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REVIEW PAPER

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KINETIC MODELS OF REACTION SYSTEMS FOR THE *IN SITU* EPOXIDATION OF UNSATURATED FATTY ACID ESTERS AND TRIGLYCERIDES

Mathematical models that describe the kinetics of reaction systems for the in situ epoxidation of unsaturated fatty acid esters or triglycerides with organic peracids are reviewed in this paper. The advantages and inadequacies of each model are discussed. A mono–phase pseudo–first order kinetic model was compared with a two phase model based on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) postulates proposed by the authors of this paper. The comparison was performed on the experimentally determined values for the in situ epoxidation of soybean oil by peracetic acid in the presence of different quantities of ion exchange resin used as the catalyst. It was concluded that a complete model for in situ epoxidation in the presence of ion exchange resin as the catalyst was still not given for perorganic acid formation. In particular, we report here the possibilities of the creation of an "ideal" model for in situ epoxidation.

Epoxidation is the reaction of forming of an oxirane ring by the oxidation of olefinic or aromatic double bonds. It can be carried out by using different methods, depending on the feedstock, applied oxidation reagent, catalyst and solvent. Epoxy compounds are valuable commercial products due to a large number of reactions they can undergo to form different types of products such as glycols, alcohols, carbonyl compounds and polymers (polyesters, polyurethanes, and epoxy resins). The epoxides obtained from higher linear olefins, esters and triglycerides of unsaturated fatty acids can be used as plasticizers and stabilizers in plastics and coatings. For example, triglycerides of unsaturated fatty acids that are the main constituent of vegetable oils, a widely available and renewable feedstock, can be successfully epoxidized to produce plasticizers for PVC. The common vegetable oil used for this purpose is soybean oil.

Epoxidation is usually performed with an organic peracid because hydrogen peroxide is not soluble in oil. The use of organic peracids for the epoxidation of vegetable oils was established in the 1940s, and all the methods developed since then can be classified into two main groups – those with preformed peracid and those with *in situ* formed peracid. When organic peracid is preformed, there are some handling problems, as the concentrated peracid is unstable and explosive. For that reason, the *in situ* method is widely used. Peracetic acid is mostly used as an oxidation reagent because it is cheap and available. It is obtained by the reaction of acetic acid and hydrogen peroxide in the presence of an acid catalyst. The resulting reaction system is multi–phase. Peracid formation occurs in water (diluted hydrogen peroxide is used) and epoxidation in the oil phase. If sulphuric acid, as a homogeneous catalyst, is used, the system is two phase (water with inorganic acid – oil), but if an acidic ion exchange resin is used as the catalyst, the third phase – a solid phase is introduced into the system (water – resin – oil).

The reaction of peracid formation is slow, slower than epoxidation. As epoxidation is very exothermic, hydrogen peroxide is usually added gradually at temperatures lower than those at which epoxidation occurs. Following this, epoxidation is allowed to proceed at higher temperatures for several hours. In this case, mass and heat transfer can be serious limitations to process performance. Furthermore, by–products can be formed, as a consequence of oxirane cleavage, which is possible in an acid medium. The degree of side reactions depends on several factors, such as the type and quantity of the catalyst, reactant ratio and the presence of solvent.

To obtain economically optimal conditions for epoxidation, in order to obtain a product with the required characteristics, a reliable kinetic model of this complex multi–phase system with parallel and consecutive reactions is more than necessary. The mechanism and the kinetics of epoxidation of unsaturated fatty acid esters and triglycerides have been studied for many years, although more rigorous kinetic models have been published in the last few years. Nevertheless, a complete, theoretically valid kinetic model for *in situ* epoxidation in the presence of ion exchange resin used as a catalyst still cannot be found in the literature. The aim of this paper is to give an overview of the different kinetic models published in the literature, as well as to compare some of them by fitting the experimental data. In particular, necessary further actions in developing a rigorous and more applicable kinetic model are pointed out.

REACTIONS OF *IN SITU* EPOXIDATION

It is generally accepted that the mechanism for *in situ* epoxidation in the presence of a homogeneous catalyst can be described as follows:

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- Peracid formation in the water phase in the presence of a catalyst;
- Mass transfer of peracid from water to the oil phase;
- The reaction of peracid with double bonds in the oil phase producing epoxide and the corresponding acid;
- Side reactions of oxirane cleavage in the oil phase and at the interfacial area;
- Mass transfer of acid from the oil to the water phase.

When ion exchange resin is used as the catalyst, the step of peracid formation includes different sub–steps, such as reactant diffusion into the catalyst, adsorption, reaction at the catalyst surface, desorption and product diffusion from the catalyst to the reaction mixture.

In general, the following reactions can occur in the system:

Peracid formation:

$$R_1 - COOH + H_2O_2 \xleftrightarrow{H^+} R_1 - COOOH + H_2O \qquad (1)$$

Epoxidation:

$$\underset{(D)}{R_2 - CH = CH - R_3} + \underset{(P)}{R_1 - COOOH} \rightarrow$$

$$\rightarrow \underset{(E)}{R_2 - CHOCH - R_3} + \underset{(A)}{R_1 - COOH} \qquad (2)$$

Different side reactions in the oil phase and/or at the interfacial area are possible:

$$R_2 - CHOCH - R_3 + R_1 - COOH \xrightarrow{H^+}$$

$$\xrightarrow{H^+} R_2 - CH(OH) - CH(OOC - R_1) - R_3 \qquad (3)$$

$$R_2 - CHOCH - R_3 + R_1 - COOOH \xrightarrow{H^+}$$

$$\xrightarrow{H^+} R_2 - CH(OH) - CH(OOOC - R_1) - R_3 \qquad (4)$$

$$R_2 - CH(OH) - CH(OOC - R_1) - R_3 + H_2O \xrightarrow{H^+}$$

$$\xrightarrow{H^+} R_2 - CH(OH) - CH(OH) - R_3 + R_1 - COOH \qquad (5)$$

$$R_2 - CHOCH - R_3 \xrightarrow{H^+} R_2 - CO - CH_2 - R_3 \qquad (6)$$

$$R_2 - CHOCH - R_3 + H_2O \xrightarrow{H^+}$$

$$\xrightarrow{H^+} R_2 - CH(OH) - CH(OH) - R_3 \qquad (7)$$

$$R_2 - CHOCH - R_3 + H_2O_2 \xrightarrow{H^+}$$

$$\xrightarrow{H^+} R_2 - CH(OH) - CH(OOH) - R_3 \qquad (8)$$

Furthermore, for extremely long duration of epoxidation a reaction between the formed hydroxyl and epoxy groups is also possible, in which case internal or oligomeric ethers are formed [1].

KINETIC MODELS

One–Phase Kinetic Model

In many studies the reaction of epoxidation, i.e. the double bond conversion designated in equation (2), was assumed to be second order, first order in respect to each reactant [2–11]:

$$-\frac{dC_D}{dt} = k_2 C_D C_P \qquad (9)$$

The authors of the first kinetic models for *in situ* epoxidation based their work on the fact that the rate of peracid formation was slower than the rate of epoxidation. Therefore, they assumed that the concentration of peracid in the system was very small and constant. Such an assumption allowed the consideration that the reaction of the double bond with peracid is pseudo–first order. Reactions (3) and (5), combined in one, were used for oxirane cleavage. The model is described by the following equations:

$$\frac{d[D]}{dt} = -k_2^o [D] \qquad (10)$$

$$\frac{d[E]}{dt} = k_2^o [D] - k_{35} [E] [A] \qquad (11)$$

$$\frac{d([H] + [G])}{dt} = k_{35} [E] [A] \qquad (12)$$

where square brackets denote the concentration in respect to the total volume.

Although the above assumption, as well as the calculated total concentrations instead of the local phase concentrations cannot be applied to the complex multiphase *in situ* epoxidation system, such an approach has been used even nowadays, totally or partially, in kinetic analysis [1,3,4,10–14].

The side reactions were examined in separate experiments by using glacial acetic acid and epoxidized palm oil methyl esters [12] in one case and epoxidized soybean oil [15] in another one. It was found that oxirane destruction (formation of by–products) was first order in respect to the epoxy group concentration and second order in respect to acetic acid:

$$\frac{dC_S}{dt} = -\frac{dC_E}{dt} = k_S C_E C_A^2 \qquad (13)$$

In the case of the *in situ* epoxidation performed under other conditions, first order kinetics in respect to acetic acid were also applied [2,11].

Two–Phase Kinetic Model

The first kinetic model that took into consideration the existence of two phases during the *in situ* epoxidation of oleic acid with peracetic acid in the presence of sulfuric acid as the catalyst was given by Chou and

Chang [5]. They assumed that the mechanism consisted of seven steps for the reactions of peracid formation and epoxidation, and for the mass transfer between the phases. However, they did not consider the side reactions of oxirane cleavage. With appropriate assumptions, regarding the steady state, they defined the rate of epoxide formation as follows:

$$r_E = \frac{dC_E}{dt} = p_1 C_A C_{H_2O_2} C_{H^+} C_D / X \quad (14)$$

where:

$$X = p_2 C_{H^+} C_{H_2O} + p_3 C_{H^+} C_{H_2O} + p_4 C_D + p_5 C_D C_{H_2O} + p_6 C_D C_{H_2O_2} + p_7 C_D C_{H_2O} C_{H^+} \quad (15)$$

p_1–p_7 are the parameters generated as a combination of the rate constants for particular (forward and reverse) elementary steps.

Chou and Chang [5] assumed that the limiting step of the overall rate was the reverse reaction of peracid formation and that the rates of the other reaction steps were very low. Therefore, equation (14) could be simplified and rewritten as follows:

$$r_E = \frac{dC_E}{dt} = k C_A C_{H_2O_2} C_{H^+} \quad (16)$$

Such an assumption was experimentally confirmed. Namely, under the conditions when mass transfer limitation did not exist they found that the following rate equation was valid for the initial epoxidation rate:

$$r_{E,0} = k C_A^{0.97} C_{H_2O_2}^{1.05} C_H^{1.02} \quad (17)$$

Rangarajan et al. [9] noticed several problems in the study of Chou and Chang [5]. They found that hydrogen peroxide was added slowly at an unspecified rate, which limited the reactions, and that the reactor was not equipped with baffles, which made it difficult to estimate how well the system was mixed and what the size of the interfacial area was. The concentrations were also expressed in respect to the overall volume. For that reason Rangarajan et al. somehow improved the epoxidation procedure by adding hydrogen peroxide at once and by applying better mixing of the reaction mixture in order to eliminate the effects of mass and heat transfer. They also used the local phase concentrations in a two–phase kinetic model for the *in situ* epoxidation of soybean oil with sulfuric acid as the catalyst. They considered oxirane cleavage, but only in the reaction with acetic acid according to equation (13). Their assumption was that sulfuric acid did not influence the previous reaction and that other side reactions did not take place on the interfacial area. Taking into account the above assumptions, the following model, based on the mass balance of the components in both the water and oil phases was derived:

$$\frac{dC^w_{H_2O_2} V^w}{dt} = -k_1 C^w_A C^w_{H_2O_2} C^{w}_{H^+} V^w + k^w_{-1} C^w_P C^w_{H_2O} C^{w}_{H^+} V^w \quad (18)$$

$$\frac{dC^w_P V^w}{dt} = k_1 C^w_A C^w_{H_2O_2} C^{w}_{H^+} V^w - k^w_{-1} C^w_P C^w_{H_2O} C^{w}_{H^+} V^w - k_{L,P}\, a\, (K_P C^w_P - C^O_P)\, V^O \quad (19)$$

$$\frac{dC^w_A V^w}{dt} = -k_1 C^w_A C^w_{H_2O_2} C^{w}_{H^+} V^w + k^w_{-1} C^w_P C^w_{H_2O} C^{w}_{H^+} V^w + k_{L,A}\, a\, (C^O_A - K_A C^w_A)\, V^O \quad (20)$$

$$C^w_{H_2O} V^w = (C^w_{H_2O_i} + C^w_{H_2O_{2i}})\, V^w_i - C^w_{H_2O_2} V^w \quad (21)$$

$$\frac{dC^O_D V^O}{dt} = -k_2 C^O_D C^O_P V^O \quad (22)$$

$$\frac{dC^O_E V^O}{dt} = k_2 C^O_D C^O_P V^O - k_3 C^O_E (C^O_A)^2 V^O \quad (23)$$

$$\frac{dC^O_P V^O}{dt} = k_{L,P}\, a\, (K_P C^w_P - C^O_P)\, V^O - k_2 C^O_D C^O_P V^O \quad (24)$$

$$\frac{dC^O_A V^O}{dt} = -k_{L,A}\, a\, (C^O_A - K_A C^w_A)\, V^O + k_2 C^O_D C^O_P V^O - k_3 C^O_E (C^O_A)^2 V^O / Y_A \quad (25)$$

In separate experiments the authors determined the intrinsic rate constant (k_2) of epoxidation and the phase partition coefficient for acetic acid (K_A), while the phase partition coefficient for peracetic acid (K_P) was only assumed. The other kinetic parameters were calculated by fitting the experimental data for *in situ* epoxidation. The agitation intensity was set up in order to eliminate the mass transfer limitation, which was confirmed by determining the initial rate of epoxidation at different rotation speeds.

The model predicted a too high consumption of acetic acid for the oxirane cleavage because the reactions of epoxide degradation on the interfacial area had not been considered. This was adjusted by introducing an empirical coefficient Y_A (Y_A = 1.65).

Although the initial epoxidation rates did not change with increasing mixing intensity beyond a certain value, the influence of the agitation rate on the rate of epoxidation and epoxy yield became apparent during epoxidation, which was also obtained in our experimental investigations [16]. The reason for such an effect is that, by varying the agitation intensity, a different drop size and interfacial area can be obtained. Therefore, a correlation between the mixing intensity and interfacial area is necessary and must be incorporated into the equations of the reaction rates.

The discussed model successfully predicts the influence of an inert solvent, such as benzene and toluene that are often used in epoxidation experiments. The inert solvent stays in the oil phase and has no

influence on the reaction of the peracid formation. However, due to the dilution of the oil phase, the solvent indirectly decreases the rate of reactions in that phase, for instance, oxirane cleavage.

The first more rigorous kinetic model for the *in situ* epoxidation of soybean oil in the presence of an ion exchange resin as the catalyst was given in the papers of Sinadinović–Fišer [17–19] and Sinadinović–Fišer et al. [11,20]. The Langmuir–Hinshelwood–Hougen–Watson (LHHW) [21–23] approach was applied to model the catalytic reaction of peracetic acid formation (1). Several models were analyzed and the model that fit the best experimental data was based on the following chemisorption mechanism:

$$A + s \leftrightarrow A \cdot s \tag{26}$$

$$A \cdot s + H_2O_2 \xrightarrow{k_{sr}} P \cdot s + H_2O \tag{27}$$

$$P \cdot s \leftrightarrow P + s \tag{28}$$

Besides the reaction of peracetic acid formation, the derived model included the reaction of epoxidation (2), and the reactions of oxirane cleavage (3) and (7). The model was described by the following rate equations:

$$\frac{d\,[H_2O_2]}{dt} = -\frac{M_k C_s k_{sr} K_{S,A}\,[A]\,[H_2O_2]}{1 + K_{S,A}[A] + K_{S,P}[P]} \tag{29}$$

$$\frac{d\,[A]}{dt} = \frac{d\,[H_2O_2]}{dt} + k_2[P]\,[D] - k_3[E]\,[A] \tag{30}$$

$$\frac{d\,[P]}{dt} = \frac{d\,[H_2O_2]}{dt} - k_2[P]\,[D] \tag{31}$$

$$\frac{d\,[D]}{dt} = -\,k_2[P]\,[D] \tag{32}$$

$$\frac{d\,[E]}{dt} = k_2[P]\,[D] - k_3[E]\,[A] - k_7[E]\,[H_2O] \tag{33}$$

$$\frac{d\,[H_2O]}{dt} = -\frac{d\,[H_2O_2]}{dt} - k_7[E]\,[H_2O] \tag{34}$$

$$\frac{d\,[S]}{dt} = k_3[E]\,[A] + k_7[E]\,[H_2O] \tag{35}$$

where the square brackets denote the concentrations in mol/100g of oil. The parameters of the kinetic model were simultaneously estimated by fitting the experimental data: time changes of both the concentration of double bonds in the oil and those of epoxy oxygen.

The simultaneous calculation of the kinetic parameters instead of their successive determination from the data of separate experiments, as Rangarajan et al. [9] had done, and the usage of the total instead of the local phase concentrations of the reactants and products, led to the obviously wrong conclusion. A model accepted as the appropriate one was those which assumed that in the catalytic reaction of peracetic acid formation only acetic and peracetic acids were adsorbed on the catalyst surface, and that reaction was irreversible. The kinetic model that predicted this reaction as a reversible one yielded a very large value for the chemical equilibrium constant K (in the order of magnitude of 10^9) after fitting the experimental data. This value suggested that the catalytic reaction might be considered irreversible, since epoxy compound formation, involving the consumption of peracetic acid, was fast enough and that the equilibrium in the reaction of peracetic acid formation was shifted to the right [11]. Therefore, as mentioned previously, the kinetic parameters for each reaction should be determined by fitting the data of the separately performed reactions (1) and (2), and by using the calculated value for the chemical equilibrium constant. Because of the fact that the water phase is non–ideal, activities should be used rather than concentrations of the reactants and products, as Rehfinger and Hoffmann did in their kinetic model derived for MTBE synthesis in the presence of an ion exchange resin [24]. The UNIQUAC method could be applied.

Musante et al. [25] gave a detailed kinetic model of one of the sub–systems that exist during epoxidation. They described the kinetics of the formation of peracetic acid in the presence of an ion exchange resin. The authors considered selective sorption and resin swelling that led to the conclusion that the component concentrations i.e. activities were different in the aqueous and polymer phases. Accordingly, they defined the system as a two–phase one that consisted of an aqueous phase with N components in equilibrium with a high viscosity liquid polymer phase, which contained N+1 components (the N+1st component is the swollen polymer). They used the UNIFAC LLE method of group contributions to determine the activity coefficients of components in the water phase [26]. The extended Flory–Huggins model [27] was applied for the activities in the polymer phase:

$$\ln a_i^R = 1 + \ln v_i - \sum_{j=1}^{N+1} m_{ij} v_j + \sum_{j=1}^{N+1} \chi_{ij} v_j - \sum_{j=1}^{N+1} \sum_{k=1}^{j-1} m_{ik} v_j v_k \chi_{kj} + \eta V_i \left(\frac{5}{3} v_R^{1/3} - \frac{7}{6} v_R \right) \tag{36}$$

The reaction rate of peracetic acid formation was expressed as a time change of the degree of conversion. It was given in respect to the dry resin content, in order to avoid dealing with continuous changes of the volume of the polymer phase (due to swelling of the resin). The following expression was obtained:

$$\frac{d\xi_1}{dt} = R k a_A^R a_{H_2O_2}^R \left(1 - \frac{a_P^R\, a_{H_2O}^R}{K_1\, a_A^R\, a_{H_2O_2}^R} \right) \tag{37}$$

This kinetic equation, together with the mass balances:

$$n_i^R + n_i^w = n_{i,0} + \nu_{i,1}\,\xi_1 \qquad i=1,2,\ldots,N \tag{38}$$

and the equilibrium equations for multi–compound sorption:

$$a_i^w = a_i^R \qquad i=1,2,\ldots,N \tag{39}$$

form the kinetic model.

The interaction parameters in equation (36) and the rate constant k in expression (37) were determined separately, either by fitting the data for separate experiments, or were assumed (for peracetic acid). The influence of the mass–transfer resistance was eliminated during the experiments. Since the standard Gibb's free energy of peracetic acid formation cannot be defined with sufficient accuracy, according to the authors [25], the chemical equilibrium constant K_1 was determined by fitting experimental data. The following condition of chemical equilibrium was used:

$$K_1 = \left(\frac{a_P^R\, a_{H_2O}^R}{a_A^R\, a_{H_2O_2}^R}\right)_{eq} \tag{40}$$

The only question related to the previous model was whether the UNIFAC method could be used for the determination of the activity coefficients of the components in the mixtures that contained hydrogen peroxide and peracetic acid, considering the fact that the data for the group contributions for these compounds could not be found in the literature [26]. That meant that the data for the liquid–liquid equilibrium of hydrogen peroxide and peracetic acid were not used for the determination of the group interaction parameters. In the absence of the specified parameters, Musante et al. [25] probably treated H_2O_2 as if it consisted of two OH groups and CH_3COOOH as if it consisted of CH_3COO and OH groups. That could have been a wrong assumption because the interaction parameters for the OH group were determined from data for alcohols [26].

COMPARISON OF THE KINETIC MODELS

In this study we compared a mono–phase pseudo–first order kinetic model (Model 1 given by equations (10)–(12)) to a two–phase model based on the Langmuir– Hinshelwood–Hougen–Watson (LHHW) postulates proposed by the authors of this paper (Model 2 described by equations (29)–(35)). The comparison was based on the experimentally determined values for the *in situ* epoxidation of vegetable oil by peracetic acid formed from acetic acid and hydrogen peroxide in the presence of different quantities of ion exchange resin used as the catalyst.

The kinetic experimental data for the *in situ* epoxidation of soybean oil (the initial iodine number was 130 and corresponded to the concentration of 0.5122 moles of double bonds in 100 g of oil) at 75°C, with 1.1 moles of hydrogen peroxide (30% aqueous solution) and 0.5 mole of acetic acid, in the presence of 2, 5 and 15 wt% (in respect to the sum of the weights of the applied acetic acid and hydrogen peroxide) of dry Amberlite IR 120, were taken from the literature [17]. The Marquardt method [28] was used to fit the experimental data and the Runge–Kutta method of the IV order was applied to solve the system of differential equations.

The results of this comparison are presented in Figures 1–3, each referring to a different quantity of applied catalyst. The figures show the time change of both the experimentally determined values of the iodine number (IN) and the epoxy oxygen content (EO) and the calculated ones, as points and curves, respectively, in both model 1 and 2. The theoretical maximum content of epoxy oxygen calculated from the conversion of the

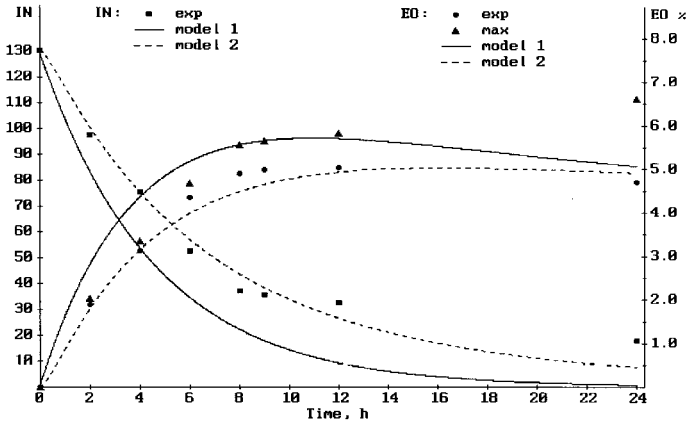

Figure 1. Time dependence of the experimentally determined values (points) and curves calculated by model 1 and model 2 of the iodine number (IN) and epoxy oxygen content (EO) for the in situ epoxidation of soybean oil at 75°C with peracetic acid in the presence of 2% (1.283 g/100g of oil) of Amberlite IR 120

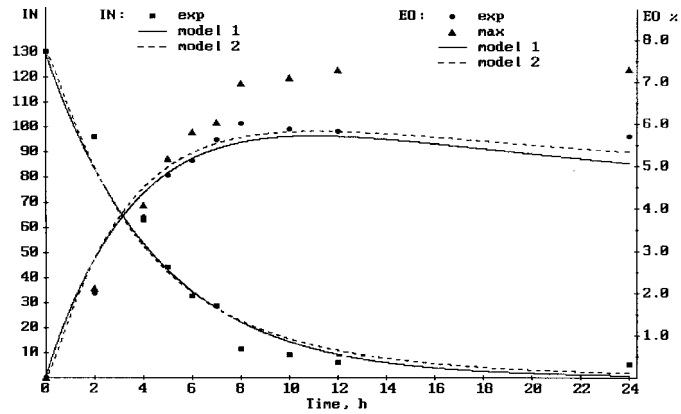

Figure 2. Time dependence of the experimentally determined values (points) and curves calculated by model 1 and model 2 of the iodine number (IN) and epoxy oxygen content (EO) for the in situ epoxidation of soybean oil at 75°C with peracetic acid in the presence of 5% (3.963 g/100g of oil) of Amberlite IR 120

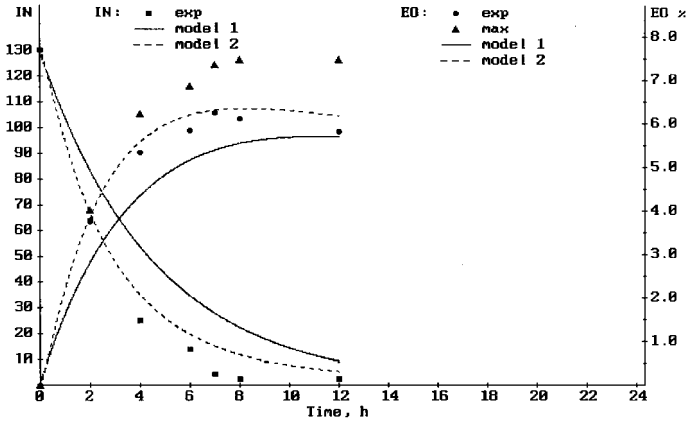

Figure 3. Time dependence of the experimentally determined values (points) and curves calculated by model 1 and model 2 of the iodine number (IN) and epoxy oxygen content (EO) for the in situ epoxidation of soybean oil at 75°C with peracetic acid in the presence of 15% (11.889 g/100g of oil) of Amberlite IR 120

double bonds of the oil reached at a particular time is also presented in the figures. The difference between the theoretical maximum and the experimentally measured content of epoxy oxygen indicated the extent of occurrence of side reactions, i.e. ring opening reactions during epoxidation. It is obvious that model 2 matches the experimental values of the measured variables significantly better than model 1. This may be explained by the impossibility of including the quantity of applied catalyst as a variable to model 1. The first attempt we made to obtain satisfactory data adequate for model 1 was to multiply particular terms in equations (10)–(12) with the value of the applied catalyst concentration. The result was a higher value of the square deviation of the calculated values from the experimental ones. The second approach to solve the problem was the inclusion of the catalyst concentration as a variable by determining a distinct set of parameter values in equations (10)–(12) for each concentration, which would be unacceptable.

THE "IDEAL" MODEL FOR *IN SITU* EPOXIDATION

Based on the discussed requirements for modelling the kinetics of the *in situ* epoxidation of unsaturated fatty acid esters or triglycerides and according to the proposed kinetic models so far, the requirements that could be included in deriving the "ideal" mathematical model could be presented as follows:

• The rate of epoxidation of unsaturated fatty acids depends on the structure of the acids e.g. on the number of double bonds, on their position in respect to the carboxyl group, and on *cis*– or *trans*– isomers, as shown in papers [3,4]. Since most of the vegetable oils that are commercially used for epoxidation contain a small number of these acids, it would be convenient to determine the kinetic parameters for the epoxidation of each acid. Finally, based on the oil composition, the overall rate constant for the epoxidation of the vegetable oil could be calculated.

• The activity of the components in all phases should be used rather than the concentrations in the expressions of the reaction rates, due to the fact that the system is non–ideal. However, an additional examination should be done for the *in situ* formation of peracid in the presence of ion exchange resin in order to determine whether the approach with activity coefficients in both aqueous and polymer phases, recommended by Musante et al., is really necessary; or, as a small quantity of catalyst is usually used, the simpler LHHW approach, which requires only activities in the aqueous phase, can be applied.

• The intensity of agitation of the reaction mixture that influences the mass transfer coefficients should be correlated with droplet size and the interfacial area, and these values should be related to the reaction rates.

CONCLUSION

The reaction system for the *in situ* epoxidation of unsaturated fatty acid esters or triglycerides, by perorganic acid is multi–phase. The formation of peracid occurs in the aqueous phase (diluted hydrogen peroxide is applied), and epoxidation takes place in the oil phase. To facilitate the formation of perorganic acid, an acidic homogeneous (traditionally sulphuric acid) or heterogeneous (an ion exchange resin) catalyst can be used. In the latter case a third phase – a solid phase is introduced into the system. Besides the mentioned reactions, secondary (acid–catalysed) side reactions of oxirane cleavage do appear.

The description of the kinetics of the heterogeneous three–phase system is not easy. Kinetic models that treated epoxidation only as a pseudo mono– or two– phase system have been reported in the literature. In this paper the two–phase model based on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) postulates was compared to a mono–phase pseudo–first order model. The first one fits the experimental data significantly better, although it also has some erroneous aspects.

Based on the critical discussion of the kinetic models reviewed in this paper, it was concluded that a rigorous model for *in situ* epoxidation in the presence of an ion exchange resin as the catalyst for perorganic acid formation has still not been given. That is why some requirements for the creation of an "ideal" model are defined in this paper, while the necessary experiments and calculations for extending the existing model, given by the authors of this paper, are in progress [16,29].

NOMENCLATURE

A – acetic acid
a_i – activity of the *i*th species
C – concentration, mol/l
C_s – concentration of active sities, g^{-1}
D – double bond
E – epoxy group
EO – epoxy oxygen content, %
G – glycol
H – hydroxy acetate
IN – iodine number
K_j – chemical equilibrium constant of the *j*th reaction
K_A, K_P – partition coefficient between oil and water for acetic acid and peracetic acid, respectively
K_S – sorption equilibrium constant
k_j – rate constant of the *j*th reaction
k_La – mass transfer coefficients
k_{sr} – rate constant of the surface reaction
M_k – mass of the catalyst, g/100g oil
m_{ij} – molar volumes ratio of the *i*th and *j*th species
N – total number of species
n_i – number of moles of the *i*th species
P – peracetic acid
R – resin, g
r_j – rate of the *j*th chemical reaction, mol/Lmin
s – active catalytic site
S – side products
t – time, min
V – volume, L
V_i – molar volume of the *i*th species, L/mol
v_i – volume fractions of the *i*th species
Y_A – empirical coefficient

Greek Letters

η – number of moles of active elastic chains per unit volume, L^{-1}
$\nu_{i,j}$ – stoichiometric coefficient of the *i*th component in the *j*th reaction
ξ_j – degree of conversion of the *j*th reaction
χ_{ij} – molecular interaction between components *i* and *j*

Superscript

O – oil phase
W – aqueous phase
R – resin

Subscript

A – acetic acid
D – double bond
E – epoxy group
P – peracetic acid
S – side products

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IZVOD

KINETIČKI MODELI REAKCIONIH SISTEMA ZA *IN SITU* EPOKSIDOVANJE ESTARA I TRIGLICERIDA NEZASIĆENIH MASNIH KISELINA

(Pregledni rad)

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Reakcioni sistem za *in situ* epoksidovanje estara i triglicerida nezasićenih masnih kiselina, koji su osnovni sastojak biljnih ulja, peroksiorganskom kiselinom je višefazni sistem. U njemu se kiselo katalizovana sinteza perkiseline odvija u vodenoj fazi (koristi se vodeni rastvor vodonik peroksida), dok se epoksidovanje odvija u uljnoj fazi. Za formiranje perkiseline može da se koristi ili homogeni (obično je to sumporna kiselina) ili heterogeni (neka jonoizmenjivačka smola) kiseli katalizator. U ovom poslednjem slučaju se u sistem uvodi i treća – čvrsta faza. Pored formiranja perorganske kiseline i osnovne reakcije epoksidovanja, u ovom višefaznom reakcionom sistemu se odvija i niz sporednih kiselo katalizovanih reakcija otvaranja nastalog epoksi prstena.
Opisivanje kinetike ovog heterogenog trofaznog reakcionog sistema nije lako. U literaturi su se do sada pojavili kinetički modeli koji su sistem definisali kao pseudo mono– ili dvofazni sistem. U ovom radu je upoređen dvofazni model zasnovan na Langmuir–Hinshelwood–Hougen–Watson (LHHW) postulatima sa jednim jednofaznim modelom pseudoprvog reda. Dvofazni model mnogo bolje fituje eksperimentalne podatke, iako i sam ima neke, u radu diskutovane, nedostatke.
Na osnovu kritičke diskusije kinetičkih modela prikazanih u radu zaključeno je da do sada još nije predložen rigorozni model koji bi opisivao *in situ* epoksidovanje u prisustvu jonoizmenjivačke smole kao katalizatora za formiranje perorganske kiseline. Zato su definisani neki uslovi potrebni da bi se postavio "idealni" model, dok se neophodni dodatni eksperimenti i proračuni izvode u cilju poboljšanja već postojećeg modela datog od strane autora ovog rada [16,29].

Ključne reči: Epoksidovanje • Kinetika • Matematički model • Trigliceridi nezasićenih masnih kiselina •

Key words: Epoxidation • Kinetics • Mathematical model • Unsaturated fatty acid triglycerides •