Model for a Cascade Continuous Epoxidation Process

Xiaomin Hang and Hong Yang*
Deptartment of Biology Science and Technology, School of Life Science
and Biotechnology, Shanghai Jiaotong University, Shanghai 200240, China

ABSTRACT: A steady-state mathematical model was developed to analyze the performance of a cascade continuous epoxidation process that was applied to the epoxidation of unsaturated compounds with *in-situ*-formed performic acid. The model equations were nonlinear, and the model prediction was calculated by solving the model equations using a numerical solution procedure. The experimental results supported the model prediction in that good agreement between the model predictions and experimental results was achieved. The model is necessary for precise operation control, process estimation, and operating parameter optimization and regulation, and will provide a theoretical foundation and research method for automatic control and engineering scale-up.

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KEY WORDS: Cascade, continuous epoxidation, epoxidation, model, optimization, performic acid.

The epoxidation of unsaturated fatty acid derivatives, primarily soybean oil and other vegetable oils, is carried out on an industrial scale, producing plasticizers that are compatible with polyvinyl chloride (PVC) and which also act as PVC stabilizers, primarily against heat degradation. In general, the degree of compatibility and stability of an epoxidized oil increases with increasing purity and oxirane number. The iodine value (IV) is a measure of the number of double bonds, while the oxirane value (EPO) is an indication of the percentage content (%, by wt) of epoxide oxygen. The quality of the epoxidized oil is better the higher the oxirane value and the lower the iodine number (1–3).

Several processes are available for the preparation of epoxidized oils. The most widely used process is the epoxidation of unsaturated compounds with either pre- or *in-situ*-formed organic peracids. *In-situ* epoxidation using hydrogen peroxide with either acetic or formic acid as the peroxygen carrier has achieved commercial importance (4–7). With hydrogen peroxide and acetic acid, however, acid catalysts, such as sulfuric acid or strong cation exchange resins, are needed to speed up peracid formation, whereas performic acid formation requires no strong acid. In our laboratory, the previous study of the kinetics and mechanism of the epoxidation of oils with *in-situ*-formed performic acid, as well as the kinetics of oxirane cleavage of epoxidized silkworm pupae oil, showed that formation as well as cleavage of the oxirane ring occurred simultaneously during the epoxidation process. The results indicate that the net yield of epoxides is determined by rates of both reactions, which depend on several factors, such as organic acid concentration and reaction temperature (8,9).

Compared with a batch process, a continuous process has three advantages: (i) stable product quality; (ii) convenience, because of use of automatic control; and (iii) lower production costs. Additionally, the continuous process is useful for controlling by-product formation and improving reaction selectivity and yield by changing material contacting time and reaction temperature.

Although the epoxidation of unsaturated oils has been extensively investigated, mathematical modeling of a continuous epoxidation process is limited. The purpose of the present paper is to develop the mathematical model of a continuous stirred-tank cascade epoxidation process. It is aimed also at establishing a steady-state mathematical model to describe the process and providing a theoretical foundation and research method for the automatic control and engineering scale-up.

MATERIALS AND METHODS

Materials. Silkworm pupae oil (SWO) was refined from fresh silkworm pupae (Zhenjiang Jinhua Silkworm Pupae Process Factory, Zhenjiang, China) by pressing, extracting, degumming, and alkali refining. Hydrogen peroxide (~30%) was obtained from Jiangyin Chemical Reagent Factory (Jiangsu, China). Formic acid (98%) was obtained from Yixing Chemical Reagent Factory (Jiangsu, China).

Cascade continuous epoxidation process. The flow chart of the epoxidation process is shown in Figure 1.This process includes three or four stirred-tank epoxidation reactors with the same volume, a continuous feed and sampling outlet, and temperature and stirring controllers. Unsaturated oil, formic acid, and hydrogen peroxide were continuously introduced into the first reactor, then the reaction mixture was continuously fed to the next reactor, and finally the crude product from the last reactor was placed in a separator. The aqueous layer was drawn off, and the ester layer was washed in successive steps as described elsewhere (8,9) until acid-free. The final product was analyzed for the iodine (10) and oxirane (11) values according to AOCS methods.

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*To whom correspondence should be addressed.
E-mail: hongyang@online.sh.cn

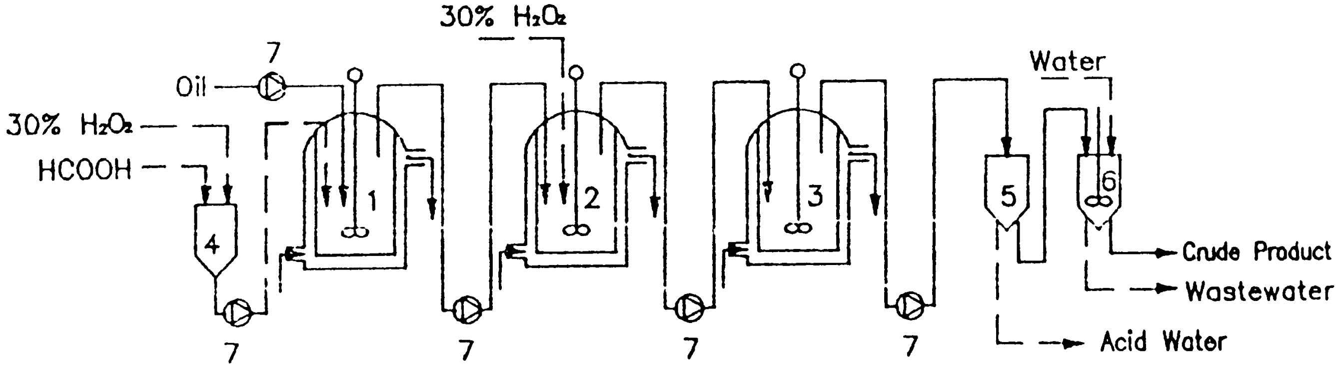

FIG. 1. Flow chart of continuous stirred-tank cascade epoxidation process. 1,2,3, stirred-tank reactor; 4, storage tank; 5, sedimentation tank; 6, washing tank; 7, pump.

RESULTS AND DISCUSSION

Notation. U, unsaturated double bonds; H, hydrogen peroxide; F, formic acid; P, peroxyformic acid; E, oxirane bond; B, by-product from the cleavage of oxirane ring; M_0, moles of one reactant introduced into the first reactor per minute, mol/min; $V_{r,0}$, volume flow rate of total reactants introduced into the first reactor, L/min; C_0, concentration of one reactant introduced into the first reactor, mol/L; reactors designated as $i = 1, 2, 3$; M_i, $V_{r,i}$, C_i, outlet moles of one reactant per min (mol/min), outlet volume flow rate (L/min), and concentration (mol/L) of one reactant from reactor i, respectively; V_i, volume of total reactants, L; T_i, average residence time, min; r_i, reaction rate of oxirane formation, mol × L^{-1} × min^{-1}; $r_{c,i}$, reaction rate of oxirane ring cleavage, mol × L^{-1} × min^{-1}; X_i, conversion (% by mole); $R_{V,i}$, volume flow ratio of total reactants introduced into reactor $(i - 1)$ to i.

Mathematical model development. Based on the prior study (8,9), an equal mixed-flow model was applied to analyze the performance of a cascade continuous epoxidation process. A material account for reactants in reactor i is proposed as follows: Moles of each reactant introduced into reactor i are expressed as $M_{i-1} = V_{r,i-1} \times C_{i-1}$; if hydrogen peroxide is added in batches, moles of hydrogen peroxide introduced into reactor i can therefore be expressed as:

$$M_{H,i-1} = V_{r,i-1} \times C_{H,i-1} + W_i;$$

$$W_i = (V_{r,i} - V_{r,i-1}) \times 1.1 \times 30\% \times 1000/34 = 9.706(V_{r,i} - V_{r,i-1})$$

where W_i is moles of fresh hydrogen peroxide added to reactor i per minute, mol/min; 1.1, specific gravity of 30% hydrogen peroxide, kg/L; 34, molecular weight of hydrogen peroxide. Moles of each reactant exiting from reactor i are expressed as $M_0(1 - X_i) = V_{r,i}C_i$; for two reactants, U and H, moles of each reacted in reactor i are indicated as r_iV_i; whereas, for F, its moles reacted in reactor i are $r_{C,i}V_i$; and moles of each reactant accumulated in reactor i are zero. In reactor i, when this system is at steady state, moles of each reactant introduced into reactor i should be equal to the sum of moles of each reactant exiting from reactor i and of each reactant reacted and accumulated in reactor i. Therefore, $M_{i-1} = M_0(1 - X_i) + r_iV_i$ (or $r_{C,i}V_i$, in calculations for F) + 0; a material balance for each kind of reactant in reactor i yields

for U, $$V_{r,i-1}C_{U,i-1} - V_{r,i}C_{U,i} - r_iV_i = 0 \qquad [1]$$

for H, $$V_{r,i-1}C_{H,i-1} + 9.706(V_{r,i} - V_{r,i-1}) - V_{r,i}C_{H,} - r_iV_i = 0 \qquad [2]$$

for F, $$V_{r,i-1}C_{F,i-1} - V_{r,i}C_{F,i} - r_{C,i}V_i = 0 \qquad [3]$$

A material account for products in reactor i is proposed as follows: moles of each product introduced in reactor i are expressed as $M_{i-1} = V_{r,i-1}C_{i-1}$; moles of each product exiting from reactor i are indicated as $M_0X_i = V_{r,i}C_i$; moles of oxirane ring formation are $(r_i - r_{C,i})V_i$; moles of by-product generated from the cleavage are $r_{C,i}V_i$; and moles of each product accumulated in reactor i are zero. In reactor i, when this system is at steady state, the sum of moles of each product exiting from reactor i and each product accumulated in reactor i is equal to the sum of moles of each product introduced and generated in reactor i. Thus, the following equation is obtained at steady state: for E, $M_0X_i + 0 = M_{i-1} + (r_i - r_{C,i})V_i$, and for B, $M_0X_i + 0 = M_{i-1} + r_{C,i}V_i$; a material balance for products in reactor i can be described by

$$V_{r,i}C_{E,i} - V_{r,i-1}C_{E,i-1} - (r_i - r_{C,i})V_i = 0 \qquad [4]$$

$$V_{r,i}C_{B,i} - V_{r,i-1}C_{B,i-1} - r_{C,i}V_i = 0 \qquad [5]$$

where $$r_i = k_iC_{H,i}C_{F,i} \qquad [6]$$

$$r_{C,i} = k_{C,i}C_{E,i}C_{F,i}^2 \qquad [7]$$

Equations 6 and 7 occurred in the epoxidation process simultaneously and were proposed by the previous work (8,9). By substituting Equations 6 and 7 into Equations 1 to 5,rearranging, and defining k as the reaction rate constant, we find

$$R_{V,i}C_{U,i-1} - C_{U,i} - k_iC_{H,i}C_{F,i}T_i = 0 \qquad [8]$$

$$R_{V,i}C_{H,i-1} + 9.706(1 - R_{V,i}) - C_{H,i} - k_iC_{H,i}C_{F,i}T_i = 0 \qquad [9]$$

$$R_{V,i}C_{F,i-1} - C_{F,i} - k_{C,i}C_{E,i}C_{F,i}^2T_i = 0 \qquad [10]$$

$$-R_{V,i}C_{E,i-1} + C_{E,i} - (k_iC_{H,i}C_{F,i} - k_{C,i}C_{E,i}C_{F,i}^2)T_i = 0 \quad [11]$$

$$-R_{V,i}C_{B,i-1} + C_{B,i} - k_{C,i}C_{E,i}C_{F,i}^2T_i = 0 \quad [12]$$

Equations 8 to 12 are a mathematical model describing the performance of reactor *i* at steady state. This set of equations is nonlinear. Solution requires knowledge of concentrations of reactants, input, and operational parameters; and the model predictions were calculated by solving the model equations using a numerical solution procedure.

Continuous epoxidation experiments, Experiment 1. As shown in Figure 1, all reactants were continuously introduced into the first reactor. First, silkworm pupae oil and formic acid were added at the same time into the first reactor (maintained at 50°C), hydrogen peroxide was added slowly into the first reactor, and then it was maintained at 70°C for 1 h. Finally, the mixture of 1.4 mol hydrogen peroxide per 0.35 mol formic acid and silkworm pupae oil were continuously introduced into the first reactor, and the flow ratio of the aqueous phase to oil phase was controlled at a constant temperature to guarantee that U/H/F = 1.0:1.4:0.35 (mol). The reaction mixture reacted in the first reactor continuously overflowed into the second and third reactors, which were maintained at 70°C. The average residence time in each reactor was 1 h. The reaction mixture exited continuously from the third reactor to the sedimentation tank, then the upper phase went to a washing tank, and finally to a crude product tank, where samples were taken periodically and the IV and oxirane oxygen content of samples were analyzed.

Experiment 2. The procedure was the same as in Experiment 1, except that the reactors were maintained at different temperatures. The first reactor was at 60°C, the second at 70°C, and the third at 80°C. The average residence time was 1 h in the first two reactors and 45 min in the third.

Experiment 3. The procedure was the same as in Experiment 1, except that the H_2O_2 added was in batches. Hydrogen peroxide (1.0 mol) per mol of double bond was introduced into the first reactor as soon as the reaction mixture overflowed the third reactor; 0.4 mol hydrogen peroxide per mol of double bond was continuously added into the second reactor. The residence times corresponded to those of Experiment 1.

Model verification and simulation. Based on the process flow chart (Fig. 1), the whole continuous epoxidation process was controlled by the mathematical model at steady state. The model-predicted concentrations were calculated as follows: Known composition of reactants and operational parameters → Calculated concentrations of reactants at the outlet of the first reactor from the model → Calculated concentrations of reactants at the outlet of the second reactor from the model → → → Calculated concentrations of reactants at the outlet of the reactor $n - 1$ from the model → Calculated concentrations of reactants at the outlet of the reactor *n* from the model. The parameters used in simulation and model predictions are listed in Table 1.

Table 2 shows the comparison between the experimental results obtained in a cascade continuous epoxidation process and the results predicted from the above model. It can be seen that the relative mean error of yields is 2.50%, and the relative greatest error is 2.83%. Good agreement between the model predictions and experimental results was achieved. The yield measured by the experiments was a little lower than the model predictions because the temperature might result in the spoilage of hydrogen peroxide during the course of epoxidation.

Model application. (i) Guidance of the automatic control of the process. During the course of epoxidation, when one or more parameters were changed, the others could be adjusted according to model predictions, thereby determining the desired operational conditions for practical production. For example, epoxidized soybean oil would be synthesized by a three-tank cascade continuous process. The original concentrations of reactants were $C_{U,0} = 2.653$ mol/L, $C_{H,0} = 3.717$ mol/L, $C_{F,0} = 1.063$ mol/L, $C_{E,0} = 0$, $C_{B,0} = 0$. The required characteristics of epoxide were: IV ≤ 4.0, EPO ≥ 6.0%.

TABLE 1
The Parameters Used in Simulation and Model Predictions[a]

Experiment	Reactor[b]	$C_{U,i}$	$C_{H,i}$	$C_{F,i}$	$C_{E,i}$	$C_{B,i}$	T_i	$R_{V,i}$	k_i	$k_{C,i}$
1	0	2.508	3.514	0.893	0	0				
	1	1.205	2.211	0.784	1.194	0.109	60	1	12.531	2.471
	2	0.468	1.474	0.665	1.813	0.228	60	1	12.531	2.471
	3	0.121	1.115	0.604	2.070	0.335	60	1	12.531	2.471
2	0	2.531	3.545	0.902	0	0				
	1	1.598	2.612	0.842	0.874	0.060	60	1	7.074	1.613
	2	0.684	1.698	0.716	1.661	0.186	60	1	12.531	2.471
	3	0.064	1.078	0.598	2.163	0.304	45	1	21.400	3.394
3	0	2.859	2.861	1.006	0	0				
	1	1.715	1.717	0.887	1.025	0.119	60	1	12.531	2.471
	2	0.674	1.686	0.680	1.666	0.221	60	0.896	12.531	2.471
	3	0.164	1.175	0.578	2.074	0.324	60	1	12.531	2.471

[a] Concentrations, mol/L; T_i, min; k_i, $10^3(\text{mol/L})^{-1}\text{min}^{-1}$; $k_{C,i}$, $(\text{mol/L})^{-2}\text{min}^{-1}$.
[b] Zero represents original concentrations; 1,2, and 3 represent the first, second, and third reactors, respectively.
[c] Outlet concentrations (mol/L) of reactants *U, H, F, E,* and *B,* respectively, from reactor *i. U,* unsaturated double bonds; *H,* hydrogen peroxide; *F,* formic acid; *E,* oxirane bond; *B,* by-product from the cleavage of oxirane ring; $R_{V,i}$, volume flow ratio of total reactants introduced into reactor $(i - 1)$ to *i*; *k,* reaction rate constant.

TABLE 2
Comparison of Model Predictions with Experimental Results

				Predicted (%)[a]			Experimental (%)[a]		
Experiment	Reactor	$C_{U,i}$	$C_{E,i}$	C	S	Y	C	S	Y
1	1	1.205	1.194	51.95	91.63	47.60	51.23	91.16	46.70
	2	0.468	1.813	81.34	88.87	72.29	79.67	87.19	69.46
	3	0.121	2.070	95.18	86.72	82.54	94.24	85.53	80.60
2	1	1.598	0.874	36.86	93.68	34.53	34.86	92.18	32.13
	2	0.684	1.661	72.98	89.93	65.63	71.65	89.05	63.80
	3	0.064	2.163	97.47	87.68	85.46	96.32	86.81	83.82
3	1	1.715	1.025	40.01	89.60	35.85	39.17	88.90	34.82
	2	0.674	1.666	73.37	89.71	65.82	72.60	88.86	64.51
	3	0.164	2.074	93.52	87.61	81.93	93.27	86.62	80.79

[a] *C*, conversion; *S*, selectivity; *Y*, yield. For other abbreviations see Table 1.

The operational parameters were determined by model predictions as follows: (i) If each reactor were maintained at 70°C, average residence time was 40, 50, and 60 min in the first, second, and third reactor, respectively, the values obtained would be: IV = 2.14, EPO = 6.51%. (ii) If the first, second, and third reactor were maintained at 60, 70, and 80°C, respectively, and average residence time was 60, 60, and 30 min, respectively, the values obtained would be: IV = 3.53, EPO = 6.42%.

(ii) *Determining the optimal ratio of reaction volumes.* Once the number of reactors and the characteristics of epoxide (EPO and IV) are determined in a stirred-tank cascade continuous process, many repetitions of the model calculation are required to find the optimal ratio of reaction volumes when total reaction volume was nearly the smallest, practically, which would be very useful for the scale-up design of epoxidation process. For example, it was known that the number of reactors, n, was 3, $R_{V,1} = R_{V,2} = R_{V,3} = 1$, the reaction temperature of each reactor was 70°C, and original concentrations were: $C_{U,0} = 2.538$ mol/L, $C_{H,0} = 3.553$ mol/L, $C_{F,0} = 1.017$ mol/L, $C_{E,0} = 0$, $C_{B,0} = 0$, and the characteristics of epoxidized silkworm pupae oil required were: IV ≤ 4.0, EPO $\geq 6.0\%$.

The optimal ratio of reaction volumes between reactors was sought based on the model, and the result indicated that the ratio of first reactor/second reactor/third reactor = 3:4:5 was optimal. When the total residence time was 3 h, the characteristics of the final epoxide were obtained: IV = 3.17, EPO = 6.16%.

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