amberlite IR-120H. The proposed model fits the corresponding experimental data reasonably well.

Comparison of the proposed model with the pseudo-homogeneous model reported in the literature

The kinetic model proposed in this study is established assuming the pseudo-homogeneity of the catalyst with respect to the aqueous phase. Unlike the other pseudo-homogeneous models found in the literature [16,31,44], it takes into consideration the partitioning of acetic acid and peracetic acid between the organic and aqueous phases, as well as the changing of the phases' volumes during the process. The model also takes into account the occurrence of the reactions during the incremental addition of the oxidizing agent solution and defined temperature changes during the epoxidation process. These phenomena were already considered in the pseudo-homogeneous model developed for the *in situ* epoxidation of castor oil [16]. In order to compare the latter pseudo-homogeneous model with the model proposed in this study, the experimental data obtained

for the epoxidation of soybean oil under defined reaction conditions (Table 1) were fitted. In both models, the beginning of the addition of hydrogen peroxide solution to the reaction mixture was considered as the zero reaction time. Also, the variation of the chemical equilibrium constant for peracetic acid formation with temperature was defined with the same expression. Further, the temperature dependencies of the kinetic parameters were defined with the same Arrhenius type model. The same objective function *F* was applied for both regressions. The least sum of squares of 0.06519 obtained for the model developed in this study is more than 44% lower than those of 0.11800 obtained for the reported model when the second order of the epoxy ring opening reaction with respect to acetic acid was assumed (Table 3). This confirmed that the improved model better describes the reaction system for the epoxidation of soybean oil conducted under the investigated conditions. Since it was shown in the literature [16] that the model developed for the epoxidation of castor oil fits the experimental data better than the two pseudo-homogeneous kinetic models proposed by other authors [31,44], it can be concluded that the model proposed in this study correlates the change of double bond and epoxy group contents during the *in situ* epoxidation of vegetable oils better than the other reported pseudo-homogeneous models.

CONCLUSION

The epoxidations of soybean oil with peracetic acid formed *in situ* from acetic acid and hydrogen peroxide in the presence of an acidic ion exchange resin as the catalyst were carried out under different temperatures of incremental oxidizing agent addition, reaction temperatures, catalyst concentrations and stirring speeds. It was determined that the highest epoxide yield was achieved at the reaction temperature of 338 K after 625 min when approximately 0.5 mol of glacial acetic acid and 1.35 mol of 30% aqueous hydrogen peroxide solution per mole of double bond of soybean oil were used. The epoxidation was catalyzed with Amberlite IR-120H in the amount of only 4.04 wt.% of oil. A kinetic model was developed assuming the pseudo-homogeneity of the catalyst with respect to the aqueous phase. The proposed model took the partitioning of acetic acid and peracetic acid between the organic and aqueous phases into consideration, as well as the changing of the phases' volumes during the process. The temperature dependency of the kinetic parameters was determined and an increase in all reaction rate coefficients with an increase in temperature was obtained. A comparison was made between the proposed model and the pseudo-homogeneous model reported in the literature. The model developed in this study fits the experimental data obtained for the *in situ* epoxidations of soybean oil run under the investigated conditions better than the kinetic model taken for the comparison.

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Nomenclature

A-acetic acid
 A_I -atomic mass of iodine
 A_O -atomic mass of oxygen
 AAD -average absolute deviation
 a -interphase area (m^2/m^3)
 $C_{H_3O^+}$ -concentration of hydronium ions (mol/L)
 C_j -concentration of component j (mol/L)
 C_s -concentration of catalytically active sites (mol/g catalyst)
 D-double bond
 E-epoxy group, *i.e.*, ring

EO-epoxy oxygen content (wt.%)
 EO_{ESO} -epoxy oxygen content in epoxidized soybean oil (wt.%)
 ESO-epoxidized soybean oil
 F -objective function
 F_j -molar flow of component j (mol/min)
 H-hydrogen peroxide
 HA-hydroxy acetate
 I_N -iodine number (g iodine/100 g oil)
 I_{N0} -initial iodine number (g iodine/100 g oil)
 $[j]$ -amount of component j (mol/100 g oil)
 K_1 -chemical equilibrium constant for peracetic acid formation
 K_j -partition coefficient for component j
 $K_{A,SO}$ -partition coefficient for acetic acid in the system soybean oil-acetic acid-water
 $K_{A,ESO}$ -partition coefficient for acetic acid in the system epoxidized soybean oil-acetic acid-water
 k_i -rate coefficient for reaction i
 $k_{i,0}$ -constant of reparameterized Arrhenius equation related to the frequency coefficient
 k_{i,E_a} -constant of reparameterized Arrhenius equation related to the activation energy
 $k_{L,j}$ -mass transfer coefficient for component j (m/min)
 M_j -molecular mass of component j (g/mol)
 m -mass of the catalyst (g)
 m_{HS} -mass of the hydrogen peroxide aqueous solution (g)
 N_j -number of moles of component j (mol)
 NR -total number of reactions
 NRN -number of runs
 NS_k -number of samples in run k
 P-peracetic acid
 R -universal gas constant (J/mol·K)
 r_i -rate of reaction i
 REY -relative epoxy yield (%)
 S -stirring speed (rpm)
 SE -selectivity
 SO-soybean oil
 T -temperature (K)
 T_a -average temperature of runs (K)
 t -reaction time (min)
 t_{HS} -period of hydrogen peroxide aqueous solution addition (min)
 t_{T1} -period of temperature increase (min)
 V -volume (L)
 v -volume (L/100 g oil)
 W-water
 w_H -mass fraction of hydrogen peroxide in its aqueous solution
 X -conversion of double bond (%)

Greek letters

α_j -stoichiometric coefficient of component j in the reaction i

ρ_j -density of component j (g/L)

ρ_o^o -density of oil in the oil phase (g/L)

ρ_{SO} -density of soybean oil (g/L)

ρ_{ESO} -density of epoxidized soybean oil (g/L)

Subscript

0-initial value

m-maximum value

th-theoretical value

Superscript

aq-aqueous phase

calc-calculated value

exp-experimentally determined value

n -order of reaction

o-organic phase

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NAUČNI RAD

KINETIKA EPOKSIDOVANJA SOJINOG ULJA PERSIRČETNOM KISELINOM FORMIRANOM *IN* *SITU* U PRISUSTVU JONOIZMENJIVAČKE SMOLE: PSEUDO-HOMOGENI MODEL

Predložen je kinetički model epoksidovanja biljnih ulja persirčetnom kiselinom formiranom in situ iz sirčetne kiseline i vodonik-peroksida u prisustvu jonoizmenjivačke smole kao katalizatora. Model je pseudo-homogen u odnosu na katalizator. Pored osnovnih reakcija formiranja persirčetne kiseline i epoksidne grupe, model opisuje i sporednu reakciju otvaranja epoksidne grupe sa sirčetnom kiselinom. U modelu se razmatraju i raspodela sirčetne i persirčetne kiseline između vodene i organske faze sistema i promena zapremine faza tokom odvijanja procesa epoksidovanja. Temperaturna zavisnost prividnih koeficijentata brzina reakcija je opisana reparametrizovanom Arrhenius jednačinom. Kinetički parametri predloženog modela su izračunati fitovanjem eksperimentalnih podataka dobijenih tokom epoksidovanja sojinog ulja izvođenih pri definisanim reakcionim uslovima. Najveći prinos epoksida od 87,73% je postignut pri temperaturi od 338 K kada je molski odnos nezasićenost ulja:sirčetna kiselina:vodonik-peroksid iznosio 1:0.5:1.35 i kada je primenjena količina katalizatora Amberlite IR-120H bila 4,04 mas.% u odnosu na ulje. U poređenju sa publikovanim pseudo-homogenim modelima, model predložen u ovom radu bolje koreliše promene sadržaja dvostrukih veza i epoksidnih grupa tokom procesa epoksidovanja.

Ključne reči: sojino ulje, epoksidovanje, persirčetna kiselina, jonoizmenjivačka smola, kinetika.