Lipase-catalyzed transesterification of epoxidized soybean oil to prepare epoxy methyl esters

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SUMMARY: Epoxidized soybean oil methyl esters could be efficiently prepared with the transesterification of epoxidized soybean oil (ESBO) with a lower dosage of methanol using lipase Novozym 435 as catalyst. The optimum parameters were as follows: the molar ratio of 5:1 (methanol to ESBO), 5% Novozym 435 as catalyst, at 45 °C for 14 h, with a stirring speed of 600rpm, under which the epoxidized soybean oil methyl esters (ESBOME) could be obtained at a 95.7% yield. During the enzymatic transesterification process, the oxirane oxygen values were kept unchangeable, which indicated that excellent functional group tolerance could be achieved under such mild reaction conditions. In addition, the recyclability of the immobilized enzyme Novozym 435 in this transesterification process was examined and the results showed that the biocatalyst could be reused ten times without losing any reaction activity or selectivity. And the final products of ESBOME were also identified by IR and NMR analysis. The kinetic data obtained followed the Ping-Pong Bi mechanism model (V_{max} = 6.132 mol·L^{-1}min^{-1}, $K_{m,S}$ = 0.0001 mol·L^{-1}, $K_{m,A}$ = 796.148 mol·L^{-1}, $K_{i,A}$ = 0.0004 mol·L^{-1}) with competitive inhibition by methanol.

KEYWORDS: *Bio-based products; Epoxidized soybean oil; Epoxy methyl esters; Lipase; Transesterification*

RESUMEN: *Transesterificación catalizada por lipasa en aceite de soja epoxidado para preparar epoxi metil ésteres.* Los ésteres metílicos de aceites de soja epoxidados pueden prepararse eficientemente mediante la transesterificación del aceite de soja epoxidado (ESBO) con una menor dosificación de metanol utilizando la lipasa Novozym 435 como catalizador. Los parámetros óptimos fueron los siguientes: relación molar 5:1 de metanol:ESBO, 5% de Novozym 435 como catalizador, 45 °C durante 14 h, velocidad de agitación de 600 rpm, bajo la cual los ésteres metílicos de aceites de soja epoxidados (ESBOME) pueden obtenerse con un rendimiento del 95,7%. Durante el proceso de transesterificación enzimática, los valores de oxígeno de oxirano se mantuvieron inalterables, lo que indicó que se logra una excelente estabilidad del grupo funcional en tales condiciones de reacción suaves. Además, se examinó la reciclabilidad de la enzima inmovilizada Novozym 435 en este proceso de transesterificación y los resultados mostraron que el biocatalizador podría reutilizarse durante diez veces sin perder ninguna actividad de reacción o selectividad. Los productos finales de ESBOME se identificaron por IR y análisis de RMN. Los datos cinéticos obtenidos siguieron el modelo de mecanismo Ping-Pong Bi (V_{max} = 6,132 mol·L^{-1}min^{-1}, $K_{m,S}$ = 0,0001 mol·L^{-1}, $K_{m,A}$ = 796,148 mol·L^{-1}, $K_{i,A}$ = 0,0004 mol·L^{-1}) con inhibición competitiva por metanol.

PALABRAS CLAVE: *Aceite de soja epoxidado; Epoxi metil ésteres; Lipasa; Productos de base biológica; Transesterificación*

1. INTRODUCTION

With the increasing for green processes from the modern chemical industry, bio-based products have become more and more attractive as biodegradable, nontoxic, and renewable chemical sources (Zhang *et al.*, 2011) which can be widely used in fuels, polymers, coatings, and other specialty products. Soybean oil (SBO) is one of the most common vegetable oils used as substrates in the oleo-chemical industry, due to its cheaper price and higher output in the world's oil market.

Epoxidized soybean oils can be synthesized on a large scale with the epoxidation of soybean oil in the presence of hydrogen peroxide (H_2O_2) and an acid catalyst (Liu *et al.*, 2016). Epoxidized soybean oil is usually used as lubricants, plasticizers, rubber-like materials and polymer stabilizers in industry (Biermann *et al.*, 2008; Wu *et al.*, 2000; Hwang and Erhan, 2001; Sharma *et al.*, 2006; Campanella *et al.*, 2010; Noor Armylisas *et al.*, 2017). With the rapid development of the oleochemical industry and increasing demand for renewable materials, the interest in using the epoxidized vegetable oil methyl esters as the chemical intermediate is increasing continually, such as carbonate esters and polymers (Mazo and Rios, 2013; Martini *et al.*, 2009; Ahn *et al.*, 2011; Mustata *et al.*, 2014).

Recently, the transesterification of vegetable oil or animal fat with short chain alcohols (eg. methanol, ethanol) has been extensively studied. The transesterification process can usually be catalyzed by a chemical method or an enzymatic method; while the chemical method can be divided into acid or base catalysts, such as sulfuric acid (Souza *et al.*, 2016), chlorhydric acid (Pastore *et al.*, 2015) and sulfonic acid (Alhassan *et al.,* 2015) as acid catalyst, or NaOH (Almeida *et al.*, 2015), KOH (Ullah *et al.*, 2015) and $NaOCH_3$ (Holser, 2008) as base catalyst. With the aim of green processing in the oleo-industry, the disadvantages of these chemical methods, such as harsh reaction conditions and corrosive catalysts, retarded the development of the oleo industry. As an efficient bio-catalyst, the lipase-catalyzed transesterification of oil to prepare biodiesel (fatty acid methyl esters) has been generally accepted as a green manner by the academic and industrial world. (Bajaj *et al.*, 2010; Guldhe *et al.*, 2015; Gutiérrez-Arnillas *et al.*, 2016) For example, Zheng *et al.* (Zheng *et al.*, 2009) reported that the lipase catalyzed transesterification of soybean oil with methanol to prepare biodiesel production in an organic solvent (eg. tert-amyl alcohol), showed the highest biodiesel conversion of 97% and was obtained at 40 °C for 15h.

Epoxidized soybean oil methyl esters can be prepared through the transesterification of epoxidized soybean oil (ESBO) with methanol in the presence of sodium methoxide as a strong base catalyst (Holser, 2008). Considering the moisture sensitivity of $NaOCH_3$ and the possible dangers in large scale processes (Kwok *et al.*, 2013; Kai *et al.*, 2014; Lin *et al.*, 2014), sustainable and green methods (eg. enzymatic method) are highly desirable for the transesterification of epoxidized vegetable oils to prepare epoxy methyl ester products under mild conditions (Scheme 1).

In this work, we chose one of the most commonly used commercial immobilized lipases for biodiesel production, Novozym 435, as a biocatalyst to prepare epoxidized soybean oil methyl ester (ESBOME) with epoxidized soybean oil and methanol in a solvent-free system. The effects of catalyst loading, reaction time, methanol to oil molar ratio, reaction temperature and stirring speed on the transesterification yield were investigated. The recyclability of the biocatalyst Novozym 435 in this transesterification process was also evaluated.

2. MATERIALS AND METHODS

2.1. Materials

Epoxidized soybean oil was purchased from Aladdin Chemical Reagent (Shanghai, China). Novozym 435 (Candida antarctica lipase immobilized on polyacrylic resin, 10,000 PLU/g) was purchased from Novozymes A/S (Bagsvaerd,
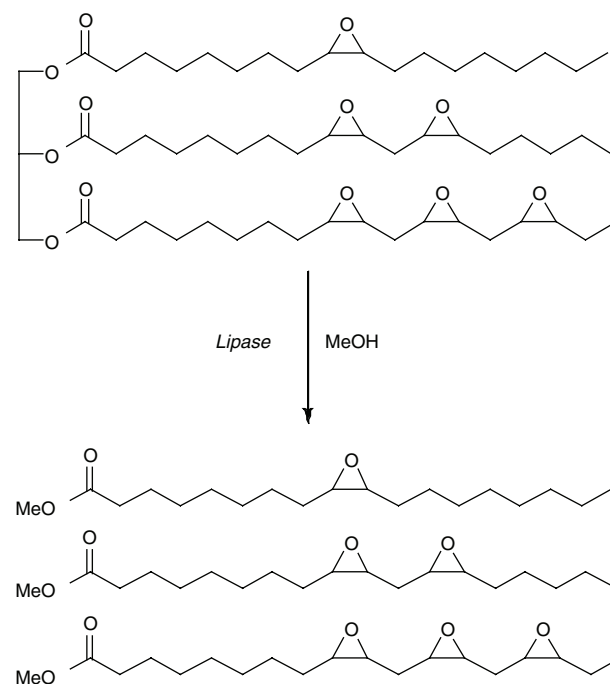
SCHEME 1. Enzymatic transesterification of ESBO with methanol.

Denmark). Methanol and n-hexane were analytical reagent grade and purchased from Kermel Chemical Reagent (Tianjin, China). Monoglyceride (analytical standard), diglyceride (95%) standards were purchased from Sigma-Aldrich Co. (St. Louis, MO). Triglyceride (> 99%, soybean oil) was purchased from a local supermarket (Zhengzhou, China).

2.2. Transesterification

Transesterification reactions were performed in 50mL round-bottom flasks. Epoxidized soybean oil (10.0g) was introduced to the flask and a certain amount of Novozym 435 catalyst and methanol were added. Then the mixture was magnetically stirred at a controlled temperature for 6-18h. To note, the sample was a mixture in stirring. After stopping stirring for 3-5 minutes, a phase separation between the formed glycerol and the FAME was observed. After completion of the reaction, the Novozym 435 was removed by filtration, then the product was washed with saturated brines to remove the remaining methanol and glycerol. The remaining water was dried by anhydrous sodium sulfate (Na_2SO_4). Finally, the product was dried under reduced pressure for 1h at room temperature.

2.3. Oxirane oxygen titrations

Epoxy oxygen group content (EOC) was determined by the titration method with a hydrobromic acid solution in acetic acid following AOCS standard test method Cd 9-57 (AOCS, 1998).

2.4. Gas chromatography analysis

Samples were analyzed with an Agilent 7890 gas chromatograph (GC) using a DB-1HT column (30m×0.25mm×0.1μm, J&W Scientific, Folsom, CA). The carrier gas was Nitrogen flowing at 5mL·min^{-1}. The oven was programmed from an initial temperature of 50-180 $^{\circ}$C at 15 $^{\circ}$C·min^{-1}, increased to 230 $^{\circ}$C at 7 $^{\circ}$C·min^{-1}, and then to 380 $^{\circ}$C at 30 $^{\circ}$C·min^{-1} with a 15 min hold for a total run time of 35 min. The injection volume was 1 μL with the inlet set to splitless mode. The detection of eluents was made by the flame ionization detector (FID) and identified by comparing the retention times to known standards. Fatty acid esters, monoglyceride, diglyceride, and triglyceride standards were used. The ESBOME yield was calculated based on the following equation (Silitonga *et al.*, 2016):

$$\text{ESBOME Yield (wt\%)} = \frac{\text{Weight of ESBOME produced (g)}}{\text{Weight of ESBO used (g)}} \times 100\%$$

2.5. Kinetic experiment

Six experiments were performed at different molar ratios of oil to methanol from 1:1 to 1:7.5 in 50 mL round-bottom flasks. At pre-determined times, 0.3 mL samples were taken, dissolved in 5 mL n-hexane, and centrifuged to obtain the upper layer for gas chromatography analysis, 17:0 methyl ester as internal standard.

2.6. ^{1}HNMR analysis

Samples were analyzed with a Bruker AVANCE III NMR. 1HNMR spectra were obtained at 500 MHz. And $CDCl_3$ was used as solvent for the sample. The chemical shifts were quoted in parts per million (ppm) and referenced to as 0 ppm for internal tetramethylsilane (TMS).

3. RESULTS AND DISCUSSION

3.1. Effect of reaction time

Reaction time is one of the most important factors affecting enzymatic transesterification reactions. According to previous work on enzymatic transesterification (Kwok *et al.*, 2013), the optimum reaction time was determined to be 24 h. Therefore, 6 h to 18 h were selected as the reaction times in this experiment. As shown in Figure 1, when the enzymatic transesterification reaction time was increased from 6 to 16 h, the yield of ESBOME was increased from 75.4 % to 90.1 %. When the reaction time was increased to 18h, the yield of ESBOME exhibited a slight decrease (85.2%). The oxirane oxygen value was reduced from 6.1 wt% to 5.8 wt% when the reaction time changed from 6 h to 16 h. The oxirane oxygen value of ESBO
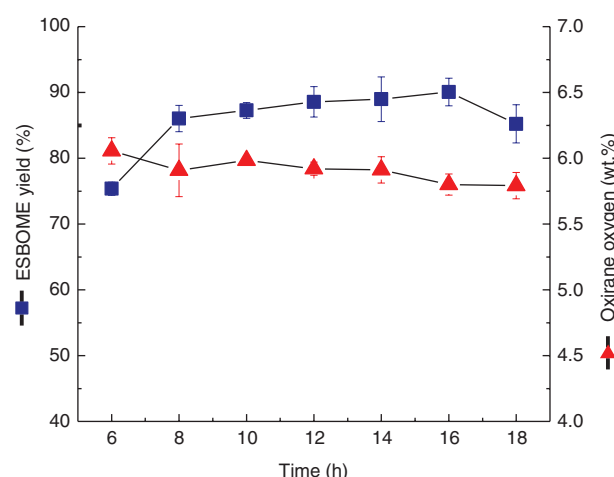

FIGURE 1. Effect of reaction time on transesterification reactions and oxirane oxygen values (Reaction conditions: 55 $^{\circ}$C, 6:1 of methanol to oil molar ratio, 10% (wt% of oil) of Novozym 435, stirring speed 600rpm). Error bars indicate the SD of the mean of three replicates (n=3).

was lower than 5.8 wt% after reaction for 16 h. Considering a longer reaction time would lead to the hydrolysis of the epoxide group. The optimal transesterification reaction time was 14h and the yield of ESBOME could reach to 89.0% under such reaction conditions. In addition, the contents of monoglycerides and diglycerides in the final products were analyzed by GC after 14 h (Figure 2), and the results showed that the methyl ester content of ESBOME could reach 98.6%. Though trace amounts of MG may be present, the purity of the methyl ester product after the simple purification was relatively higher.

3.2 Effect of catalyst loading

Novozym 435 is one of the most effective and widely used bio-catalysts in many organic transformations (Zheng *et al.*, 2009; Gutiérrez-Arnillas *et al.*, 2016; Rosa *et al.*, 2009), which could lower the activation energy for the reactant and increase activated molecules in the reaction system. In this experiment, ESBOME was prepared through the transesterification of ESBO at 55 °C for 14 h with Novozym 435 as bio-catalyst and different catalyst loading (1%-15%) was investigated. As shown in Figure 3, when the amount of Novozym 435 was increased from 1 % to 10 %, the ESOME yield was gradually improved. However, when the amount reached 15 %, the ESOME yield was slightly lower, because the excess amount of Novozym 435 could also accelerate the side reactions at the same time. When the amount of Novozym 435 was increased from 5 % to 10 %, the ESOME yield was slightly enhanced from 93.2 % to 93.9 %. With the increase in the amount of Novozym 435, oxirane oxygen values were maintained at around 6.0wt %. Considering the reaction activity and the cost of scalable production for bio-based products, a 5 % amount of Novozym 435 was chosen as the optimal amount of bio-catalyst used in the following experiments.

3.3. Effect of methanol/oil molar ratio

The molar ratio of methanol/ESBO strongly affects the transesterification reaction rate and conversion. Because the stoichiometric molar ratio of methanol to epoxidized soybean oil (ESBO) was 3:1 according to the transesterification reaction, an excess of methanol was used to ensure the complete conversion of epoxidized soybean oil. However, a higher methanol ratio would lead to the denaturation and inactivation of the lipase. In this experiment, the different molar ratios of methanol/ESBO ranged from 3:1 to 7:1 and were evaluated in Figure 4. In general, a greater amount of methanol (5:1 molar ratio of methanol to ESBO) used in the
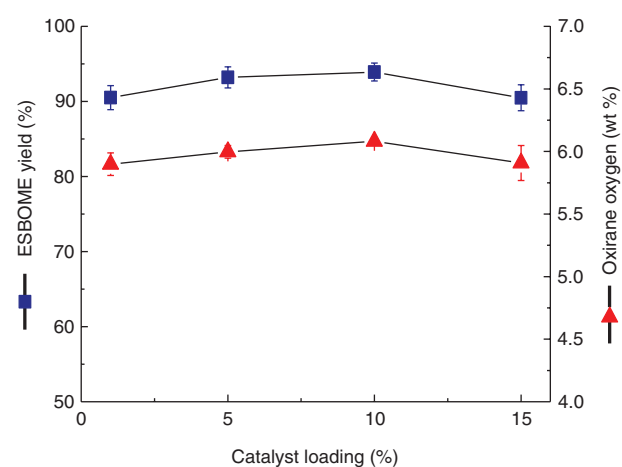
FIGURE 3. Effect of catalyst loading on transesterification reactions and oxirane oxygen values (Reaction conditions: 55 °C, 14h, 6:1 of methanol to oil molar ratio, stirring speed 600rpm). Error bars indicate the SD of the mean of three replicates (n=3)

FIGURE 4. Effect of methanol/oil molar ratio on transesterification reactions and oxirane oxygen values (Reaction conditions: 55 °C, 14h, 5% of Novozym 435, stirring speed 600rpm). Error bars indicate the SD of the mean of three replicates (n=3)
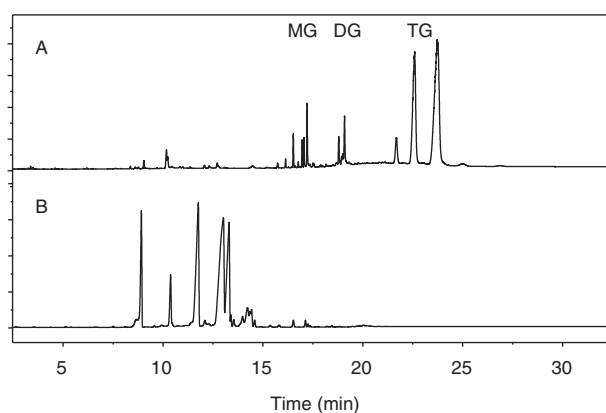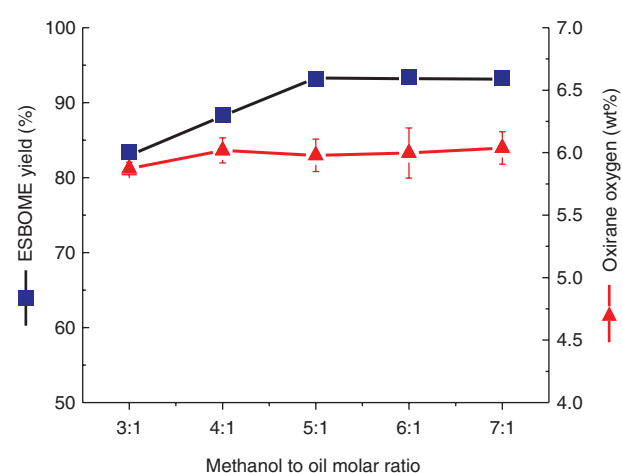

FIGURE 2. Gas Chromatograms of: (A) monoglyceride (MG), diglyceride (DG), and triglyceride (TG) standard compounds; (B) transesterification of epoxidized soybean oil after 14h.

transesterification reaction led to a higher yield of ESBOME (93.3 %). With a continuing increase in the molar ratio of methanol to ESBO from 5:1 to 7:1, the methyl ester yield had practically no change. It is important to note that the change in molar ratio of methanol to EBSO could not affect the epoxide group, which indicated that this established enzymatic transesterification method was mild enough for such unstable epoxide groups. Therefore, the optimal molar ratio of methanol to ESBO was 5:1 and the yield of ESBOME was able to reach 93.3 %.

3.4. Effect of reaction temperature

The reaction temperature not only affects the activity of Lipase Novozym 435, but also the percent of activated molecules in the reactants such as methanol and triglycerides. Moreover, the increase in reaction temperature can decrease the viscosity of ESBO and affect the thermodynamic equilibrium of enzyme-catalyzed reactions (Rosa *et al.*, 2009). Based on the studies involving Novozym 435 as catalyst (Zhang *et al.*, 2011), a range of reaction temperature (25 °C-55 °C) was investigated in this work (Figure 5). When the reaction temperature was increased from 25 °C to 45 °C, the ESBOME yield was improved from 90.7% to 95.7%. The ESBOME yield was similar at 55 °C. Meanwhile, the oxirane oxygen values did not change when the reaction temperature changed from 35 °C to 55 °C. Therefore, 45 °C was selected as the optimal reaction temperature and the yield of ESBOME reached 95.7% under such reaction conditions.

3.5. Effect of stirring speed

The stirring speed can make contact in the substrates more efficient, so that stirring can improve the reaction rate in most cases (Gharat *et al.*, 2013).

It could be seen from Fig. 6 that with an increase in stirring speed from 200 rpm to 600 rpm, the yield of ESBOME increased from 69.9 % to 95.7 %. With the increase in stirring speed, the oxirane oxygen values were changed from 6.3wt % to 6.0wt%. Considering 600 rpm as the maximum stirring speed in this experiment, 600 rpm was selected as the optimal stirring speed and the highest yield of methyl esters was 95.7 % under such reaction conditions.

3.6. Recycling of Novozym 435

The reusability of Novozym 435 in the transesterification reactions was also investigated based on the selected conditions obtained above. The changing trend of the ESBOME yield, the methyl ester content and the oxirane oxygen values are shown in Figure 7 when the Novozym 435 was reused. From Figure 7, it can be determined that the lipase could be used at least 10 times without losing any activity, as the ESBOME yield, the methyl ester content and the oxirane oxygen values were changed within very small ranges, from 95.7 % to 96.7 %, from 98.7% to 100.0%, from 5.7wt % to 6.3wt %, respectively. The above results suggested that the activity of Novozym 435 could be well kept due to the mild reaction temperature (45 °C) and lower dosage of methanol solvent (5:1 of methanol/oil molar ratio) in the reaction system.

3.7. Determination of molecule structure of methyl esters by IR and NMR

The final product of the transesterification of epoxidized soybean oil (ESBO) with methanol was identified by IR and ^{1}H NMR (Figures 8 and 9). The characteristic absorption peaks of ESBOME (carbonyl group, ester group and epoxy group)
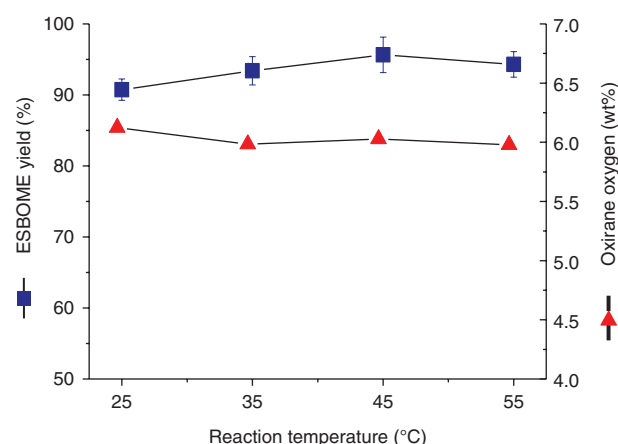
FIGURE 5. Effect of reaction temperature on transesterification reactions and oxirane oxygen values (Reaction conditions: 5:1 of methanol to oil molar ratio, 5% of Novozym 435, 14h, stirring speed 600rpm). Error bars indicate the SD of the mean of three replicates (n=3)
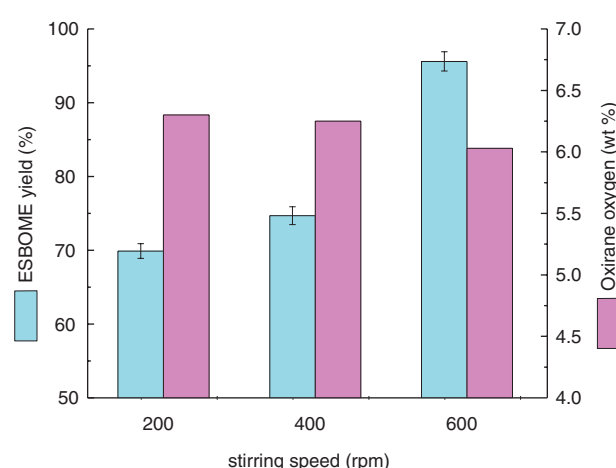
FIGURE 6. Effect of speed agitation on transesterification reactions and oxirane oxygen values (Reaction conditions: 45 °C, 5:1 of methanol/oil molar ratio, 5% of Novozym 435, 14h). Error bars indicate the SD of the mean of three replicates (n=3).
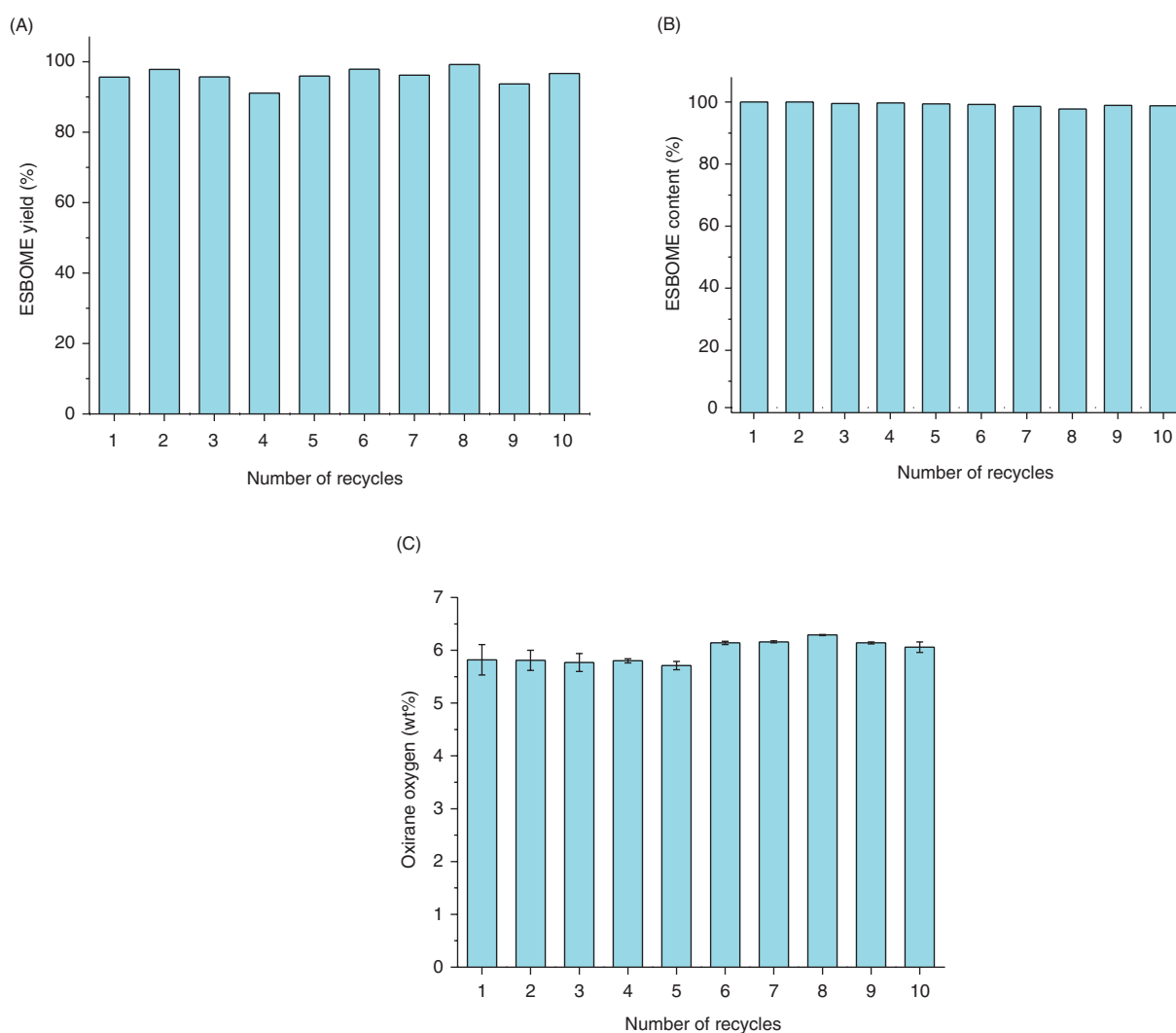
(A)

(B)

(C)

FIGURE 7. Effect of Novozym 435 recycling on transesterification reactions: ESBOME yield (A); ESBOME content (B) and oxirane oxygen values (C). (Reaction conditions: 45 °C, 5:1 of methanol/oil molar ratio, 5% of Novozym 435, 14h, stirring speed 600 rpm). Error bars indicate the SD of the mean of three replicates (n=3)
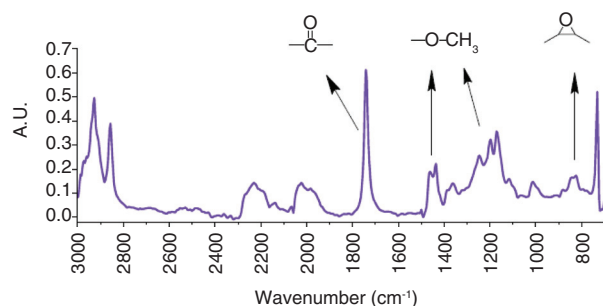

FIGURE 8. IR spectrum of epoxy oil methyl esters

appeared on its FT-IR spectrum. As shown in Figure 9, the protons of the epoxy groups (a) were at 3.0 ppm and methyl ester protons (ME) (b) were at 3.6 ppm, which undoubtedly suggested that epoxidized soybean oil methyl esters (ESBOME) could be obtained without a loss in epoxide function. The above results obtained by NMR were similar to those reported by Knothe (Knothe *et al.*, 2001) and Y. C. Sharma. (Sharma *et al.*, 2010).

3.8. Kinetic analysis of transesterification

A kinetic model was established for the transesterification of ESBO with methanol catalyzed by Novezym-435 lipase. The process for ESBOME concentration-time profiles for different methanol concentrations is shown in Figure 10. In this system, methanol concentrations gradually increased, and the amount of ESBO should be fixed. When the ratio of oil to methanol was below 1:5, the reaction rate obviously increased. When the ratio of oil to methanol was higher than 1:5, the reaction rate decreased, due to the inhibition of methanol (Trinh *et al.*, 2018). The optimal ratio of oil to methanol as
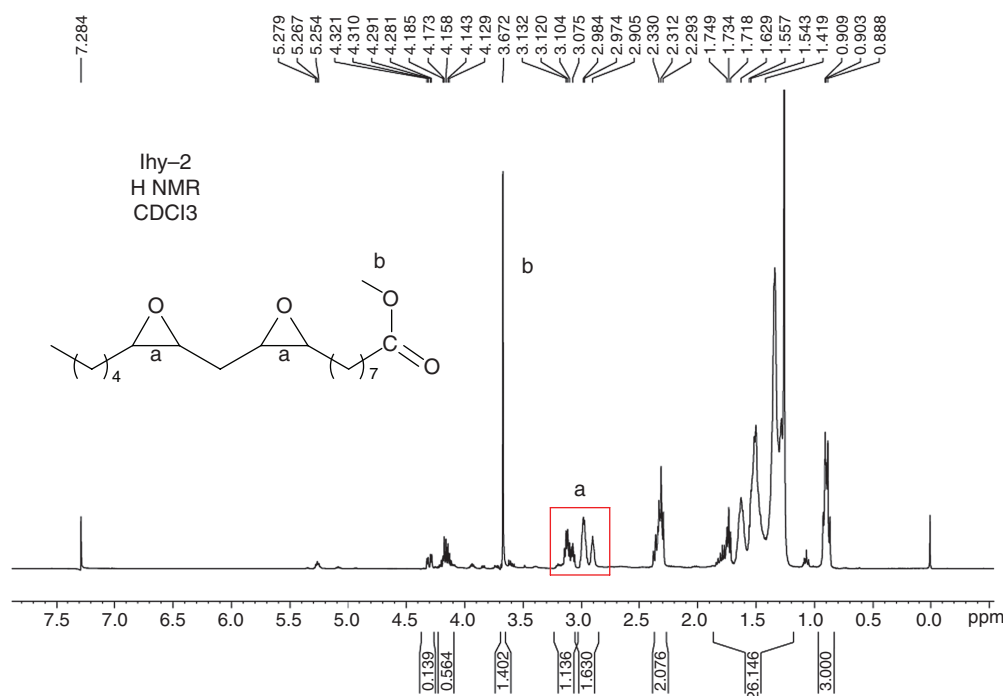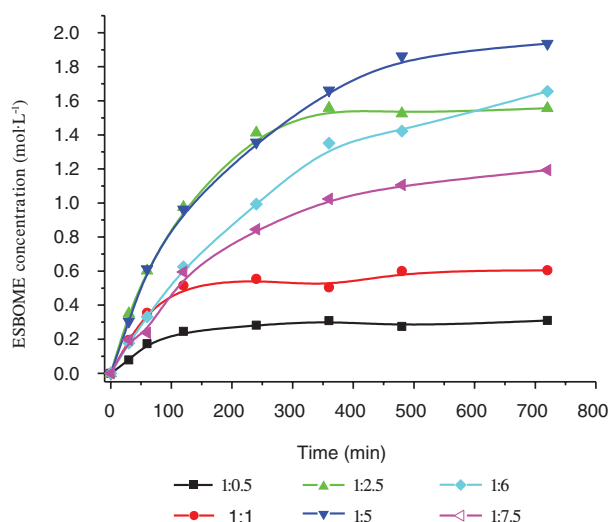
FIGURE 9. ^{1}H NMR of epoxy oil methyl esters

FIGURE 10. ESBOME concentration-time profiles for different methanol concentrations. (Reaction conditions: 45 °C, 5% of Novozym 435, 14h, stirring speed 600 rpm)

TABLE. 1. Comparison of kinetic parameters with related transesterification reactions.

Parameters	value
V_{max} (mol·L^{-1} min^{-1})	6.132
$K_{m, S}$ (mol·L^{-1})	0.0001
$K_{m, A}$ (mol·L^{-1})	796.148
$K_{i, A}$ (mol·L^{-1})	0.0004

initial stage of the reaction, the production was low and the inhibition of ESBOME and glycerin was ignored. (3) One of the substrates was oil without inhibition to Novezym-435, but another substrate was methanol with obvious inhibition.

The Ping Pong mechanism inhibition of methanol can be expressed as follows:

$$v = \frac{v_{max}}{1 + \dfrac{K_{m,A}}{[A]} + \dfrac{K_{m,s}}{[S]}\left[1 + \dfrac{[A]}{K_{i,A}}\right]}$$

Here [S] denotes the oil concentration, [A] the methanol concentration, $K_{m, S}$ and $K_{m, A}$ denote the dissociation constants of oil and methanol, respectively, and $K_{i, A}$ the inhibition constants of methanol.

The data were analyzed by non-linear regression and the kinetic parameters were determined by the Origin, as shown in Table 1. The values obtained for the kinetic data were Vmax = 6.132 mol·L^{-1}min^{-1}, $K_{m,S}$ = 0.0001 mol·L^{-1}, $K_{m, A}$ = 796.148 mol·L^{-1},

seen in Figure 10 was same as the result of the single factor optimal reaction. Previously it was suggested that the enzymatic transesterification of triglycerides could be described by a Ping-Pong Bi mechanism with methanol inhibition (Ilmi *et al.*, 2016).

The kinetic model was set-up on the basis of the following assumptions: (1) The polarity of epoxidized soybean oil was better than soybean oil for mutual solubility with methanol. Under stirring, the mix was a homogeneous mixture. (2) In the

$K_{i, A}$ = 0.0004 mol·L^{-1}. This suggests that the proposed model for the Novezym 435 catalyzed transesterification of ESBO and methanol is valid.

4. CONCLUSIONS

Epoxidized soybean oil methyl esters could be efficiently prepared through the transesterification of epoxidized soybean oil (ESBO) with methanol in a solvent-free system using lipase Novozym 435 as catalyst. The optimized conditions were as follows: lower dosage of methanol (the molar ratio of methanol to ESBO 5:1), 5% Novozym 435 as catalyst, at 45 °C for 14 h, with a stirring speed of 600 rpm, under which the epoxidized soybean oil methyl esters (ESBOME) could be obtained at a 95.7% yield. During the enzymatic transesterification process, the oxirane oxygen values were kept unchangeable, which indicated that excellent functional group tolerance could be achieved under such mild reaction conditions. In addition, the recyclability of Novozym 435 in this transesterification process was examined and the results showed that the bio-catalyst could be reused ten times without losing any reaction activity or selectivity. The final product of ESBOME was identified by IR and ^{1}HNMR analysis. This established enzymatic transesterification of epoxidized soybean oil will provide an efficient method to produce multipurpose bio-based products. And the obtained kinetic data followed the Ping-Pong Bi mechanism model (Vmax = 6.132mol·L^{-1}min^{-1}, $K_{m,S}$ = 0.0001 mol·L^{-1}, $K_{m, A}$ = 796.148 mol·L^{-1}, $K_{i, A}$ = 0.0004 mol·L^{-1}) with competitive inhibition by methanol.

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