ORIGINAL ARTICLE

Optimization of the oxirane ring opening reaction in biolubricant base oil production

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Abstract This study has successfully optimized the conversion of monoepoxide linoleic acid (MEOA) into biolubricant via oxirane ring opening reaction using oleic acid (OA) with *p*-toluene sulfonic acid (PTSA) as a catalyst. The four main factors were studied according to a D-optimal design at three levels. These factors were OA/MEOA ratio, PTSA/MEOA ratio, temperature and reaction time. This analysis evidenced the best operating conditions of the oxirane ring opening reaction performed at the following condition; OA/MEOA ratio of 0.30:1 (w/w), PTSA/MEOA ratio of 0.50:1 (w/w), reaction temperature at 110 °C and reaction time at 4.5 h, an optimum yield of 84.61% and OOC of 0.05%. This model results showed a good agreement with the predict value, demonstrating that this methodology may be useful for industrial process optimization.

1. Introduction

The development of new efficient lubricants and environmentally benign pathways, which can lead to new value added products, has still a high potential (Baumann et al., 1988). Furthermore, vegetable oil based products have become more cost competitive with their petroleum derived counterparts as crude petroleum oil prices have increased dramatically in recent years due to a number of geopolitical factors (Moser et al., 2007).

Due to the high reactivity of the oxirane ring, the epoxidation of the double bonds opens up a wide range of feasible reactions that can be carried out under moderate reaction conditions. A variety of chemical modifications of epoxidized vegetable oils and fatty acids are possible through epoxy moiety, and one of the most commonly used is the ring opening reaction (Lozada et al., 2009).

The oxirane ring opening takes place through cleavage of one of the carbon–oxygen bonds. It can be initiated by either electrophiles or nucleophiles, or catalyzed by either acids or bases. The acid catalyzed of an epoxide is a useful procedure for preparing hydroxy ester compounds (Von, 2002). The nucleophilic addition of a carboxyl group to the epoxide center can easily be promoted by protonation using solid acid catalysts (Fig. 1). Nonetheless, the rate of the oxirane ring opening

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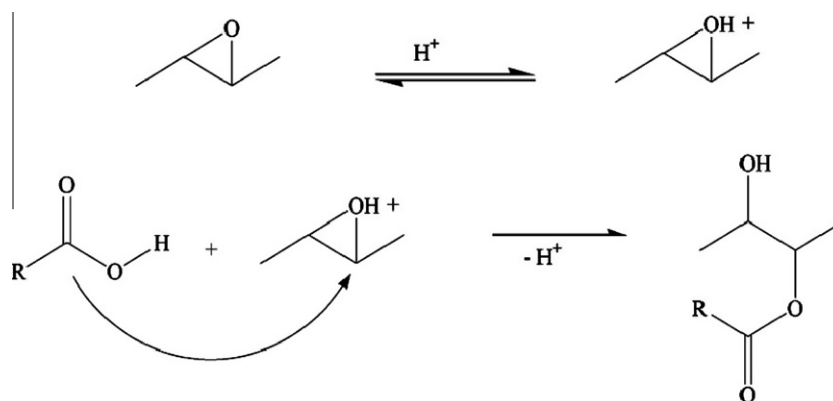E-mail address: jumat@ukm.my (J. Salimon).

Figure 1 Nucleophilic addition of a carboxyl group to the epoxide promoted by protonation using acid catalysts.
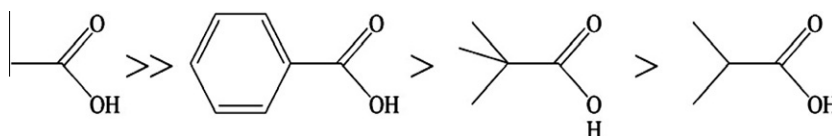

Figure 2 Nature and structure of the carboxylic acid toward the oxirane ring opening.

of epoxidized fatty acids strongly depends on the nature and structure of the carboxylic acid (Fig. 2) (Schuster et al., 2008).

Many nucleophilic reagents are known to add to an oxirane ring, resulting in ring opening (Salimon et al., 2011). These ring-opening reactions could result in branching at the oxirane ring opening (earlier sites of unsaturation in LA). The appropriate branching groups would interfere with the formation of macro-crystalline structures during low-temperature applications and would provide enhanced fluidity to plant oils. TAGs that are hydrogenated to eliminate polyunsaturation will solidify at room temperature as a result of alignment and stacking of adjacent molecules (Hwang and Erhan, 2001).

The aim of the present work is the determination of the feasibility, reliability and best operating conditions for the oxirane ring opening reaction process using D-optimal design on the optimization of the process variables. Fig. 3 demonstrates the scheme for the oxirane ring opening reaction of MEOA.

2. Methodology

2.1. Experimental procedure

The oxirane ring opening reaction was carried out using oleic acid (OA) and *p*-toluene sulfonic acid (PTSA) as catalyst to prepare 9,12-hydroxy-10,13-oleioxy-12-octadecanoic acid (HYOOA) (Salimon et al., 2011). Table 1 shows the different OA/MEOA ratio, different PTSA/MEOA ratio, different reaction temperature and different reaction time using D-Optimal design. Factors (variables) such as ratio OA/MEOA (w/w, X_1), PTSA/MEOA (w/w, X_2), reaction temperature (°C, X_3) and reaction time (h, X_4) were performed under the same experimental conditions. MEOA (1.55 g, 0.0052 mol) and ratio PTSA/MEOA (0.2:1–0.5:1 w/w) were dissolved in toluene (10 mL) in a 250-mL three-neck flask equipped with a cooler,

Table 1 Independent variables and their levels for D-optimal design of the oxirane ring opening reaction.

Independent variables		Variable levels		
		−1	0	+1
1. OA/MEOA (w/w)	X_1	0.30	0.45	0.60
2. PTSA/MEOA (w/w)	X_2	0.2	0.35	0.5
3. Temperature (°C)	X_3	90	100	110
4. Time (h)	X_4	3	4.5	6

dropping funnel and thermometer. The mixture was kept at 50 °C. OA/MEOA ratio (0.30:1–0.60:1 w/w) was added during 1.5 h in order to keep the reaction mixture temperature under 70–80 °C. The reaction mixture was subsequently heated to different temperatures 90–110 °C and refluxed at different times 3–6 h at this temperature range. After reaction termination, the heating was stopped and the mixture was left to stand overnight at ambient temperature. The mixture was washed with water and the organic layer was dried over anhydrous sodium sulfate and the solvent was removed using the vacuum evaporator. The oxirane ring content (OOC%), yield % and iodine value (IV mg/g) were measured.

2.2. Experimental design and statistical analysis

A quadratic polynomial equation by central composite design was developed to predict the response as a function of independent variables and their interaction. In general, the response for the quadratic polynomials is described below:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \sum \beta_{ij} X_i x_j \qquad (1)$$

where β_0; β_i; β_{ii} and β_{ij} are constant, linear, square and interaction regression coefficient terms, respectively, and x_i and x_j