Characterizing the epoxidation process conditions of canola oil for reactor scale-up

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ABSTRACT

Novel epoxidized vegetable oils are of current interest for a variety of applications in coatings and polymeric materials. Samples are needed at quantities beyond gram scale to test such applications. However, scale-up of this very exothermic reaction requires an increased understanding of actual reaction temperature (T_r), which may be much higher than the water bath temperature (T_b). Canola oil (300 g) was epoxidized at three H_2O_2 addition rates (4.6, 2.3, and 1.2 g min^{-1} mol^{-1} unsaturation); at three T_b (55, 65, and 75 °C); and at three reaction times (2.5, 4, and 5.5 h). The addition rates were obtained by adding 180 g of H_2O_2 over 0.5, 1, and 2 h. Maximum ΔT (T_r–T_b) was attained within 30–40 min of reaction time; thereafter, reactor temperatures gradually declined even though H_2O_2 addition continued. The maximum ΔT (8.7–15.8 °C) increased as the T_b and H_2O_2 addition rate increased; but, no clear trend was observed in the time maximum ΔT values were attained. The ΔT vs time profile was a useful indicator of the extent of epoxidation and can be used as a criteria to stop epoxidation reaction. The greatest source of variation in oxirane content was from T_b and reaction time. Therefore, T_r must be maintained within the optimal range during the high exothermic periods, if high resin quality and minimal process time is to be achieved during scale-up.

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1. Introduction

Vegetable oil is one of the most abundant biobased feedstocks and has fatty acid chains with unsaturated double bonds that can be used to produce a wide variety of valuable products (Saurabh et al., 2011). In an effort to address the rising cost and increasing demand for petroleum-based epoxy resin, and transition to sustainable alternatives, epoxidized vegetable oil (EVO) has been successfully used in coatings, polymers, and material science (Tan and Chow, 2010). The epoxy groups are highly reactive and can be directly crosslinked or converted to other valuable functional groups like hydroxyl (polyols), hydroxyl ester, polyurethane, and carbonyl groups, which are used as plasticizers and stabilizers for polymers, lubricants, and resins in composite materials (Guo et al., 2000; Pan and Webster, 2012). The potential modifications to EVO also include substitutions for its glycerol backbone, which can greatly improve the thermal and mechanical strength of composite materials and coatings made from EVO (Pan and Webster, 2012). However, knowledge and equipment are needed to produce novel EVOs and their derivatives in sufficient quantities (much more than gram scale) for product application trials.

There are four major categories of epoxidation processes (Table 1): conventional sulfuric acid, acidic ion exchange resin (AIR), chemo-enzymatic, and metal-catalyzed epoxidation, based on the type of catalyst used (Tan and Chow, 2010). Each of these processes has its advantages, but the AIR process has been the most often reported in the epoxidation of vegetable oil, because of ease of catalyst separation and refining, and the low number of side reactions (Sinadinovic-Fiser et al., 2001). Table 1 also shows that the AIR process gives the best conversion for varied oil type, batch size, and process conditions. In order to have consistent resin properties from batch to batch, the process conditions needed to produce epoxy bonds must be the same irrespective of the batch size and oil type. The epoxidation reaction with peracetic acid formed in the presence of a catalyst is shown in Fig. 1.

The reaction is very exothermic, which poses a challenge to scale-up. Producing greater batch size requires increasing the reactor size and quantities of reactants but this could result in an excessively high reactor temperature, depending on the H_2O_2 addition rate and reaction time. Controlling reaction temperature (T_r) in a scaled-up reactor is critical to maximize oxirane conversion and minimize reaction time. Most studies in Table 1 assumed that the reactor temperature was the water bath temperature (T_b) or temperature of heating unit. Meanwhile, the one study that monitored

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Table 1
Summary of epoxidation processes and conditions for various types of vegetable oil reported in the scientific literature. The temperature reported was the bath temperature, except where noted otherwise.

Epoxidation process	Vegetable oil	Batch size (g)	Process conditions			Conversion (%)	References
			Temperature (°C)	H_2O_2 addition duration (h)	Reaction time (h)		
Conventional	Soybean	150	45, 55, 65, 75	12	12	nd	(Cai et al., 2008)
	Jatropha	nd	30, 50, 70, 85	0.5	3.4, 4.5, 10	35–88	(Goud et al., 2010)
	Cottonseed	nd	30, 45, 60, 75	0.5	4	80	(Dinda et al., 2008)
AIR	Canola	22.6	40, 55, 65, 75	0.5	7	50–90.8	(Mungroo et al., 2008)
	Canola	50, 300	50–60	0.5	5	95–98	(Espinoza-Pérez et al., 2009)
	Soybean	100	30, 60, 75	0.5	8	73.1–97.7	(Sinadinovic-Fiser et al., 2001)
	Sucrose ester of fatty acid	170	55–65*	variable	nd	99.4–99.9	(Pan et al., 2011)
	Rubber, neem, mee	40, 1000	50–60	1, 2.5	5.5, 8	86–91	(Gamage et al., 2009)
Chemo-enzymatic	Soybean	25	50	0.083	24	50–98.9	(Vlček and Petrović, 2006)
	Soybean, sunflower, linseed, rapeseed	7.8	RT	54 µl every 7.5 min	16	88–99	(Rüsch gen. Klaas and Warwel, 1999)
Metal-catalyzed	fatty acid	11.7	30	2	2	31–96	(Cai et al., 2009)
	soybean	30	RT	nd	1–2	16–92	(Gerbase et al., 2002)

RT – room temperature; nd – no data; AIR – acidic ion exchange resin.
*Reaction temperature.

the actual reactor temperature used it as a means to control H_2O_2 addition rate, and did not show the temperature–time profile (Pan and Webster, 2012). At a scale <150 g, which was the scale in most of these studies, the difference between T_r and T_b may not be significant; therefore, it is easier to maintain reactor temperature closer to T_b during the exothermic activities. However, as the scale increases, the heat flux from the reaction mixture through the wall of the reactor may become insufficient. This could significantly increase T_r to a level well above the optimal epoxidation level. Therefore, it is worthwhile to determine temperature behavior at different H_2O_2 addition rates and T_b at bench-scale.

Hydrogen peroxide addition duration, which is inversely proportional to H_2O_2 addition rates (R), has not been commonly discussed in epoxidation reports. H_2O_2 was almost always added into the reaction mixture at a fixed addition rate and duration (Table 1) irrespective of the T_r. In one instance, addition rate was variable based on T_r control within 55–65 °C (Pan et al., 2011). Typical H_2O_2 addition rates and durations might be problematic in scale up, because the chemical bonds release more heat relative to the ability of the reactor to dissipate it. In the case of varying H_2O_2 addition rates as a function of the T_r, it has been observed that total reaction time increases during scale up because of prolonged cooling time (Gerlach and Geller, 2004). Therefore, reaction scale-up requires a better understanding of the T_r as affected by different combinations of H_2O_2 addition rates and T_b, and at a given reaction time. The characterization of T_r at the different process conditions, such as those in Table 1, has not been reported.

Other process conditions that could affect oxirane formation, but which are not included in Table 1, are stirring speed and

molar ratio of oil unsaturation: acetic acid: H_2O_2. In terms of stirring speed, different optimum stirring rates have been reported; however, the difference in threshold speed was mainly due to the different quantity of oil epoxidized and/or stirrer used (Tan and Chow, 2010). The most important consideration is that stirring should be sufficient to ensure that the reactants mix properly and assist heat transfer, and increasing stirring speed above this minimum does not influence epoxidation (Dinda et al., 2008; Espinoza-Pérez et al., 2009). The molar ratio of oil unsaturation: acetic acid: H_2O_2 has been explored in some studies. The ratio of 1:0.5:2 was shown to be optimal (Espinoza-Pérez et al., 2009; Goud et al., 2007), and has been used in most epoxidation studies where the ratio was not the subject of interest. Therefore, stirring speed and molar ratio were not varied in our study.

The overall goal is to scale up production while maintaining or reducing batch time and achieving high conversion and low degradation. Our objective was to evaluate the effect of different H_2O_2 addition rates T_b, and reaction time on oxirane formation and to characterize the temperature–time profile at these different process conditions. These conditions and results will be used as a benchmark for further reactor scale-up.

2. Materials and methods

2.1. Materials

Commercial edible-grade canola oil was acquired locally. The ion exchange resin catalyst, Amberlite IR120, was purchased from Acros Organics (Morris Plains, NJ). Aqueous H_2O_2 (50%), pyridine,
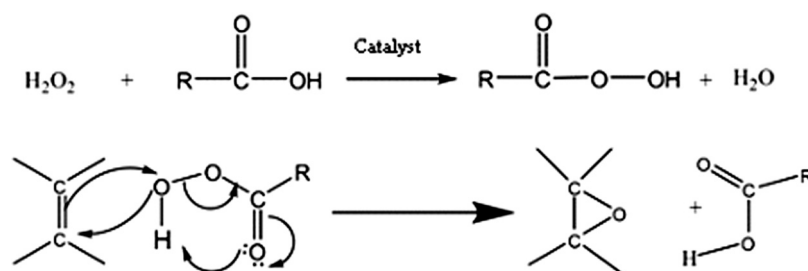

Fig. 1. Epoxidation reaction (Gamage et al., 2009).