

Article

Synthesis of Biolubricant Basestocks from Epoxidized Soybean Oil

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Abstract: This work deals with the preparation of biolubricant basestocks through the ring-opening reaction of epoxidized soybean oil (ESO) by alcohols in presence of solid acid catalysts (SAC-13 resin). To this end, different experimental runs were carried out in a lab-scale reactor, analyzing the effect of the alcohol (methanol, ethanol, 2-propanol, 2-butanol), catalyst mass loading (from 1 to 10 wt % with respect to the oil mass) and operating temperature (60–90 °C). The main focus of investigation was oxirane conversion. The study was complemented by FT-IR, ¹H NMR and kinematic viscosity characterization of the different products of the ring-opening reaction. Experimental conversion data were fitted through a suitable kinetic model. Values of the best-fitting parameters in terms of rate constant, activation energy and catalyst reaction order were obtained, and were potentially useful for the design of an industrial process.

Keywords: biolubricants; acid exchange resin; epoxidized soybean oil; ring opening reaction; kinetic modelling

1. Introduction

During the last decade, efficient new technologies aimed at new renewable products have been developed to replace petroleum-derived chemicals due to increasing sustainability and environmental-health concerns. In this context, vegetable oils represent suitable substitutes for replacing conventional mineral oil-based lubricants due to their biodegradability and non-toxicity. In fact, compared to mineral oils, biolubricants have a higher flash point, viscosity index and lubricity, and lower evaporative loss [1,2]. On the other hand, the applicability of biolubricants is partially limited due to their thermo-oxidative hydrolytic instabilities, as well as their low-temperature fluidity. Nevertheless, there are many methods for improving these undesirable properties, such as the genetic modification of vegetable oil fatty acids; the direct addition of antioxidants, viscosity modifiers, pour point depressants and emulsifiers; and the chemical modification of vegetable oils [3]. Among these methods, the last seems to be the most interesting for improving thermal stability. Chemical modifications mainly involve altering the acyl (C=O) and alkoxy (O-R) functional groups and unsaturations of the triglyceride molecules.

Esterification and transesterification reactions are commonly used to modify the acyl group through the formation of new esters with better physical properties [4].

The epoxidation reaction of the double bond contained in vegetable oils, followed by oxirane ring opening by an acid or alkaline catalyzed reaction with organic acid or alcohol, improves the poor stability of oils caused by the presence of unsaturations. Moreover, modification of the molecular structure triglycerides can improve the chemical and physical properties of the final products.

Epoxidized vegetable oils can be produced via conventional reaction of the double bonds of oil with peracids, which act as oxidizing agents. The latter are obtained in situ by the reaction of corresponding carboxylic acids with hydrogen peroxide in presence of soluble mineral acids or, alternatively, acidic ion-exchange resins, as catalysts [5–7]. Epoxidized vegetable oils show better performances than vegetable oils for application as lubricants in certain temperature ranges. Indeed, they show a better thermal and oxidative stability due to their better acidity value and lubricity, increased viscosity, and higher pour-point temperature [8]. Adhvaryu and Erhan [8] reported epoxidized soybean oil (ESO) as a potential candidate for high-temperature lubrication, considering the good thermal, oxidative and frictional behavior observed. Moreover, epoxidized vegetable oils are promising intermediates, since the oxirane group is easily functionalized by reaction with different nucleophilic reagents, leading to a wide number of products that are interesting from the point of view of biodegradable lubricant formulations. Chemically modified soybean oils, with improved thermal and oxidative stability, were obtained by the ring-opening reaction of epoxidized soybean oil with alcohols in presence of acid catalysts, followed by esterification of the hydroxyl group in the opened-ring product with anhydride [9–11]. Sulphuric acid has been widely employed as a homogeneous catalyst in the modification of epoxidized oil. Campanella [12] proposed an alternative synthesis route, consisting of ring-opening reaction of the epoxidized soybean oils with acetic acid or short-chain aliphatic alcohol (methanol or ethanol) in presence of fluoroboric acid as catalyst in aqueous media. However, the use of acidic homogenous catalysts, mainly mineral acids, poses severe problems due to the potential corrosion of the reactor vessel, as well as waste stream-handling problems. Heterogenous catalysts or alternative methods of solid removal based on magnetic nanostructured materials [13–15] allow these limitations to be overcome. To this end, acidic ion exchange resin catalysts have been proposed for epoxidation and for the following modification reaction [6]. In this work, an optimization of the preparation of biolubricants through the acid-catalysed ring-opening reaction of epoxidized soybean oil with alcohols, using SAC-13 as solid acid catalyst, is proposed. The effect of the addition of alcohols, with different chain length and type, on the tribological features of the final products is investigated. Finally, after having selected the product with the highest viscosity, some reaction parameters—such as catalyst loading and temperature—were studied, in order to detect the best reaction conditions and to present a kinetic model that could be useful for the eventual design of an industrial process.

2. Results and Discussion

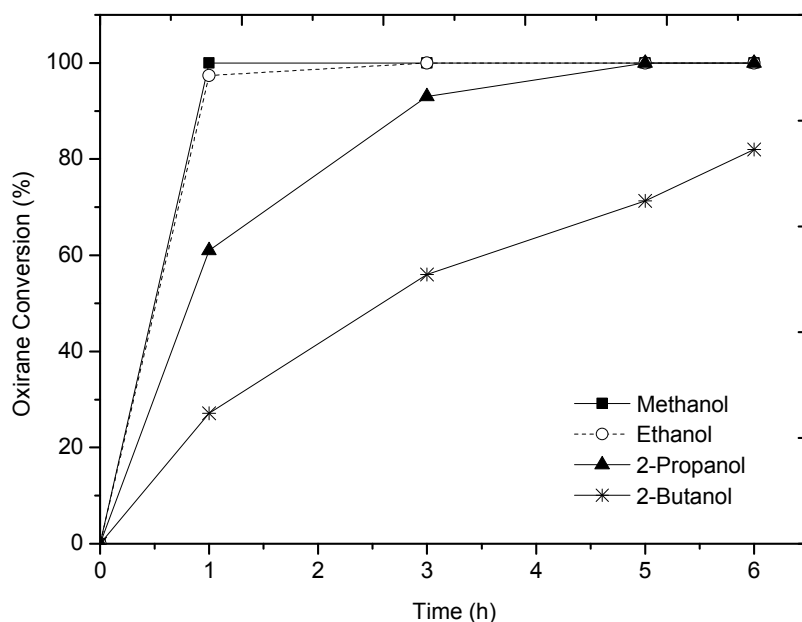
2.1. Alcohol Effect

To compare the effect of the alcohol structure on the ring-opening reaction rate, various alcohols with different structures and chain sizes were used as nucleophilic agent (Table 1, Runs# 1–4). The length of the alkyl group and the possible presence of branches are important factors for the thermal stability and the viscosity of the final biolubricant products. In fact, the presence of branching attached to the epoxy sites imposes spacing on triacylglycerol molecules, thus inhibiting crystallization, which results in a lower pour point.

Figure 1 shows the effect of different alcohols (methanol, ethanol, 2-propanol and 2-butanol) on the ESO conversion as a function of time (up to 6 h), with SAC-13 resin as solid catalyst. Among the alcohols, methanol and ethanol showed the largest activity, having almost completed the conversion to epoxidized oil after 1 h. Longer and branched alcohols impose longer reaction times.

Table 1. List of ring-opening runs with related experimental conditions.

RUN #	Alcohol	Alcohol/ESO (mol/mol)	Catalyst	Catalyst/ESO (wt %)	T (°C)
1	methanol	10	SAC-13 ^a	10	65
2	ethanol	10	SAC-13 ^a	10	78
3	2-propanol	10	SAC-13 ^a	10	80
4	2-butanol	10	SAC-13 ^a	10	80
5	2-butanol	10	SAC-13	10	80
6	2-butanol	10	No catalyst	-	80
7	2-butanol	10	SAC-13	2	80
8	2-butanol	10	SAC-13	4	80
9	2-butanol	10	SAC-13	1	80
10	2-butanol	10	SAC-13	4	60
11	2-butanol	10	SAC-13	4	70
12	2-butanol	10	SAC-13	2	80
13	2-butanol	10	SAC-13	2	80

^a SAC13 was used in pellets.**Figure 1.** Oxirane conversion as a function of time and for different alcohols. Catalyst: SAC-13 resin. Runs #3–6. See Table 1 for the operating conditions.

2.2. Characterization of Products

The ring-opening reaction of epoxidized soybean oil was monitored through the oxirane content value by titration of the purified product. A viscous and yellow-colored oil was obtained in all cases. The nature of the hydroxyl-ether product was confirmed by FT-IR and ¹H NMR analysis.

FT-IR spectra of epoxidized soybean oil, and of the products of the ring-opening reaction with methanol, ethanol, 2-propanol and 2-butanol are shown in Figure 2. The ESO spectrum shows a characteristic band at 819 cm⁻¹, which is attributed to the quaternary carbons of the epoxy ring C–O–C stretching, in accordance with the literature [16]. The spectra of hydroxyl-ether products when using different alcohols show the disappearance of the epoxy band, and the corresponding appearance of the band relative to the hydroxyl groups (3500 cm⁻¹), further confirming the product nature.

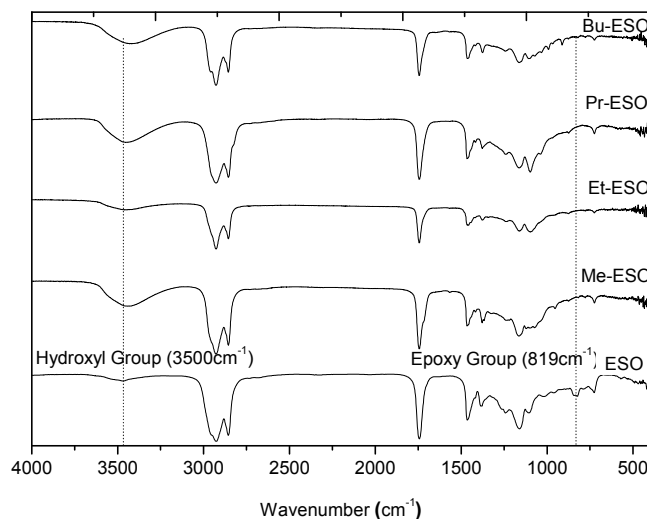


Figure 2. Comparison of infrared spectra for: ESO, and product of ring opening reaction of ESO with methanol (Me-ESO), ethanol (Et-ESO), 2-propanol (Pr-ESO) and 2-butanol (Bu-ESO).

Figure 3 presents the ^1H -NMR spectra of epoxidized soybean oil, and the product of ring-opening reaction with ethanol, 2-propanol and 2-butanol. The ^1H -NMR spectrum of ESO (Figure 3a) shows a chemical shift in the 2.7–3.1 ppm region, which corresponds to proton attachment to the oxygen atom of the oxirane group, which is in accordance with the literature [16]. Signals of the methylene protons of the glycerol backbone appear in the 5–5.2 ppm region; this aspect is important with regard to the biodegradability of the product [17], since it permits decomposition by microorganisms into nontoxic products (carbon dioxide and water), and which depends on the starting product. The ring-opening reaction products retain (Figure 3b–d) the backbone structure, confirmed by the signal at 5.2 ppm, while the peak of hydrogen attached to the epoxy group (2.7–3.1 ppm) disappears.

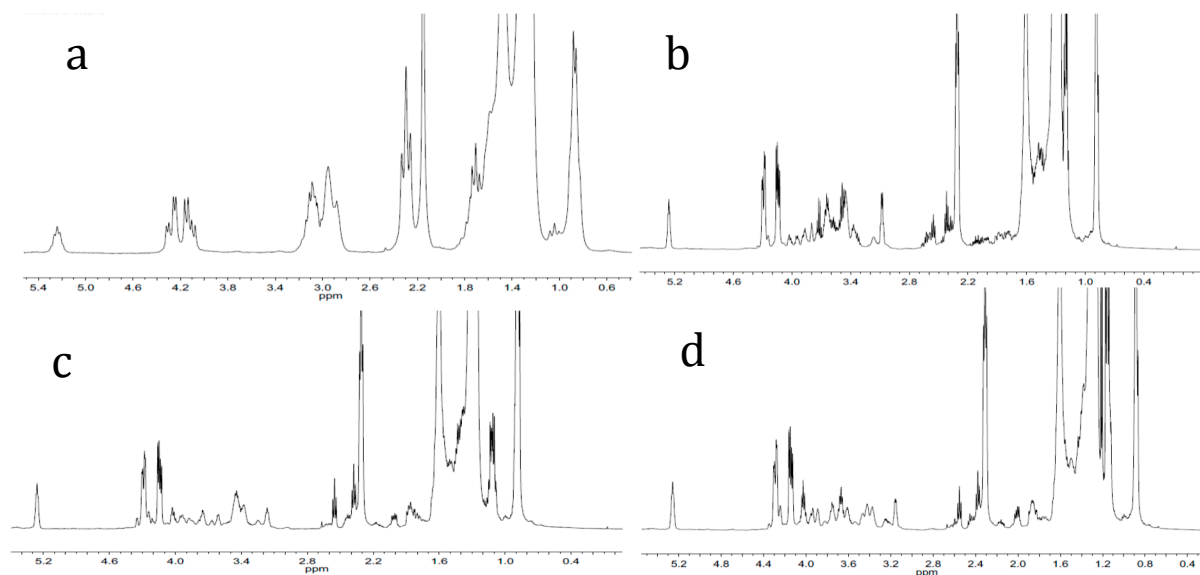


Figure 3. Comparison of ^1H NMR spectra for: (a) ESO, product of ring opening reaction of ESO with (b) ethanol, (c) 2-propanol, and (d) 2-butanol.

The kinematic viscosity (dynamic viscosity per density) of these products was measured in order to evaluate their suitability as lubricants. The results are displayed in Figure 4. A higher viscosity was observed for the products, compared to the value (circa $200 \text{ mm}^2 \text{ s}^{-1}$) for epoxidized soybean oil. In

particular, Bu-ESO proved to be the most viscous fluid (about $600 \text{ mm}^2 \text{ s}^{-1}$) due to the presence of branching in the starting alcohol (2-butanol). For this reason, even though it was characterized by slower kinetics behavior (see Figure 1), 2-butanol was used for successive runs, and for deepening the kinetics and mass transfer aspects, as reported below.

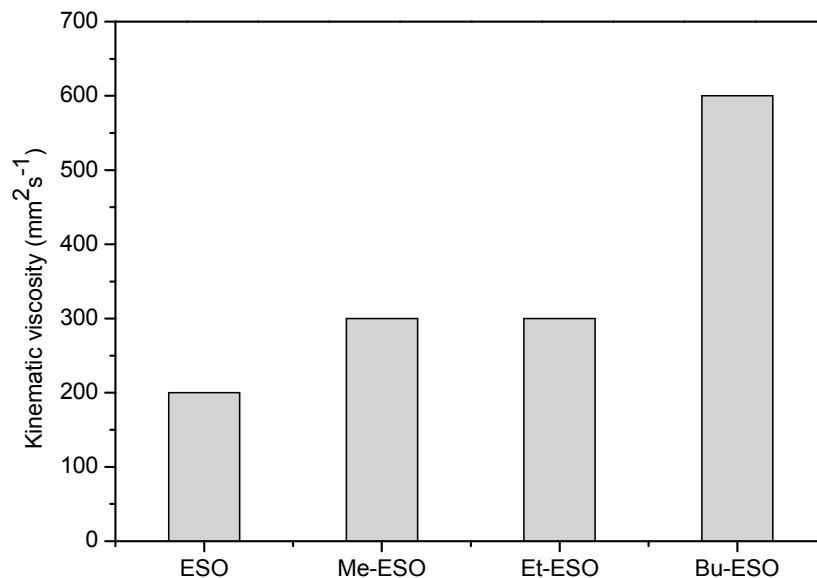


Figure 4. Kinematic viscosity for: ESO, and product of ring-opening reaction of ESO with methanol (Me-ESO), ethanol (Et-ESO), and 2-butanol (Bu-ESO).

2.3. Kinetics

2.3.1. Diffusion Resistances

To evaluate the influence of catalyst dimension, the catalyst pellets were grounded to obtain a powder. The diffusion effects were evaluated by comparing the results for the ring-opening reaction of epoxidized oil with butanol at 80°C (see Table 1) with SAC-13 in pellet- (Run #4) and in powder form (Run #5). The ring-opening reaction in presence of SAC-13 in pellets was strongly affected by internal diffusion. In fact, the conversion value after 1 h was 27.1% (see Figure 1), significantly lower than the corresponding value found when the powder was used (around 100%).

For this reason, parameter estimation analysis was carried out on the two experimental tests performed with the catalyst in powder and pellet form, under the same experimental conditions, and using a power-law reaction rate expression (see Equation (1)). The ratio between the two kinetic constants is $k_{\text{powder}}/k_{\text{pellets}} = 0.006$, which is clearly related to mass transfer phenomena occurring either in the liquid-solid film or for intraparticle diffusion. Therefore, to investigate the intrinsic kinetics of the reaction, the kinetic study of the ring-opening reaction was performed using SAC-13 resin in powdered form.

2.3.2. Effect of Catalyst Loading and Temperature

The effect of catalyst loading on the ESO ring-opening reaction with 2-butanol was studied by varying the catalyst (SAC-13) content (see Table 1): no catalyst (Run #6, no observed activity); and 1, 2 and 4 wt % for the catalyst/ESO ratio (Runs #9, #7 and #8, respectively, time-conversion results reported in Figure 5). A larger amount of catalyst leads to a larger oxirane conversion, due to the increase in available catalyst active sites. Conversion values of around 95% after 1 h were observed when the largest catalyst amount was used.

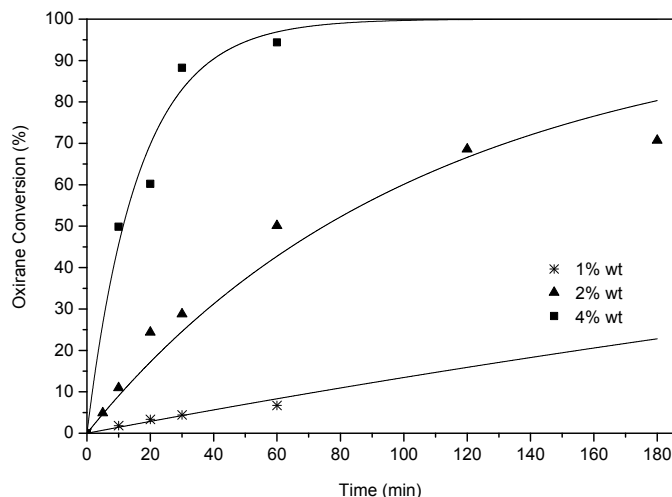


Figure 5. Oxirane conversion as a function of time and for different values of catalyst loading (SAC-13 powder resin). Runs #7–9. See Table 1 for the operating conditions. Symbols = experimental data; curves = model predictions.

To check the data reliability, Run #7 was repeated three times (with the tags Run #7, #14 and #15, the last two of which are not reported in the Table 1 list); no deviation in the oxirane conversion values was observed, indicating the reproducibility of the process under investigation.

The effect of temperature was investigated by using a 4 wt % catalyst/ESO ratio. T -values from 60 °C to 80 °C were investigated (Runs #8, #10, and #11, with time-conversion results reported in Figure 6). The temperature had a rather strong effect in terms of ameliorating the conversion values; taking a 1-h reaction time as reference, oxirane conversions of 10%, 48% and 93% were observed at 60, 70 and 80 °C, respectively.

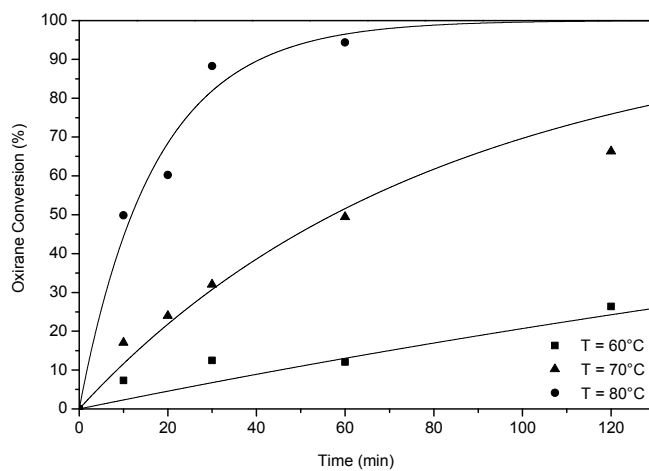


Figure 6. Oxirane conversion as a function of time and for different temperature values. Runs #8, #10, and #11. See Table 1 for the operating conditions. Symbols = experimental data; curves = model predictions.

2.3.3. Reuses Tests

The stability of the SAC13 resin was studied by repeating the ring-opening reaction using the same catalyst. The reaction was carried out as described above. At the end of the reaction, the catalyst was removed by filtration, air-dried, and reused. The reusability of the catalyst was evaluated by performing three sequential experiments with the same catalyst, with filtration occurring after each

experiment. The reuse tests for SAC-13 (see Figure 7) indicate that this catalyst can be reused without significant losses in activity.

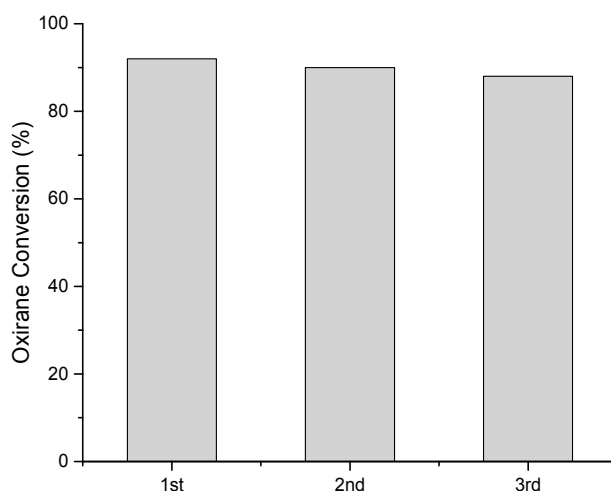
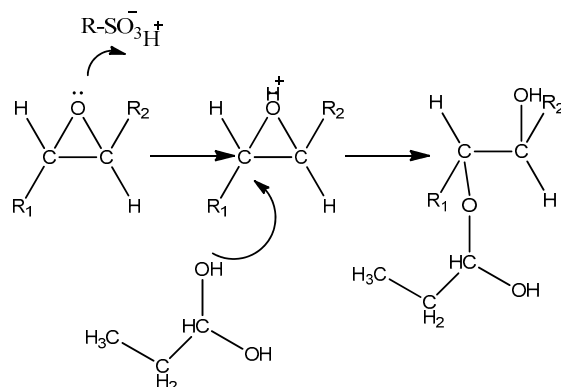


Figure 7. Oxirane conversions as a function of number of reuses. Runs #5, #12, and #13. See Table 1 for the operating conditions.

2.3.4. Development of a Kinetic Model and Reaction Mechanism for the Ring-Opening Reaction of Epoxidized Soybean Oil to Hydroxyl-Ether Products

The results of the ESO ring-opening reaction in presence of 2-butanol were interpreted with a lumped mechanism, which takes into account the reaction between the alcohol and the oxirane rings, Scheme 1.



Scheme 1. Mechanism of ring-opening reaction of the oxirane group with 2-butanol.

The reaction is hypothesized to occur by an initial electrophilic attack on the epoxy-oxygen by the acid catalyst, with a subsequent nucleophilic attack by the alcohol hydroxyl on the protonated oxirane group. As no competitive adsorption term was considered, the described mechanism leads to an overall second-order kinetic rate expression (please refer to the included list of symbols):

$$r = kC_{CAT}^nC_{OR}C_B \quad (1)$$

where, in particular, the oxirane ring concentration was calculated starting from the oxirane number definition. The partial reaction orders for both ESO and 2-butanol were assumed to be equal to one. To take into account the non-linear dependency of the catalyst concentration of the reaction rate, an adjustable partial reaction order, n , was considered for the resin concentration [18–20].

To take into account the kinetic constant dependence with temperature, the Arrhenius equation was implemented in the model, considering, as reference, the temperature of 353 K:

$$k = k_{ref} \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (2)$$

The modelling strategy followed was:

- the evolution of the concentration of the oxirane ring and 2-butanol was followed along with time, r being the time-derivative of the above concentrations, through the solution of an ordinary differential 2-equation system (ode45 MATLAB algorithm);
- n , k_{ref} and E_a were obtained by parameter estimation activity, implanting the lsqnonlin function present in the MATLAB library. 95% confidence intervals were calculated by implementing the nlparci MATLAB function.

The agreement between the experimental and retro-fitted data is reported in Figures 5 and 6, with an overall error window of about 15%. The values of the best-fitting parameters are reported in Table 2, together with the correlation matrix, from which it is evident that the estimated parameters are not correlated.

Table 2. Best-fitting values of the parameters used in the kinetic model.

Parameter	Value	Unit
k_{ref}	$2.84 \times 10^{-5} \pm 1.32 \times 10^{-6}$	$L^{n+1} g^{-n} mol^{-1} min^{-1}$
E_a	154.47 ± 10.50	$kJ mol^{-1}$
n	2.7 ± 0.1	-
Correlation Matrix		
	E_a	k_{ref}
E_a	1	
k_{ref}	-0.5	1
n	0.6	0.7

The activation energy of about $155 kJ mol^{-1}$ confirms (cf. Figure 6) a strong temperature effect on the reaction rate.

Moreover, the catalyst reaction order was found to be about 3. This has also been observed by other authors [18–20], and seems to be a characteristic value for acid-catalyzed reactions in the presence of resins, such as ether synthesis by reaction between alcohols and olefins. In general, the non-linear dependence of the reaction rate on the catalyst concentration ($n = 2.7$) is not straightforward to explain. In particular, different kinds of mechanisms have been applied in the related literature, such as Langmuir–Hinshelwood or Eley–Rideal mechanisms, but without giving good results. Actually, as it is evident from findings in the literature [20], the protonating power of the resin does not linearly depend on the concentration of sulphonic groups, explaining the non-linear dependency of the reaction rate on the catalyst concentration.

3. Experimental

3.1. Materials

Epoxidized soybean oil (ESO, acidity number of $0.14 mg_{KOH}/g_{sample}$, oxirane number of $6.52 g_{O_2}/100 g_{sample}$) was purchased from K Chimica (Mirano, Italy) and used as received, without any further purification and processing.

Unless otherwise specified, all other chemicals, including alcohols and SAC-13 resin (Fluorosulfonic acid polymer Nafion[®] on silica) (acidity = 0.22 meq^{H+}/g specific surface area = 200 m² g⁻¹ particle dimension = 1 mm), were purchased from Sigma Aldrich.

3.2. Analytical Methods

The oxirane number ($ON = g_{O_2}/100 g_{sample}$) was determined by potentiometric titration with perchloric acid in acetic acid, using cetyltrimethylammonium bromide (CTAB, 0.1 M in acetic acid) as reagent [21]. A METROHM end potentiometric titrator was used to calculate the oxirane number. By repeating each measurement thrice, the average error of the analysis was calculated to be about 1%.

Infrared (IR) spectra were recorded with a Fourier transform IR Avatar apparatus by Thermo Fisher. All the spectra were acquired, in transmittance mode, by spreading the samples between KBr plates. ¹H-NMR spectra were recorded using a Varian VXR200 FT spectrometer with CDCl₃ as solvent.

Kinematic viscosity was measured at 40 °C using a Bruker viscometer (model LV).

3.3. Ring-Opening Reaction

Table 1 lists the experimental conditions under which the eighteen runs reported in this paper were carried out. The ring-opening reaction was carried out in a three-neck round-bottom flask placed in an oil bath, and equipped with a reflux condenser and a thermometer for temperature control. Stirring was achieved by a Teflon magnetic bar.

In a typical experiment, alcohol (either methanol, ethanol, 2-propanol or 2-butanol) and catalyst were mixed and heated to the desired temperature T (60–90 °C); then, ESO was added to start the reaction (alcohol/ESO molar ratio = 10; catalyst/ESO mass ratio = 1–10%). The choice of the operating conditions was based on the study of pre-existing literature [9–12], and with the observance of the sustainability criteria of a chemical process. Samples were withdrawn periodically, quenched and centrifuged to separate the solid catalyst. The residual solvent was then evaporated by heating at 80 °C under high vacuum.

The oxirane conversion was calculated as $(ON_i - ON_f)/ON_i$, where ON_i and ON_f are the initial and final oxirane numbers, respectively.

4. Conclusions

The current work focused on the optimization of the synthesis of biolubricant basestock from epoxidized soybean oil and alcohol using a solid acid catalyst, SAC-13 resin. The study confirmed that the ring-opening reaction strongly depends on both the branching and the length of the alcohol used. The highest-viscosity product was obtained using 2-butanol as alcohol for the opening reaction. For this reason, the use of 2-butanol was chosen for a more detailed investigation, finding an interesting behavior when increasing catalyst concentration. As a result of a parallel kinetic modelling activity, the resulting rate of the ring-opening reaction was, in fact, strongly nonlinear with catalyst concentration. Thus, a kinetic study was performed on this system. Firstly, it was evident that, by using the catalyst in pellet forms, the overall rate was affected by mass transfer limitation. A second-order rate expression was used to interpret the collected data, finding a non-linear dependency of reaction rate on catalyst concentration, a fact that was described by adopting a power-law expression, which led to an exponent of 2.7.

The results obtained using the same catalyst three times showed no significant difference, indicating the good stability of SAC-13 resin in the reaction conditions. These findings could represent the first step in future process optimization for the low-temperature production of biolubricants.

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Author Contributions: Rosa Turco and Riccardo Tesser conceived and designed the experiments; Rosa Turco and Rosa Vitiello performed the experiments; Rosa Turco, Martino Di Serio and Vincenzo Russo analyzed the data; Salvatore Andini contributed reagents/materials/analysis tools; Rosa Turco wrote the paper; Martino Di Serio coordinated the work.

Conflicts of Interest: The authors declare no conflict of interest.

List of Symbols

C_B	2-butanol concentration, [mol L ⁻¹]
C_{CAT}	Catalyst concentration, [g L ⁻¹]
C_{OR}	Oxirane ring concentration, [mol L ⁻¹]
E_a	Activation energy, [kJ mol ⁻¹]
k	Kinetic constant, [L ⁿ⁺¹ g ⁻ⁿ mol ⁻¹ min ⁻¹]
k_{ref}	Kinetic constant at 353 K, [L ⁿ⁺¹ g ⁻ⁿ mol ⁻¹ min ⁻¹]
n	Catalyst reaction order, [-]
ON	Oxirane number, [mol oxirane ring/100 g substrate]
r	Reaction rate, [mol L ⁻¹ min ⁻¹]
\mathcal{R}	Ideal gas constant, [kcal K ⁻¹ mol ⁻¹]
T	Temperature, [K]
T_{ref}	Reference temperature, [K]

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