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Macroscopic kinetics modelling of liquid–liquid reaction system: Epoxidation of fatty acid methyl esters



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ABSTRACT

In industry, mass transfer limitation is a major and widespread problem in most of vegetable oil epoxidation reactors. To improve the quality of products and the efficiency of production, it is essential to understand the law of mass transfer in the epoxidation reaction system. In present work, epoxidation of fatty acid methyl esters with performic acid generated in situ was studied in a stirred vessel at 50-80 °C. At first, the Sauter mean diameter (D₃₂) was determined and correlated, the correlation can predict the D₃₂ evolution of the reaction. Then, individual experiments were performed to separately determine the intrinsic kinetic parameters and the mass transfer parameters. Finally, a macroscopic kinetic model was developed, which can well describe the effect of droplet size on the reaction. Noteworthy, the mass transfer limitation was significantly increased when reaction temperature rises to 80 °C.

1. Introduction

Biodiesel emerges as a renewable resource has good prospects for application. The majority of the commercially available biodiesel is prepared through transesterification of natural sources such as vegetable oil, with short chain alcohol in the presence of base or acid catalysts (Lee et al., 2014). However, the relatively high production cost made biodiesel less competitive as compared to petro-diesel (De Haro et al., 2016). Thus, new applications should be developed for biodiesel as a cheap feedstock to produce valuable fine chemical products. Many researchers work on converting biodiesel into biodegradable products. One of these pathways is to transform the double bonds of fatty acid methyl esters (FAMEs) into epoxy groups. Epoxides have been used for many commercial applications, including additives in lubricant (Adhvaryu and Erhan, 2002; Salimon et al., 2010), co-stabilizer and plasticizers in polymer (Metzger, 2009), stabilizers in chlorine-containing resins (Benaniba et al., 2003), pharmaceuticals (Grinberg et al., 2010), and biofuel additives (Sharma et al., 2007).

The epoxidation of vegetable oils and fats can be carried out on various catalysts, including ion exchange resins (Goud et al., 2007; Jankovic et al., 2014), titanium-based catalysts (Guidotti et al., 2009; Kumar and Ali, 2012), phase transfer catalysts (Cheng et al., 2015), alumina (Hernandez et al., 2017), etc. In industry, the epoxidation of FAMEs is performed by reacting the double bonds with peracetic acid

(PAA) or performic acid (PFA) generated in situ (Santacesaria et al., 2011). Zheng et al., (2016) has given a detailed introduction to the use of PAA or PFA as oxidant during epoxidation. The use of PAA or PFA is a compromise between process safety, energy integration, and kinetics. In this study, the motivations to use PFA are high exothermic reaction system leading to better energy integration, and no need to incorporate acid catalyst. Fig. 1 shows the simplified mechanism of the epoxidation of the FAMEs. In this liquid-liquid reaction system, PFA is generated in situ by reacting FA and H_2O_2 ; then unsaturated group of the oil reacts with PFA which diffuses from the aqueous phase, producing epoxy group and FA; the FA regenerated in the organic phase diffuses into the aqueous phase in the meantime, the Ring-opening reaction in the organic phase and the PFA decomposition in the aqueous phase occur.

The enthalpy of this extremely exothermic reaction is up to -196 kJ/mol (De Quadros and Giudici, 2016). To avoid runaway of reaction temperature in industrial-scale reactors, the addition time of H_2O_2 typically lasts over 2 h to the oil at a temperature of 10 °C below reaction temperature, and then the reaction will be completed after about 10–12 h. However, the total reaction time in lab-scale only takes about 8 h. It means both mass and heat transfer rate are technical bottlenecks in traditional industrial reactors. Hence, some process intensification techniques were applied to the epoxidation of vegetable oil and fats in recent years, including continues reactor (Santacesaria et al., 2012), coupling of hydrodynamic cavitation and static mixer (Wu et al.,

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Nomenclature			Volume of organic phase (L) Population balance model
FAMEs	Fatty acid methyl esters		1
EFAMEs	Epoxy fatty acid methyl esters	Greek let	ters
PFA	Performic acid		
FA	Formic acid	σ	Interfacial tension (N/m)
AA	Acetic acid	$\sigma_{\!sd}$	Standard deviation
DB	Double bond	ρ	Density (Kg/m ³)
EG	Epoxy group	Ø	Holdup
IV	Iodine value	μ	Viscosity (cP)
EV	Epoxy value	w	Mass fraction
D ₃₂	Sauter mean diameter (mm)		
D_{I}	Impeller diameter (mm)	Subscript	s and superscripts
Ν	Agitation speed (rpm)		
We	Weber number	w	Aqueous phase
VI	Viscosity number	0	Organic phase
ΔG^0	Standard dissociation free energy (J/mol)	PFA	Performic acid
ΔH	Standard enthalpy (J/mol)	FA	Formic acid
$K_{a,FA}$	Thermodynamic dissociation constant	HP	Hydrogen peroxide
K_1	Equilibrium constant of the perhydrolysis reaction	C=C	Double bond
R	Gas constant (J/(mol•K))	perh	Perhydrolysis
k_i	Rate constant of the reactions $(i = 1, 2, 3, 4, 5)$	decomp	Decomposition
$k_{\rm FA}$	Mass transfer coefficient of FA (m/min)	epox	Epoxidation
$k_{\rm PFA}$	Mass transfer coefficient of PFA (m/min)	ro	Ring-opening
V^w	Volume of aqueous phase (L)		



Fig. 1. Simplified mechanism of the epoxidation of the FAMEs.

2017), single addition of H_2O_2 (De Quadros and Giudici, 2016), microwave technology (Aguilera et al., 2016) and ultrasonic technique (Chavan et al., 2012; Chavan and Gogate, 2015). According to the characteristic of the reaction and the need of process intensification, mass transfer kinetic and thermal study should be examined in detail.

In the past few decades, the kinetics of vegetable oil epoxidation have been studied widely, considering the two-phase system as a homogeneous system (Petrović et al., 2002; Okieimen et al., 2002; Goud et al., 2006; Dinda et al., 2008; De Haro et al., 2016), a pseudohomogeneous system (Campanella et al., 2008; Zheng et al., 2016) or a heterogeneous system (Santacesaria et al., 2011; Rangarajan et al., 1995; Wu et al., 2016). Normally a two-phase model, which takes into account transport parameters, is more in line with the actual situation. Most kinetic studies in literature were mainly focused on the intrinsic kinetics of epoxidation. Santacesaria et al. (2011) and Zheng et al. (2016) systematically conducted thermal study. Though the two-phase model developed in literature considered the mass transfer parameters, only volumetric mass transfer coefficients were estimated (Santacesaria et al., 2011; Rangarajan et al., 1995) or the mass transfer area was roughly estimated (Wu et al., 2016). This information obviously is not enough for the design or scale-up of such kind of reactors (because the droplet size distribution character significantly affects the behavior of such systems.).

As we know, no kinetic model investigating mass transfer process in detail was developed for the epoxidation of vegetable oils and fats. In the study, we proposed a macroscopic kinetic model for the epoxidation of FAMEs. D_{32} study was firstly conducted using high speed camera to predict the evolution of mass transfer area with reaction advancement and temperature. Then three parts of experiments were conducted to separately determine the intrinsic kinetics and mass transfer coefficients of FA and PFA using nonlinear regression method.

2. Experimental

2.1. Materials and chemicals

The iodine value of the FAMEs was 125 (g I₂/100 g oil), which was produced from soybean oil by transesterification. Briefly, the transesterification was carried out by reacting soybean oil with methanol using KOH as a catalyst at 60 °C, and the mass ratio of soybean oil/ methanol/ KOH was 1/0.3/0.01. The composition of FAMEs is shown in Table 1. The H₂O₂ used in the work was 50 wt %, and the FA was 95 wt %. All reagents used in the analysis process were analysis-grade, and without further treatment.

2.2. Preparation of epoxy fatty acid methyl esters (EFAMEs)

150.0 g of FAMEs, 9.0 g of FA were added into a 500 ml glass reactor at 60 °C. Then, 75.3 g of H_2O_2 was introduced drop wise in 30 min. The reaction time was 10 h. Then the aqueous phase was removed after reaction. The organic phase was exhaustively washed by deionized water to eliminate acidity and dried using a rotary evaporator. The epoxy value and iodine value of the final EFAMEs were 6.03 and 1.95, respectively.

2.3. Physical properties of FAMEs, EFAMEs, FA, H₂O₂ and H₂O

The physical properties of FAMEs, EFAMEs, FA, H_2O_2 and H_2O at 50–80 °C are summarized in Table 2. Density was measured using a 5 cm³ pycnometer at atmospheric pressure. Kinematic viscosity was measured by a viscometer calibrated with pure water at atmospheric pressure. Interfacial tension was measured by Pendant drop method and Wilhelmy plate method at atmospheric pressure.

2.4. Droplet size measurement

2.4.1. Measurement method of droplet size

A wide variety of experimental techniques have been utilized to monitor droplet size in a stirred-vessel system such as photography (Wu et al., 2017), laser granulometry (Maindarkar et al., 2013), particle video microscope (Qi et al., 2015). In this research, a video technique was developed by a high-speed digital camera (PHOTRON, FASTACM SA-X2) which was used to measure the droplet size in a stirred-vessel. Fig. 2A presents the schematic drawing of the apparatus for data acquisition. The camera lens used was "AF micro-Nikkor ED 200 mm f/4 D IF" and extension tubes were used to increase the amplification constant. The substance in the glass reactor can be heated by water bath. The water/oil system can be recorded using the high speed camera after reducing the height of the lifting platform. This process takes less than 10 s, and the temperature in the reactor has little change. The frame duration was 0.08 ms in this work. In this way, 12,500 frames can be obtained per second, which guarantees the selection of images with high quality.

The images obtained need to be treated for extracting the droplet size. Fig. 2B shows the image obtained in the method. The droplet size was determined from image processing as follows: to obtain statistically reliable results, more than 500 droplets was manually performed in each condition. During production, the image was focused on the size-defined black article as shown in Fig. 2B, which means the drops filmed clearly were nearly on the same surface. Then the droplet size was determined by comparing the drops size with the size-defined black article.

2.4.2. Operating conditions

In a given stirred-vessel system, the droplet size is mainly affected by physicochemical properties of the system, agitate speed and holdup (Tavlarides and Stamatoudis, 1981). It is difficult to measure the droplet size distribution in a reaction system. It is mainly because that the oil and aqueous phase composition changes with the reaction time in the epoxidation reaction, and the corresponding properties of the system changes over the time. In addition, the poor transmittance and high holdup of the reaction system give rise to difficulties in the experimental measurement. To improve the accuracy and operability of measurement, it is necessary to simplify the system. The droplet size was investigated in the absence of FA, which means no reaction occurs.

The droplet size in H₂O/FAMEs and H₂O/EFAMEs systems was investigated at four holdups (0.05 < hold up < 0.25) and four different agitation speeds (100 < Agitation speed (rpm) < 400 rpm) at 50 °C. The droplet size in H₂O₂/FAMEs system was investigated at four different agitation speeds with two different holdups at 50 °C. To investigate the effect of temperature on droplet size, the droplet size in H₂O/FAMEs system was also carried out at four different agitation speeds with two different holdups at 70 °C. The properties (continuous phase density, disperse phase viscosity and interfacial tension) of FAMEs, EFAMEs, FA, H₂O₂ and H₂O at 50–80 °C were measured and listed in Table 2, which are important for correlation of D₃₂.

2.5. Kinetic experiments

Experiments carried out in this part were aimed at estimating the kinetic parameters involved in the reaction system. The epoxidation process mainly includes FA perhydrolysis, PFA decomposition, double bond epoxidation, Ring-opening reaction and mass transfer of FA and PFA (Rangarajan et al., 1995; Santacesaria et al., 2011; Zheng et al., 2016). Based on consulting literature, Filippis et al., (2009) and Sun et al., (2011) have made a kinetic study of FA perhydrolysis and PFA decomposition. The kinetic parameters of FA perhydrolysis and PFA decomposition obtained by Filippis were used in present work after mathematical analysis. While there is little research on epoxidation of FAMEs, Ring-opening reaction of EFAMEs and mass transfer of FA/PFA. Hence, three parts of kinetic experiments were performed separately to estimate the residual kinetic parameters.

In part I: Ring-opening reactions of EFAMEs without mass transfer limitation (Table 3 summarizes the experimental matrix) were carried out to estimate the rate constants and activation energy of EFAMEs ring-opening reaction caused by FA and H_2O .

In part II: FAMEs epoxidation without mass transfer limitation (Table 4 summarizes the experimental matrix) were carried out to estimate the rate constants and activity energy of FAMEs epoxidation reaction and EFAMEs ring-opening reaction caused by PFA.

In part III: FAMEs epoxidation with mass transfer limitation (Table 5 summarizes the experimental matrix) were carried out to estimate the mass transfer coefficients of FA and PFA.

The apparatus for experiments is the same with the reactor shown in Fig. 2A. The glass reactor (250 mL) has four necks, equipped with a thermometer, a reflux condenser, an elevated tank for adding H_2O_2 and a motor-driven agitator. Temperature control was realized by recirculating thermostatic water in a constant temperature bath, with the temperature error within 1 °C. The speed of the agitator could be set on the meter.

Table 1

Composition of the fatty acid methyl esters (FAMEs) mixtures.

Fatty acids		Composition (wt. %)
Name	Symbol	
Myristate	C14:0	0.37
Palmitate	C16:0	8.51
Stearate	C18:0	3.42
Oleate	C18:1	30.35
Linoleate	C18:2	55.46
Linolenate	C18:3	1.14
Others	C18+:0	0.89

Table 2

Physical properties of FAMEs, EFAMEs, FA (95 wt%), H₂O₂ (50 wt%) and H₂O at 50-80 °C. [a. Interfacial tension between FAMEs and H2O; b. Interfacial tension between EFAMEs and H₂O; c. Interfacial tension between FAMEs and H₂O₂.].

Substance	Density (kg/m ³) 50/60/70/80 °C	Viscosity (×10 ⁻³ Pa s) 50/60/70/80 °C	Interfacial tension (×10 ⁻³ N/m) 50/60/70/80 °C
FAMEs	860/853/847/ 840	2.96/2.48/2.12/ 1.84	26.8/27.7/28.8/29.4 ^a
EFAMEs	932/925/918/ 911	7.99/6.16/4.91/ 3.98	17.5/18.7/19.1/19.8 ^b
FA	1183/1171/ 1158/1142	1.04/0.91/0.80/ 0.70	-
H_2O_2	1170/1160/ 1152/1142	0.71/0.63/0.56/ 0.50	21.3/21.9/22.8/23.1 ^c
H_2O	988/983/978/ 972	0.55/0.47/0.41/ 0.36	-

A typical experimental procedure of ring-opening reaction (Part I) was as follows: a given mass of EFAMEs was added into the reactor and heated to the reaction temperature, then FA and water were preheated to the same temperature and added to the reactor. Samples were taken from the reactor periodically. The aqueous phase was separated from the samples by using centrifuge. The FA concentration in the aqueous phase was measured by titration with NaOH. The oil phase was thoroughly washed with deionized water, followed by desiccation with a rotary evaporator. The concentrations of double bond and epoxy group in the oil phase were measured by titration.

A typical experimental procedure of the epoxidation reactions (Part II and Part III) was as follows: a given mass of FAMEs was added into the reactor followed by the addition of FA. The mixture of FAMEs and FA was mixed driven by the agitator. Then H₂O₂ was added into the system steadily in 30 min, when the mixture temperature reached the value of reaction temperature. The treatment method of the samples is the same with part I.

2.6. Analytic methods

The analytic methods of iodine value and epoxy value were the same with our previous work (Wu et al., 2017).

3. Results and discussion

3.1. The effects of various factors on D_{32}

Fig. 3 shows the effect of agitation speed on D_{32} at four different dispersed phase holdups for a system with H₂O as disperse phase and

Table 3	
Experimental matrix for EFAMEs Ring-opening reaction.	

RUN	T (°C)	Oil mass (g)	Aqueous mass (g)	$C_{H_2O}^w$ Initia	C ^w _{FA} al value (n	C ^o _{EP} nol/L)
1	50	100.38	65.11	45.22	4.35	3.51
2	60	100.42	53.86	48.49	2.99	3.48
3	70	99.32	61.88	46.88	3.67	3.45
4	70	101.75	63.80	49.80	2.63	3.45
5	80	100.02	68.02	50.37	2.18	3.43

Table 4

Experimental matrix for FAMEs epoxidation with performic acid generated in situ without mass transfer limitation.

RUN	T (°C)	Agitation Speed (rpm)	Organic Mass (g)	H ₂ O ₂ Mass (g)	FA Mass (g)	Total duration (min)
6	50	500	89.98	45.16	5.36	600
7	60	500	90.04	45.18	5.37	600
8	70	500	90.01	45.16	5.36	480
9	80	500	90.00	45.18	5.37	240
10	50	500	90.00	39.15	7.50	600
11	60	500	90.04	54.18	8.56	600
12	70	500	89.99	51.20	3.23	480
13	80	500	90.00	36.16	3.22	240

Table 5

Experimental matrix for FAMEs epoxidation with performic acid generated in situ with mass transfer limitation.

RUN	T (°C)	Agitation Speed (rpm)	Organic Mass (g)	H ₂ O ₂ Mass (g)	FA Mass (g)	Total duration (min)
14	50	150	89.98	45.16	5.36	600
15	50	200	90.04	45.18	5.37	600
16	60	150	90.01	45.16	5.36	680
17	60	200	90.00	45.18	5.37	640
18	70	150	90.02	45.18	5.37	480
19	70	200	89.98	45.16	5.36	480
20	80	150	90.04	45.18	5.37	240
21	80	200	90.01	45.16	5.36	240

FAMEs as continue phase.

An increase in the agitation speed led to smaller D_{32} and higher drop breakage frequency. For each holdup, D_{32} was correlated with We as a function with an exponent of -0.5731, verifying the applicability of Hinze-Kolmogorov's theory to this system. Fig. 3 also shows that higher holdup leads to larger D₃₂, which is due to higher collision frequency between drops resulting from higher holdup. The results highlight the



1-lift platform; 2-water bath; 3-reactor; 4-condenser; 5-agitator; 6-thermocouple;

7-paperless recorder; 8-light source; 9-lens; 10-extension tube; 11-high-speed camera; 12-computer; Fig. 2. A-schematic drawing of the apparatus for data acquisition; B-drops in the stirred-vessel.



Fig. 3. The effects of agitation speed and holdup on D₃₂.

relevance of inter-drop coalescence in determining the behavior of liquid-liquid dispersions. These findings are consistent with results published in literature (Calabrese et al., 1986).

Figs. 4 and 5 show the effect of the composition of the oil phase and the aqueous phase on D_{32} . Based on the results, when D_{32} is plotted versus the agitation speed for each holdup (0.0595, 0.1128, 0.1618 and 0.2026), the curves present the same trend. Therefore, the figures are plotted at 0.0595 and 0.1128 of holdups and the corresponding results are reported in Figs. 4 and 5. Fig. 4 shows the effect of the continue phase composition (FAMEs and EFAMEs) on D₃₂ with H₂O as the disperse phase. The results show that the D₃₂ of EFAMEs/H₂O system is smaller than that of FAMEs/H₂O system. Fig. 5 shows the effect of the disperse phase composition (H₂O and H₂O₂) on the D₃₂ with FAMEs as the continue phase. The results show that the D₃₂ of FAMEs/H₂O₂ system is smaller than that of FAMEs/H₂O system. These findings can be explained from the aspects of interfacial tension, disperse phase viscosity and disperse phase density. Calabrese et al. (1986) and Wang and Calabrese (1986) studied the relative influence of interfacial tension and dispersed-phase viscosity on equilibrium D_{32} in a stirred-tank vessel and illuminated the surface and viscous contributions to the relative resistance to breakage and that droplet size distribution broadened as interfacial tension and viscosity increased. As shown in Table 2, the interfacial tension of EFAMEs/H₂O was smaller than that of FAMEs/H2O, which decreased the resistance to breakage of drops, hence the D₃₂ of EFAMEs/H₂O system was smaller. While comparing the FAMEs/H₂O₂ system and FAMEs/H₂O system, the viscosity of H₂O₂ was slightly larger than that of H₂O, which decreased the breakage frequency of drops. However, the interfacial tension of H2O2/FAMEs was smaller than that of H₂O/FAMEs and density of H₂O₂ is larger than that of H₂O, which increased the breakage frequency of drops, resulting in the smaller D₃₂ of FAMEs/H₂O₂ system.

Fig. 6 shows the effect of temperature on the D_{32} at holdups of 0.0552 and 0.1050 in the FAMEs/H₂O system. The result shows that the D_{32} slightly decreased with the increase in temperature. It was due to the slight decrease in interfacial tension and disperse phase viscosity with increasing temperature, which reduced the resistance to breakage of drops.

3.2. Correlation of D₃₂

The D_{32} in an agitated vessel has been correlated by many investigators. D_{32} depends on the physicochemical properties of the system, the turbulence intensity, and the holdup fraction. The most frequently reported correlation is in the form of an increasing linear of the holdup (Tavlarides et al., 1981):

$$\frac{D_{32}}{D_{\rm I}} = C_1 (1 + C_2 \emptyset) \text{We}^{C_3} \text{ with We} = \frac{\rho_c N^2 D_I^3}{\sigma}$$
(1)

where $D_{\rm I}$ is the impeller diameter, C_1 , C_2 and C_3 are constants, \emptyset is the holdup, We is the impeller Weber number, σ is the interfacial tension, ρ_c is the continuous phase density and N is the agitation speed. This equation is simple, but it usually has a large error (Khakpay et al., 2009).

Calabrese et al. (1986) developed the following correlation using a semi-empirical approach:

$$\frac{D_{32}}{D_{\rm I}} = C_1 W e^{-0.6} \left(1 + C_2 V_I \left(\frac{D_{32}}{D_I} \right)^{1/3} \right)^{0.6} \text{ with } V_I = \frac{\mu_d N D_I}{\sigma}$$
(2)

where C_1 and C_2 are constants, V_l is viscosity number and μ_d is disperse phase viscosity. The correlation shows the effects of process variables under a dilute liquid-liquid suspension, yet the effect of holdup is not included.

Khakpay et al., (2009) developed a modified correlation on the bases of Eqs. (1) and (2):

$$\frac{D_{32}}{D_1} = C_1 (1 + C_2 \varnothing) \left(1 + C_3 V_I \left(\frac{D_{32}}{D_I} \right)^{C_4} \right) W e^{C_5}$$
(3)

where C_1 , C_2 , C_3 , C_4 and C_5 are constants. The correlation considers the effects of all parameters with good accuracy. Therefore, Eq. (3) was adopted for D_{32} correlation in this work.

The constants of the correlation were calculated by the least square method using "lsqnonlin" package in MATLAB. Then the correlation for the D_{32} prediction is:

$$\frac{D_{32}}{D_{\rm I}} = 0.1422(1+1.1467\emptyset) \left(1+22658V_I \left(\frac{D_{32}}{D_I}\right)^{1.7669}\right) We^{-0.5731}$$
(4)

Fig. 7 shows the calculated D_{32} using Eq. (4) and measured D_{32} from the experiments. The results depicted that the correlation is in a good agreement with the experiment data. The average standard deviation for the 48 values is $\sigma_{sd} = 4.95\%$, where

$$\sigma_{sd} = 100 \times \left[\frac{1}{n} \sum_{i=1}^{1} \left(D_{32m} - D_{32c}\right)_{i}^{2}\right]^{1/2}$$
(5)

where *n* is the number of experiments, D_{32m} is the measured D_{32} and D_{32c} is the calculated D_{32} .

The density, viscosity and interfacial tension of the mixture vary with the reaction advancement. In case of mixture, densities and viscosities can be expressed as (Ramírez Verduzco, 2013):



Fig. 4. The effect of the continue phase composition on D_{32} .





Fig. 7. The comparison of the calculated and measured D_{32} value.

 $\rho_{\text{mixing}} = w_{\text{FAME}} \cdot \rho_{\text{FAME}} + w_{\text{EFAME}} \cdot \rho_{\text{EFAME}} \tag{6}$

 $In \mu_{mixing} = w_{FAME} \cdot In \mu_{FAME} + w_{EFAME} \cdot In \mu_{EFAME}$ (7)

The results in Table 2 show that the interfacial tension had little change with temperature. During epoxidation, the interfacial tension decreased with the increase of EFAMEs, while the consumption of H_2O_2 increased the interfacial tension. Hence, it is reasonable to consider the interfacial tension as a constant (0.02 N/m).

Overall, the evolution of D_{32} with the conversion of double bond can be calculated by combining Eqs. (4), (6) and (7).

3.3. Kinetic model

3.3.1. Reactions involved in the reaction system

Fig. 1 summarizes the main reactions and mass transfer during FAMEs epoxidation by PFA generated in situ. In the aqueous phase, the FA perhydrolysis reaction system involves FA perhydrolysis and PFA decomposition reactions. In the organic phase, epoxidation of double bond and Ring-opening reaction caused by PFA, FA and H_2O occur.

3.3.2. Kinetic equations

The rate equation for FA perhydrolysis reaction can be written as:

$$r_{FA}^{perh} = k_1 \sqrt{K_{a,FA} C_{FA}^{w}} \left((C_{FA}^{w} C_{HP}^{w}) - \frac{1}{K_1} C_{PFA}^{w} C_{H_2O}^{w} \right)$$
(8)

where $K_{a,FA}$ is the thermodynamic dissociation constant, which is determined by the following equation (Sun et al., 2011):

$$InK_{a,FA} = \frac{-\Delta G^0}{RT}, \ \Delta G^0 = 21kJ \cdot mol^{-1}$$
(9)

where ΔG^0 is the standard dissociation free energy of FA.

 K_1 is the equilibrium constant of the perhydrolysis reaction, which was determined to be equal to 0.8 at 25 °C (Filippis et al., 2009), and expressed by van't Hoff equation:

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$
(10)

where the standard enthalpy ΔH was determined to be equal to -5580 J/mol (Zheng et al., 2016).

ThePFA decomposition follows a first order kinetic, expressed as: $r_{\text{DEFA}}^{\text{decomp}} = k_2 C_{\text{DEFA}}^w$ (11)

$$p_{FA} = \kappa_2 c_{PFA}$$
 (11)

The double bond epoxidation is expressed as:

$$r_{C=C}^{epox} = k_3 C_{\rm PFA}^o C_{\rm C=C}^o \tag{12}$$

The Ring-opening reaction of EFAMEs is mainly caused by FA, PFA and H_2O in the presence of hydrogen ion, and expressed as:

$$r_{EFAMEs}^{r_0} = \sqrt{K_{a,FA}C_{FA}^w} \left(k_4 C_{FA}^w C_{C=C}^o + k_5 C_{PFA}^w C_{C=C}^o + k_6 C_{H_2O}^w C_{C=C}^o \right)$$
(13)

The mass transfer kinetic equation can be expressed as:

$$r_{FA}^{m} = \frac{6k_{FA}V^{w}}{D_{32}}(C_{FA}^{o} - C_{FA}^{w}K_{FA})$$
(14)

$$r_{PFA}^{m} = \frac{6k_{PFA}V^{w}}{D_{32}} \left(C_{PFA}^{w} - \frac{C_{PFA}^{o}}{K_{PFA}} \right)$$
(15)

where K_{FA} and K_{PFA} are equilibrium constants in two phases, which were determined to be equal to 0.035 and 0.095, respectively (Campanella et al., 2008), V^w is the volume of aqueous phase, k_{FA} and k_{PFA} are the average mass transfer coefficients of FA and PFA, respectively.

The kinetic parameters involved in the reaction system (k_{3-6} , E_{a3-6} , k_{FA} and k_{PFA}) were estimated through the optimization procedure.

3.3.3. Mass balance

Combining the intrinsic reaction part and the mass transfer part, the overall mass balance for the macroscopic kinetic model can be written as follows(mol·min⁻¹):

Aqueous phase:

$$\frac{\mathrm{d}C_{\mathrm{HP}}^{w}V^{w}}{\mathrm{d}t} = -r_{FA}^{perh}V^{w} \tag{16}$$

$$\frac{\mathrm{d}C_{\mathrm{PFA}}^{w}V^{w}}{\mathrm{d}t} = (r_{FA}^{perh} - r_{PFA}^{decomp})V^{w} - r_{PFA}^{m} \tag{17}$$

$$\frac{\mathrm{d}C_{FA}^{w}V^{w}}{\mathrm{d}t} = -r_{FA}^{perh}V^{w} + r_{FA}^{m} \tag{18}$$

$$\frac{\mathrm{d}C_{\mathrm{H_2O}}^{w}V^{w}}{\mathrm{d}t} = (r_{FA}^{perh} + r_{PFA}^{decomp})V^{w} \tag{19}$$

Oil phase:

$$\frac{\mathrm{d}C^o_{C=C}V^o}{\mathrm{d}t} = -r^{epox}_{C=C}V^o \tag{20}$$

$$\frac{\mathrm{d}C_{\mathrm{EP}}^{o}V^{o}}{\mathrm{d}t} = (r_{C=C}^{epox} - r_{EFAMEs}^{ro})V^{o} \tag{21}$$

$$\frac{\mathrm{d}C_{PFA}^{o}V^{o}}{\mathrm{d}t} = -r_{C=C}^{epox}V^{o} + r_{PFA}^{m} \tag{22}$$

$$\frac{\mathrm{d}C_{FA}^o V^o}{\mathrm{d}t} = r_{C=C}^{epox} V^o - r_{FA}^m \tag{23}$$

It was reasonable to assume that k_{FA} is approximately equal to k_{PFA} due to the similar structures of FA and PFA. For simplification, it was assumed that all the organic compounds were insoluble in the aqueous phase, and the volumes of the aqueous phase and organic phase

maintained constant during epoxidation.

3.3.4. Estimation of kinetic parameters

The high coupling relationship of reactions involved in vegetable oil epoxidation makes parameter estimation difficult. An efficient method is to estimate the kinetic parameters separately by individual experiments. The following four categories of reaction system were considered to estimate the kinetic parameters:

3.3.4.1. Synthesis of PFA by FA and H_2O_2 . FA perhydrolysis and PFA decomposition reactions occur in this category. The results of Filippis' work (Filippis et al., 2009) were adopted in the present work after analysis and comparison in subsequent kinetic study. The pre-exponential factor and activation energy for PFA formation reaction are $7.84 \times 10^5 \text{ L}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ and $43,524.2 \text{ J} \cdot \text{mol}^{-1}$. The pre-exponential factor and activation energy for PFA decomposition are $3.91 \times 10^{11} \text{ L}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ and $72,627.9 \text{ J} \cdot \text{mol}^{-1}$.

3.3.4.2. Ring-opening reactions of EFAMEs. Ring-opening reactions of EFAMEs caused by FA and H_2O were considered in this category. All the ordinary differential equations derived from the system were solved using Runge-Kutta method in the MATLAB package.

The temperature dependences of the rate constants are described by Arrhenius equation:

$$k_i = k_i^{ref} \exp\left[\frac{E_{ai}}{R} \left(\frac{1}{T^{ref}} - \frac{1}{T}\right)\right]$$
(24)



Fig. 8. Fit of the model to the experiments and simulation of epoxy value and FA concentration.

Where k_i^{ref} is the rate constant chosen at a fixed temperature (here 70 °C).

The reaction rate constants and activation energies of EFAMEs Ringopening reactions caused by FA and H_2O were obtained with the experiments listed in Table 3, using least squares method, by minimizing the difference between the experimental and predicted epoxy value and FA concentrations. The objective function was minimized by the Levenberg-Marquardt method.

Fig. 8 shows the results of the Ring-opening reactions caused by FA and water. It is found that the model fits well with the experimental data. The estimated kinetic parameters of Ring-opening reaction of EFAMEs caused by FA and H₂O at 70 °C are listed in Table 6. The parameters of Ring-opening reactions (k4, k6, Ea4 and Ea6) were calculated with confidence level of 95%, which is the frequency of possible confidence intervals that contain the true value of their corresponding parameters. It can be noticed that the confidence interval of Ea4 is relative wide (28% relative deviation), this is due to the factor that the change of FA concentration in the system is not obvious. Nevertheless, the errors of the estimated parameters in this section are acceptable. Moreover, the P-values were examined for each group of calculated values with experimental values, and the P-values for all groups are smaller than 0.0001, further illustrating the significance of the statistical analysis. Compared to the results of Campanella et al. (2008) and Zheng et al. (2016), similar trends were found, that is, Ring-opening by FA is faster than that by H_2O .

3.3.4.3. Epoxidation of FAMEs without mass transfer limitation. In this category, the kinetic parameters of FA perhydrolysis and EFAMEs Ringopening by FA and H₂O were included into the model. The volume mass transfer term $(6k_{FA}V^w/D_{32})$ was firstly assumed to be large enough to eliminate the influence of mass transfer of FA and PFA. All the experimental runs listed in Table 4 are characterized by taking 6 samples at different time. The data obtained from the analysis of these samples was subjected to mathematical regression analysis, and the method is the same with the one used in Ring-opening study. The selection of initial values is critical to the convergence and accuracy of the mathematical regression analysis. In the past few years, the intrinsic kinetics of vegetable oil has been widely investigated, and hence the initial values were selected based on literatures.

Fig. 9 shows the fit of the model to the experimental data of the concentrations of double bond and epoxy group. It can be observed that the kinetic models can well predict the trends of double bond and epoxy group concentrations. The confidence intervals of the parameters (k_3 , k_5 , Ea_3 and Ea_5) are narrow at confidence level of 95% and the P-values for each group of calculated values with experimental values are

smaller than 0.0001. The observed activation energies of double bond epoxidation and Ring-opening by PFA were 78,445 J/mol and 91,320 J/mol, respectively. Both of which illustrate the temperature has important effect on the conversion and selectivity of the reaction.

3.3.4.4. Epoxidation of FAMEs with mass transfer limitation. With the results of intrinsic kinetics and D_{32} determined in the previous sections, it is possible to determine the mass transfer coefficients through optimization procedure based on the data obtained from the experiments in Table 5. At each temperature, two epoxidation experiments with mass transfer limitation were carried out for regression analysis using the same least square method. The obtained mass transfer coefficients are shown in Fig. 10. The relative deviations (95% confidence level) for all the mass transfer coefficients are in the range of 8%-18%, which indicates the applicable for using this method to estimate the mass transfer coefficients. It can be noticed that the mass transfer coefficients were proportional to T^{0.5}, which accorded with the surface renewal theory.

Combining the rate equations, mass balance equations and all the parameters obtained, the macroscopic kinetic model of the epoxidation of FAMEs was developed.

Fig. 11 shows some data fitting results. The solid line depicts the double bond and epoxy group concentrations vs. reaction time with mass transfer limitation conditions. The imaginary line depicts the double bond and epoxy group concentrations vs. reaction time without mass transfer limitation conditions. The P-values for each group of calculated values with experimental values were smaller than 0.0001. The good agreement of calculated value with experimental value indicates the applicable of the macroscopic model. One can notice that the influence of mass transfer became increasingly pronounced with the increase in temperature. The influence of mass transfer on each temperature can be more clearly observed in Table 7. Normally, the Iodine value will be required to below 5 or 3 based on the different application in industry. It shows that the reaction time will be extended about 4 h or even more at 150 rpm as compared to 500 rpm. Similar phenomena exist in industrial reactors, that is, the reaction time in industrial reactor is longer than that in laboratory scale as the exist of mass transfer limitation. Another important outcome in Fig. 11 is worthy of attention: the influence of mass transfer on double bond conversion at 80 °C is steep increased which means higher requirement for the mixing of two phases is needed. This observation is extremely important for reactor design of high-temperature epoxidation process, which have been studied widely in recent years (Cortese et al., 2012; Santacesaria et al., 2012; Naidir et al., 2012).

For a liquid-liquid reaction system, the scale-up of reactors will be

Table 6

Kinetic p	arameters	determined	at th	he 70	°C and	l numerical	l val	ue of	othe	er parameters	of t	the mode	el.
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Parameter	Value	Unit	Notes					
k ₁	0.1845 ^a	$L^2 \cdot mol^{-2} \cdot min^{-1}$	Rate constant of FA perhydrolysis					
K ₁	0.8 at 25 °C ^a	none	Equilibrium constant of FA perhydrolysis					
ΔH	$-5580^{\rm b}$	J/mol	Standard enthalpy of FA perhydrolysis					
k ₂	3.3997 ^a	min ⁻¹	Rate constant of PFA decomposition					
k ₃	2.42542 ± 0.14100	$L \cdot mol^{-1} \cdot min^{-1}$	Rate constant of FAMEs epoxidation					
k4	0.002972 ± 0.00019	$L \cdot mol^{-1} \cdot min^{-1}$	Rate constant of Ring-opening by FA					
k ₅	0.01676 ± 0.00142	$L \cdot mol^{-1} \cdot min^{-1}$	Rate constant of Ring-opening by PFA					
k ₆	0.000273 ± 0.000015	$L \cdot mol^{-1} \cdot min^{-1}$	Rate constant of Ring-opening by H ₂ O					
Ea1	43,524 ^a	J/mol	Activation energy of FA perhydrolysis					
Ea ₂	72628 ^a	J/mol	Activation energy of PFA decomposition					
Ea ₃	$78,445 \pm 4022$	J/mol	Activation energy of FAMEs epoxidation					
Ea ₄	21463 ±5999	J/mol	Activation energy of Ring-opening by FA					
Ea ₅	$91,320 \pm 9091$	J/mol	Activation energy of Ring-opening by PFA					
Ea ₆	$38,316 \pm 7002$	J/mol	Activation energy of Ring-opening by H ₂ O					
k _{FA}	3.45	m/min	Mass transfer coefficient of FA					

^a Data from Filippis et al.'s work (Filippis et al., 2009).

^b Data from Zheng et al.'s work (Zheng et al., 2016).



Fig. 9. Experimental and model-calculated concentrations of double bond (DB) and epoxy group (EG) at different conditions (Corresponding to run 10-13).



Fig. 10. Mass transfer coefficients of FA and PFA.

easy if the following two problems can be solved.

(a) Development of macroscopic kinetic model for a specific reaction, that is, the effect of droplet size on the reaction rate can be determined. (b) Development of population balance model (PBM) for a specific reactor, that is, the droplet size distribution in the reactor can be determined.

The effect of droplet size on the FAMEs epoxidation has been determined in the present work. Hence, the optimal value of droplet size can be obtained for a specific reaction process condition. For a specific reactor, the optimal operation condition can be determined based on the PBM (the optimal operation condition for a specific reactor is to obtain the optimal value of droplet size in the reactor with minimum energy consumption).

4. Conclusions

The epoxidation of FAMEs with PFA generated in situ by reacting $\rm H_2O_2$ and FA was studied as a liquid-liquid model reaction.

Firstly, D_{32} in the liquid-liquid dispersion system was determined using high speed camera. The effects of agitation speed, holdup, composition of continue phase/disperse phase and temperature were investigated. Results shows: (1) The D_{32} was correlated with Weber number as a function with an exponent of -0.5731; (2) The increase in holdup increased collision frequency and resulted in large D_{32} ; (3) Smaller D_{32} was observed with higher content of EFAMEs in the oil phase and H_2O_2 in the aqueous phase; (4) D_{32} was slightly decreased with the rise of temperature.

Then Ring-opening reaction, epoxidation without mass transfer



Fig. 11. Effect of mass transfer of FA/PFA on the epoxidation reaction at different temperature.

 Table 7

 Comparison of the change of Iodine value (IV) vs. time at reaction temperature 50–80 °C with/without mass transfer limitation.

Time (min)	e (min) IV at 50 °C		IV at 60 °C	IV at 60 °C			IV at 80 °C		
	500 rpm	150 rpm	500 rpm	150 rpm	500 rpm	150 rpm	500 rpm	150 rpm	
120	68.42	72.04	41.92	54.72	20.87	39.37	8.72	45.5	
240	36.83	41.88	13.15	24.93	2.84	14.84	0.92	25.36	
360	20.30	24.65	4.15	12.24	1.09	6.82	-	-	
480	10.80	16.66	2.78	6.37	0.49	3.65	-	-	
600	5.64	8.37	2.10	3.89	-	-	-	-	

limitation were separately performed to determine the intrinsic rate constants and activation energies. The rate constant of Ring-opening reaction caused by FA, H₂O and PFA at 70 °C were 0.002972, 0.000273 and 0.01676 L·mol⁻¹·min⁻¹, and the corresponding activation energy were 21463, 38,316 and 91,320 J/mol, respectively. Similar trends were found in the work of Campanella et al., (2008) and Zheng et al., (2016). The rate constant and activation energy of double bond epoxidation at 70 °C were 2.43 L·mol⁻¹·min⁻¹ and 78,445 J/mol, these values were similar with the results obtained by Santacesaria et al., (2011). Finally, epoxidation with mass transfer limitation was performed, and the mass transfer coefficients of FA and PFA were determined to be 1.45–3.52 m/min at temperature 50–80 °C.

The macroscopic kinetic model makes FAMEs epoxidation associated with the droplet size, which is useful for the design and scale-up of reactors using experimental method or simulation tool (such as CFD- PBE simulation) to adjust and control the required droplet size. Aiming at getting the suitable operating condition with minimum energy consumption.

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