ORIGINAL PAPER

Kinetic Study on Oxirane Cleavage of Epoxidized Palm Oil

Ruihua Guo · Chuanguo Ma · Shangde Sun · Yuxiang Ma

Abstract A ring-opened product (EPO-HOAc) was prepared using epoxidized palm oil (EPO) and acetic acid (HOAc). The kinetics of the oxirane cleavage of EPO were investigated at 50, 60, 70, 80, and 90 °C, respectively, in the presence of HOAc. The rate equation of oxirane cleavage was as follows: $r = k[\text{Ep}][\text{CH}_3\text{COOH}]^{1.6}$ ([Ep] is the molar concentration of oxiranes, [CH_3COOH] is the molar concentration of HOAc), and the activation energy of oxirane cleavage was 40.28 kJ mol^{-1}. The structure of EPO-HOAc was confirmed by FT-IR and ^{1}H NMR. The oxidative stability of EPO-HOAc was better than that of palm oil (PO), and the pour point of EPO-HOAc was lower than that of PO and EPO, which made EPO-HOAc more suitable for biodegradable lubricant materials than PO and EPO.

Keywords Epoxidized palm oil · Oxirane cleavage · Kinetics · Acetic acid

Introduction

Owing to the unfavorable impact on the environment of mineral oil-based lubricants, there has been a steady increase in the demand for biodegradable, environmentally friendly lubricants. Vegetable oils can be used as biodegradable and non-toxic lubricants, which have high viscosity, low volatility, and low production cost. So vegetable oils are recognized as promising candidates as base fluids in environmentally friendly lubricants. However, their poor thermo-oxidative stability and poor low temperature properties limit their use as lubricant basestocks [1–3], but this can be overcome by blending the vegetable oils with diluents, such as polyisobutylene, poly-α-olefin, 2,6-di-*tert*-butyl-4-methylphenol. Another method of overcoming these problems is chemical structural modification of the vegetable oils. Epoxidized oil (EO) is a promising intermediate for this purpose, since the epoxy group is readily functionalized. Many valuable materials derived from EO by ring-opening reactions, especially epoxidized soybean oil (ESO), have been found [4, 5]. The oxidative stability and low temperature properties of EO can be improved by the ring-opened reaction of epoxy groups and the formation of hydroxyl and ethoxycarbonyl groups.

The content of unsaturated double bonds in palm oil (PO) is low, which limits the synthesis and oxirane cleavage reaction of epoxidized palm oil (EPO). However, compared with other vegetable oils, the commercial production of PO is quite larger, and the cost of PO is lower, which made the study of synthesis and oxirane cleavage of EPO more economic and practical. In our previous report [6], the EPO was prepared using PO as the raw material, and sulfuric acid as the catalyst. In this paper, assuming a single acetyl group is introduced into each oxirane and oxirane group completely convert to acetyl group, the resulting product is presented in Fig. 1. The kinetics of oxirane cleavage of EPO by acetic acid were investigated.

Materials and Methods

Materials

PO (acid value 0.09 mg g^{-1}, hydroxyl value 2.15 mg KOH g^{-1}, iodine value 70.31 g I$_2$/100 g) was purchased

R. Guo · C. Ma (✉) · S. Sun · Y. Ma
School of Food Science and Engineering, Henan University of Technology, 140 Songshan South Road, Zhengzhou 450052, Henan, People's Republic of China
e-mail: chuanguoma@hotmail.com

Fig. 1 Idealized oxirane cleavage route of EPO by acetic acid
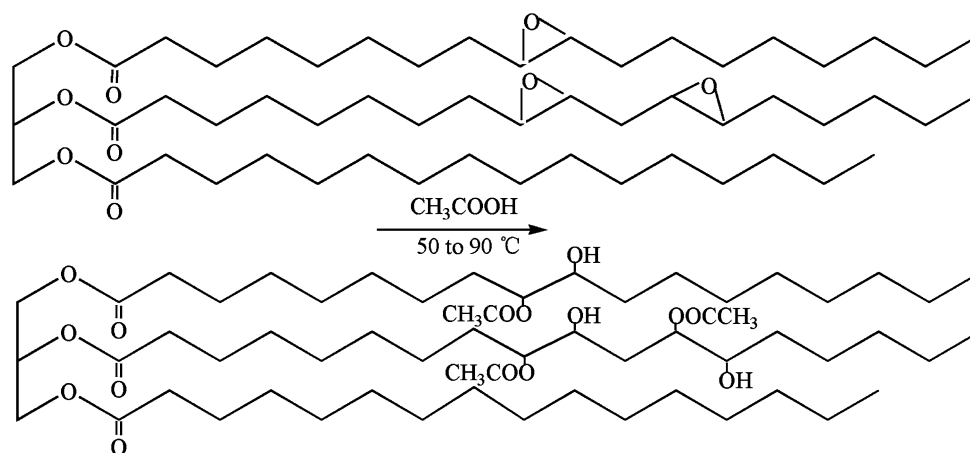
from Tianjin Longwei Grain and Oil Industry Co., Ltd (Tianjin, China). Hydrogen peroxide (30.0%, w/w), formic acid (88.0%, w/w), acetic acid (99.5%, w/w), sulfuric acid (95.0%, w/w), sodium hydroxide (96.0%, w/w) were purchased from Luoyang Haohua Chemical Co., Ltd (Luoyang, China). All other reagents were of analytical grade.

Synthesis of EPO

Formic acid (0.8 mol), hydrogen peroxide (2 mol), and sulfuric acid (0.1 mol) were placed in a round-bottomed reaction flask and continuously stirred at 40 °C for 10 min. The reaction mixture were used as epoxy agents. PO (0.2 mol) was added to a three-necked round-bottomed reaction flask equipped with a reflux condenser and was heated to 40 °C. Then, the epoxy agents (reaction mixture of 0.8 mol formic acid, 2 mol hydrogen peroxide, and 0.1 mol sulfuric acid) were added dropwise to the PO within 1 h at 40 °C. After that, the reaction was continued for 6 h at 65 °C. At the end of reaction, the crude product was washed with hot dilute alkali solution (1.0%, w/w; 45 °C) and hot distilled water (45 °C) until the pH of the product was approximately 7.0. Then the product was dried using a vacuum oven and analyzed for epoxy oxygen content. EPO (acid value 0.07 mg g^{-1}, hydroxyl value 2.08 mg KOH g^{-1}, iodine value 0.67 g I$_2$/100 g) with 3.8% epoxy value was obtained. The yield of EPO was 94.8%.

Kinetic Study of Oxirane Cleavage

EPO (100 g) was added to a three-necked round-bottomed reaction flask equipped with a reflux condenser and was heated to 80 °C in a constant-temperature water bath. Then, according to the fixed molar ratios of acetic acid to oxiranes (1:1, 2:1, 3:1, 4:1 or 5:1), acetic acid was added to the flask. Samples of the reaction mixture were withdrawn at 60 min intervals during the course of the experiment.

The samples were washed with hot dilute alkali solution (1.0%, w/w; 45 °C) and hot distilled water (45 °C) until the pH of the product was approximately 7.0. Then, the product was dried using a vacuum oven and analyzed for epoxy oxygen content, immediately.

Another series of experiments was conducted to calculate the reaction order of oxirane and the rate constant of the oxirane cleavage reaction. The experiments were conducted at 50, 60, 70, 80, and 90 °C with a molar ratio of acetic acid to epoxy group of 1:1. The residual epoxy oxygen of the ring-opened product (EPO-HOAc) was 0.05%, and all experiments were done in duplicate.

Analysis Methods

The epoxy oxygen content was determined by direct titration with HBr according to the standard method for oils and fats [7]. The hydroxyl values were determined according to the previous standard method [8].

The structure of the products were confirmed by Fourier transform infrared (FT-IR) and ^{1}H-NMR spectroscopy. The FT-IR spectra were obtained with an IR Prestige-21 FT-IR spectrometer (Japan). The ^{1}H-NMR spectra were obtained with a Bruker (Germany) DRX 400 (400 MHz), using CDCl$_3$ as solvent and tetramethylsilane as standard.

The model 743 Rancimat (Switzerland) was used for measurements of thermal oxidation stability according to a previous report [9]. The air flow was set at 20 L h^{-1}, and the temperature of the heating block was set at 110 °C. The pour points of the PO, EPO and the ring-opened product (EPO-HOAc) were measured by using a standard method [10].

Data Processing Methods

Data were analyzed by a self-compiled BASIC program based on the Lagrange interpolation [11, 12] and the numerical differential method [13, 14].

Results and Discussion

Kinetic Model

The kinetic model of oxirane cleavage of the epoxidized compounds by acetic acid [15] can be expressed as:

$$-d[Ep]/dt = k[Ep]^{n1}[HX]^{n2}$$

where [Ep] is the molar concentration of oxiranes, and [HX] is the molar concentration of acetic acid.

So the kinetic equation of EPO oxirane cleavage reaction by acetic acid can be expressed as:

$$r = -d[Ep]/dt = k[Ep]^{n1}[CH_3COOH]^{n2}$$

where r (mol L^{-1} min^{-1}) is the rate of oxirane ring opening, [Ep] is the molar concentration of oxiranes, [CH$_3$COOH] is the molar concentration of acetic acid, $n1$ and $n2$ are the reaction orders with respect to oxirane and acetic acid, and k is the rate constant of the oxirane cleavage reaction.

[Ep] and [CH$_3$COOH] can be calculated using the additive amount of EPO, the additive amount of acetic acid, the initial oxirane of EPO and the residual oxirane at different time. According to the relations between [Ep] and reaction time, using the self-compiled BASIC program based on the Lagrange interpolation and the numerical differential method, the instantaneous reaction rate of various reaction times can be calculated as $r = -d[Ep]/dt$.

The plots of ln(r/[Ep]) versus ln[CH$_3$COOH] for the oxirane cleavage of EPO by acetic acid are shown in Fig. 2. The result showed that a linear relationship between ln(r/[Ep]) and ln[CH$_3$COOH] was achieved at the different molar ratios, and the reaction order ($n2$, 1.6) of acetic acid was obtained from the slopes of the linear regressions.

The plots of ln r versus ln[CH$_3$COOH] are shown in Fig. 3. The result showed that relationships between ln r and ln[CH$_3$COOH] were fitted the linearity, and the values of ln k (i.e., the intercept of each linear regression)
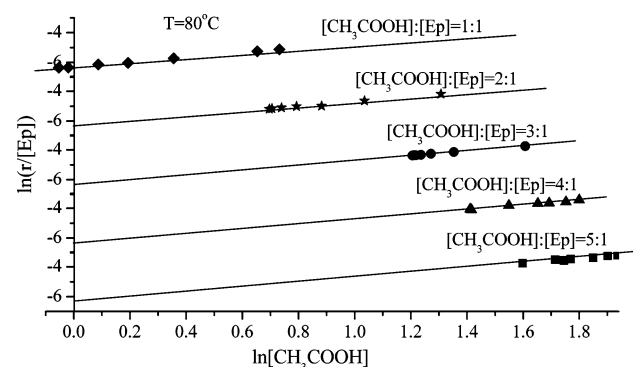
were −7.654, −7.147, −6.663, −6.318, and −6.010 at 50, 60, 70, 80, and 90 °C, respectively. The slopes of the linear regressions were all approximately 2.6 (i.e., the overall reaction order of the reactant was 2.6), then the reaction order of oxirane ($n1$) was 1.0, which can be calculated with the equation of $n1 = 2.6 - n2$.

Combining the results from these two sets of experiments, the kinetic equation of EPO oxirane cleavage reaction by acetic acid can be expressed as follows:

$$r = -d[Ep]/dt = k[Ep][CH_3COOH]^{1.6}$$

Temperature Dependence of the Cleavage Reaction

The activation energy, E_a, is an important parameter of the kinetic equation, which determines the relations between reaction rate constant (k) and reaction temperature (T).
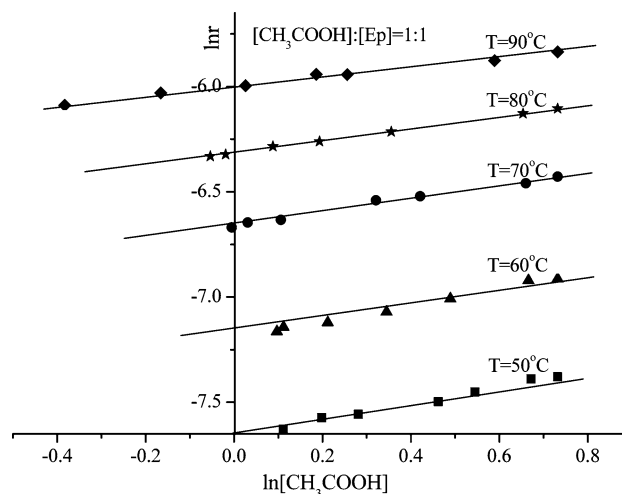

Fig. 3 Determination of the reaction order of oxirane and ln k at various reaction temperatures with the molar ratio of acetic acid to epoxy group of 1:1
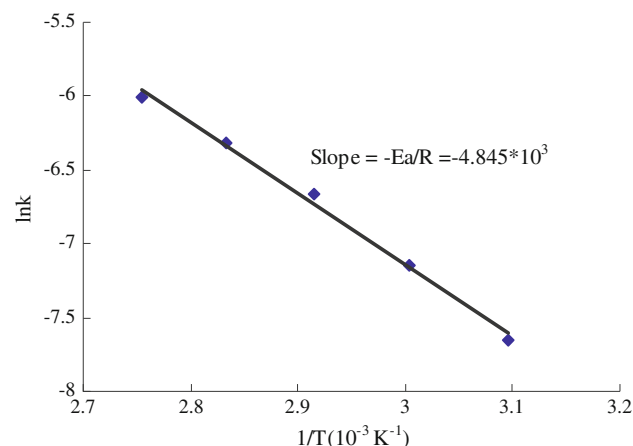

Fig. 2 Determination of the reaction order at various concentrations of acetic acid

Fig. 4 Determination of activation energy (Ea) for the oxirane cleavage of EPO

Generally, their mutual relations can be expressed by Arrhenius equation:

Integral index formula: $k = Ae^{-E_a/RT}$

Integral logarithmic formula: $\ln k = \ln A - E_a/RT$

The plots of $\ln k$ versus $1/T$ are shown in Fig. 4. The result showed that a linear relationship between $\ln k$ and $1/T$ was found, and the activation energy (E_a) of oxirane cleavage was 40.28 kJ mol^{-1}.

FT-IR and ^{1}H-NMR Spectroscopy

FT-IR spectra of the products based on the oxirane cleavage reaction are presented in Fig. 5. The formation of epoxy oxygen and hydroxyl in the products can be confirmed by the presence of peaks at 835 and 3,500 cm^{-1}, respectively. With the increasing of reaction temperature from 50 to 90 °C, the epoxy oxygen content gradually decreased, but the hydroxyl content gradually increased. This result suggested that the higher the temperature, the faster the oxirane cleavage reaction.

^{1}H-NMR spectra of PO, EPO and EPO-HOAc are presented in Fig. 6. The peaks at δ 5.3 ppm and δ 2.9–3.1 ppm are the characteristic displacements of the carbon–carbon double bonds and the epoxy groups, respectively. In the epoxidation of PO, the formation of epoxy groups was confirmed with the emergence of the peak at $\sim$3.0 ppm. In the oxirane cleavage of EPO, the formation of CH–OOC$_2$H$_5$ in EPO-HOAc was confirmed with the peak at 4.8 ppm.

Determination of Thermal Oxidation Stability

The Rancimat method determines the induction times of samples by measuring the increase of acidic volatiles released from the oxidizing oil at 110 °C and air flow of 20 L h^{-1}. Longer induction times suggest better oxidative stability of the tested samples. As shown in Fig. 7, the induction times of the PO, EPO and EPO-HOAc were
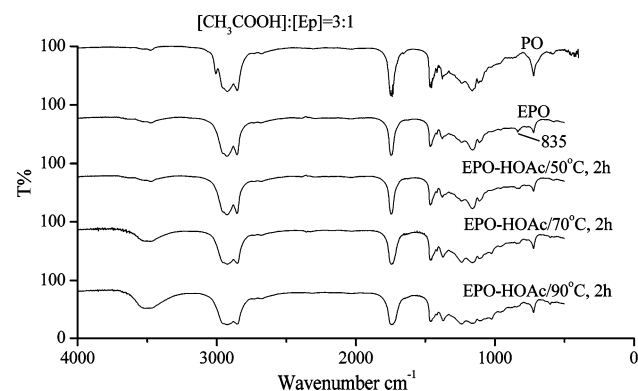
11.10, 63.92, and 37.17 h, respectively. The result suggested that though the oxidative stability of the EPO-HOAc is not so good as the EPO, it has been much improvement compared with that of PO.
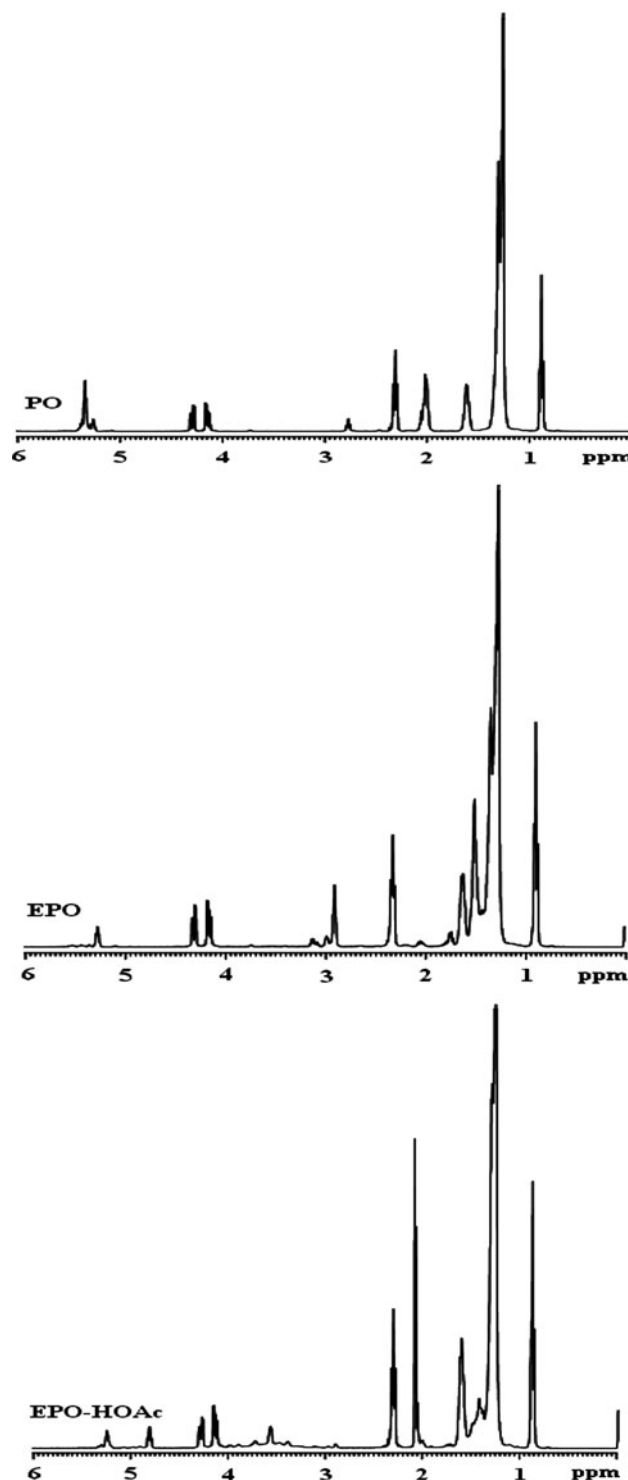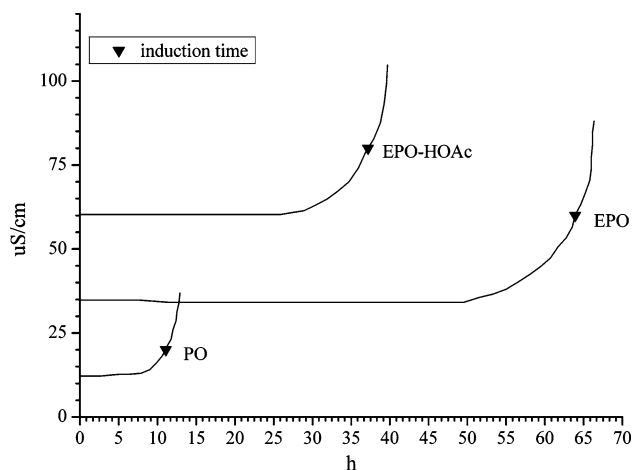

Fig. 6 ^{1}H-NMR spectra of PO, EPO, and EPO-HOAc

Fig. 5 FT-IR spectra of PO, EPO, and EPO-HOAc

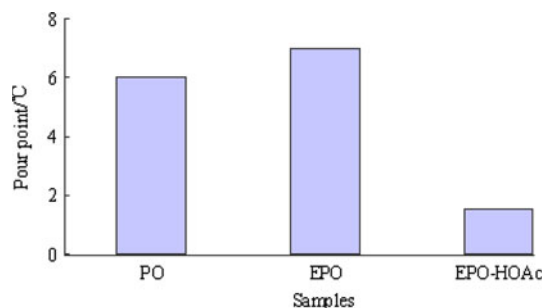**Fig. 7** Oxidative stability of PO, EPO, and EPO-HOAc

Fig. 8 Pour points of PO, EPO, and EPO-HOAc

Pour Point Determination

In industry, the pour point is one major characteristic of the low temperature properties of lubricating fluids [16]. Figure 8 showed the pour points of the PO, EPO, and EPO-HOAc without a pour point depressant. The result showed that the pour point of EPO-HOAc was lower than that of PO and EPO, which can broaden the use of PO and other vegetable oils for biodegradable lubricants.

Conclusion

The reaction rate equation of oxirane cleavage of EPO by acetic acid can be expressed as: $r = k[\text{Ep}][\text{CH}_3\text{COOH}]^{1.6}$. The relation between reaction rate constant and reaction temperature was satisfied with the Arrhenius formula, and the activation energy of oxirane cleavage was 40.28 kJ mol^{-1}. The epoxy functional groups in EPO

disappear to form hydroxyl and ethoxycarbonyl groups, which result in the improvement of oxidative stability and low temperature properties of EPO-HOAc. These result suggested that EPO-HOAc was more suitable for use as a biodegradable lubricant than PO and EPO.

References

1. Sharma BK, Adhvaryu A, Liu Z, Erhan SZ (2006) Chemical modification of vegetable oils for lubricant applications. J Am Oil Chem Soc 83:129–136
2. Wu XD, Zhang XG, Yang SR, Chen HG, Wang DP (2000) The study of epoxidized rapeseed oil used as a potential biodegradable lubricant. J Am Oil Chem Soc 77:561–563
3. Pop L, Puscas C, Bandur G, Vlase G, Nutiu R (2008) Basestock oils for lubricants from mixtures of corn oil and synthetic diesters. J Am Oil Chem Soc 85:71–76
4. Hwang HS, Erhan SZ (2001) Modification of epoxidized soybean oil for lubricant formulations with improved oxidative stability and low pour point. J Am Oil Chem Soc 78:1179–1184
5. Guo YZ, Hardesty JH, Mannari VM, Massingill JL Jr (2007) Hydrolysis of epoxidized soybean oil in the presence of phosphoric acid. J Am Oil Chem Soc 84:929–935
6. Ma CG, GUO RH, Zhang KH (2009) Study on the preparation of epoxidized palm oil with peroxyformic acid. China Oils Fats 34:58–61
7. Paquot C (1979) Standard methods for the analysis of oils, fats and derivatives: part 1, 6th edn. Pergamon, Oxford, pp 66–70
8. American Oil Chemists' Society (1997) Official and tentative methods of analysis. Section Cd 13–60
9. Jiménez AM, Martínez-Tomé M, Egea I, Romojaro F, Murcia MA (2008) Effect of industrial processing and storage on antioxidant activity of apricot (*Prunus armeniaca* v. bulida). Eur Food Res Technol 227:125–134
10. Petroleum products—determination of pour point. ISO 3016-1994
11. Carnicer JM, Gasca M (2004) Classification of bivariate configurations with simple Lagrange interpolation formulae. Adv Comput Math 20:5–16
12. Revers M (2000) Approximation constants in equidistant Lagrange interpolation. Periodica Mathematica Hungarica 40:167–175
13. Cockburn B, Dong B, Guzmán J (2009) A hybridizable and superconvergent discontinuous Galerkin method for biharmonic problems. J Sci Comput 40:141–187
14. Tselios K (2004) Symplectic methods of fifth order for the numerical solution of the radial Schrödinger equation. J Math Chem 35:55–63
15. Gan LH, Goh SH, Ooi KS (1992) Kinetic studies of epoxidation and oxirane cleavage of palm olein methyl esters. J Am Oil Chem Soc 69:347–351
16. Asadauskas S, Erhan SZ (1999) Depression of pour points of vegetable oils by blending with diluents used for biodegradable lubricants. J Am Oil Chem Soc 76:313–316