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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 (D_{32}) was determined and correlated, the correlation can predict the D_{32} 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

FAMEs	Fatty acid methyl esters
EFAMEs	Epoxy fatty acid methyl esters
PFA	Performic acid
FA	Formic acid
AA	Acetic acid
DB	Double bond
EG	Epoxy group
IV	Iodine value
EV	Epoxy value
D_{32}	Sauter mean diameter (mm)
D_I	Impeller diameter (mm)
N	Agitation speed (rpm)
We	Weber number
V_I	Viscosity number
ΔG^0	Standard dissociation free energy (J/mol)
ΔH	Standard enthalpy (J/mol)
$K_{a,FA}$	Thermodynamic dissociation constant
K_1	Equilibrium constant of the perhydrolysis reaction
R	Gas constant (J/(mol•K))
k_i	Rate constant of the reactions (i = 1, 2, 3, 4, 5)
k_{FA}	Mass transfer coefficient of FA (m/min)
k_{PFA}	Mass transfer coefficient of PFA (m/min)
V^w	Volume of aqueous phase (L)
V^o	Volume of organic phase (L)
PBM	Population balance model

Greek letters

σ	Interfacial tension (N/m)
σ_{sd}	Standard deviation
ρ	Density (Kg/m^3)
$\varnothing$	Holdup
μ	Viscosity (cP)
w	Mass fraction

Subscripts and superscripts

w	Aqueous phase
o	Organic phase
PFA	Performic acid
FA	Formic acid
HP	Hydrogen peroxide
C=C	Double bond
perh	Perhydrolysis
decomp	Decomposition
epox	Epoxidation
ro	Ring-opening

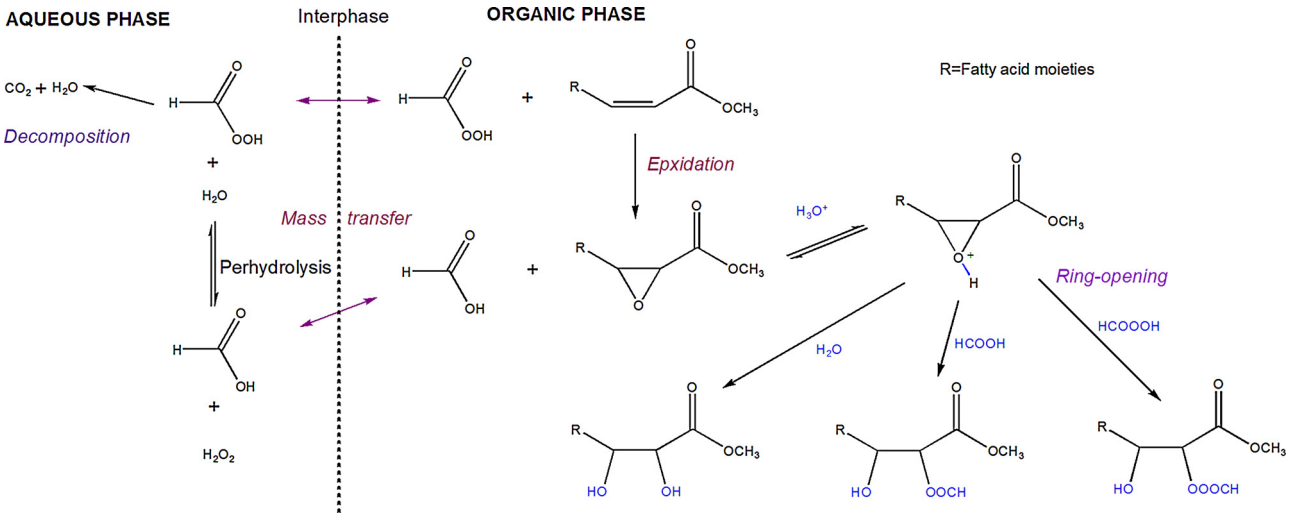

Fig. 1. Simplified mechanism of the epoxidation of the FAMEs.

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.