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Investigation of the physicochemical properties for vegetable oils and their epoxidized and carbonated derivatives

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Abstract

Vegetable oils are more and more used in industry for the production of biodiesel, biolubricant or polymer. In this context, production of polyurethane by non-isocyanate routes involves the production of epoxidized and carbonated vegetable oils. The determination of the optimum operating conditions and the scale-up of these processes require the knowledge of different physicochemical properties such as viscosity, density, refractive index or specific heat capacity. These data are rare for the epoxidized and carbonated vegetable oils and the evolution of these data with the temperature is absent in the literature. This article proposes to study the evolution of these properties with temperature and composition in double bond, epoxide and carbonated groups. It was demonstrated that density, refractive index of these oils vary linearly with temperature. Viscosity of these oils, which was found to be Newtonian fluids, is an exponential function of temperature. The ratio of specific heat capacity at a temperature to the specific heat capacity at a reference temperature follows a polynomial equation of second order with temperature.

It was demonstrated that some correlations could be used to predict the evolutions of these physicochemical properties at different compositions and temperatures based on the property knowledge of the pure compounds.

Keywords: Vegetable Oil; Epoxidized Vegetable Oil; Carbonated Vegetable Oil; Physicochemical Properties.

1. Introduction

Depletion of fossil fuel reserves and environmental issues have favored the academic and industrial research on biomass and CO₂ valorization. The example of vegetable oils for the production of biodiesel illustrates this tendency. Vegetable oils can be considered as a substitute for petroleum-derived compounds. Even though the majority of vegetable oils production is for alimentary (106 million tons in 2012), a significant part is used for the production of biodiesel (30 million tons in 2012) and for the production of chemicals (20 million tons in 2012).¹⁻² The interest of polymer industry for vegetable oils as feedstock is growing.³

Production of carbonated vegetable oils for the production of polyurethane by a non-isocyanate route is of particular interest.⁴⁻⁷ The production of such polyurethane requires different steps: epoxidation, carbonation and polymerization. This kind of production is eco-friendly because it uses renewable reactants. Furthermore, this carbon capture and utilization (CCU) leads to materials that capture CO₂ for a long period.⁸

The different steps for the production of carbonated vegetable oils are illustrated by Figure 1.

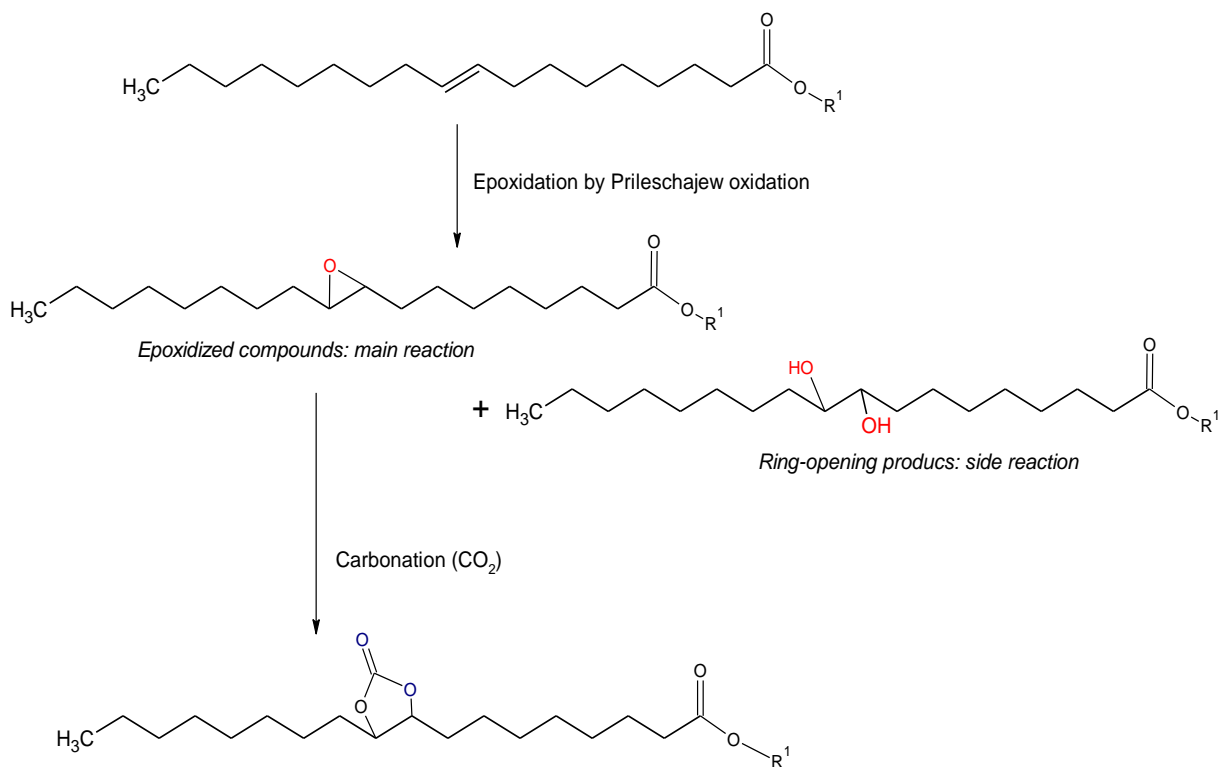


Figure 1. Different steps for the production of carbonated vegetable oils.

Epoxidation and carbonation synthesis have been described from several viewpoints in the literatures for different oils, such as cottonseed oil,⁴ unsaturated fatty acid and esters,⁹⁻¹² soybean oil,¹³⁻¹⁶ jatropha oil,¹⁷ castor oil,¹⁸ anchovy oil,¹⁹⁻²⁰ and some other oils.²¹⁻²⁴ Prileschajew oxidation is widely applied for the epoxidation synthesis through the oxidation of alkene with peracetic acid or performic acid.²⁵⁻²⁶ Nevertheless, epoxide group undergoes ring-opening side reactions.²⁷⁻³² Besides, different catalysts (homogeneous,^{4,9-12,16,18,21-27,30,32-38} heterogeneous,^{13-15,17,19-20,28-29,31,39} and enzymatic catalysts⁴⁰⁻⁴⁶) were investigated for an efficient synthesis. Moreover, process intensification with the use of microwave irradiation,⁴⁷⁻⁴⁸ or process safety⁴⁹⁻⁵² were treated by different research groups. For the carbonation reaction, tetrabutylammonium bromide (TBABr) is the most used catalyst, and the reaction temperature should be lower than 413.15 K to avoid ring-opening reaction by the catalyst decomposition products.³³

The literature concerning the physicochemical properties of vegetable oils, epoxidized vegetable oils and carbonated vegetable oils are scarce.⁵³ These data are fundamental for a better

understanding of mixing, hydrodynamics and heat transfer phenomena, and thus for process integration. For example, viscosity and density are important properties to determine mass transfer coefficients. Refractive index could also be used as an on-line analysis method.⁵⁴ Specific heat capacity data are essential for the energy balance of a chemical system.

The goal of this paper is to fill this lack of knowledge by studying the evolution of different physicochemical properties such as refractive index, dynamic viscosity, density and specific heat capacity of vegetable oils, epoxidized vegetable oils and carbonated vegetable oils at different temperatures. Three different types of vegetable oils were selected: cottonseed, linseed and soybean oils. We have chosen these vegetable oils because their compositions of unsaturated fatty acids and the iodine numbers are different (Table 1).⁵⁵

Table 1. Composition of vegetable oils in mass fraction.

	Palmitic C16:0	Palmitoleic C16:1	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Iodine value
Linseed oil	5.10	0.30	2.50	18.90	18.10	55.10	175.18
Soybean oil	10.60	-	4.80	22.50	52.30	8.20	132.16
Cottonseed oil	28.70	-	0.90	13.00	57.40	-	116.88

The second objective of this article is to investigate the influence of the functional groups on the physicochemical properties. For that, we have measured the physicochemical properties of different mixtures of soybean oil and their derivatives.

2. Experimental section

To evaluate the uncertainty of the measurement, the standard deviation of the mean $s(\theta_{mean})$ was calculated as:

$$s(\theta_{mean}) = \frac{s(\theta)}{\sqrt{N}} \times 100\% \quad (1)$$

where, $s(\theta)$ is the standard deviation of the single value and N is the number of experimental point.

2.1 Materials

Refined cottonseed oil, linseed oil and tetraethylammonium bromide (TEAB, 98 % in mass fraction) were purchased from ThermoFisher Scientific GmbH (Schwerte, Germany). Soybean oil was purchased from Sigma Company (Sigma, USA). Formic acid (purity>99 % in mass fraction), acetic acid (purity>99 % in mass fraction), hydrogen peroxide (33 % in mass fraction) and chloroform were obtained from VWR International SAS (Fontenay-sous-Bois, France). A standardized solution of 0.095 mol.kg⁻¹ of perchloric acid in acetic acid and tetra-n-butylammonium bromide (TBABr, purity>98 % in mass fraction) were obtained from Alfa Aesar (Alfa Aesar GmbH & Co., Ward Hill, MA, USA).

Epoxidized cottonseed oil (ECSO), epoxidized linseed oil (ELSO) and epoxidized soybean oil (ESBO) were produced by using the protocol developed by our group.^{32,51} Briefly, in a 500 mL jacketed-reactor, a mixture of vegetable oil, hydrogen peroxide and distilled water was stabilized at 333.15 K under agitation. When the reaction temperature was stable, formic acid was added with a volumetric flow rate of 2.9 mL.min⁻¹ for 25 min. The reaction of epoxidation for CSO, LSO and SBO lasted for one hour under these operating conditions. The molar ratios of reactants were 2:4:1:3 (double bond of oil/water/formic acid/hydrogen peroxide). Then, the organic phase was washed with a 10 % (in mass fraction) aqueous solution of Na₂CO₃ to remove residual formic acid and then with distilled water for three times to remove the residual sodium carbonate. Furthermore, the

purified organic phase was dried in a rotary evaporator and finally dried over anhydrous magnesium sulfate.

Carbonated cottonseed oil (CCSO), carbonated linseed oil (CLSO) and carbonated soybean oil (CSBO) were produced by using the same protocol described in the articles of our group.^{33,51} Briefly, epoxidized vegetable oil (ca. 0.09 kg) and the catalyst tetrabutylammonium bromide (TBABr, ca. 0.0039 kg) were introduced into a high-pressurized reactor. The reaction temperature was kept at 403.15 K and the pressure of CO₂ was 5 MPa. The reaction lasted for 50 hours.

In order to remove the TBABr catalyst, the carbonated product (CCSO, CLSO and CSBO) was diluted in ethyl acetate. Then, the mixture was washed four times with distilled water before being evaporated at 343.15 K. The residual water and solvent were removed through nitrogen-blowing.

The production of the epoxidized oils (ECSO, ELSO and ESBO) and carbonated oils (CCSO, CLSO and CSBO) are reproducible. The standard deviation of the mean for the epoxide value was 1.91 %. Table 2 shows the molar fractions of double bonds (x_{DB}), epoxide groups (x_{Ep}), ring opening groups (x_{RO}) and carbonated groups (x_{Carb}) for the different species. These molar fractions were determined as:

$$x_i = \frac{n_i}{n_{DB \text{ in } VO}} \quad (2)$$

where, n_i is the number of moles of groups (double bonds, epoxide groups) and $n_{DB \text{ in } VO}$ is the number of double bonds in the fresh vegetable oils.

Table 2. Molar fractions: X_{DB} , X_{EP} , X_{RO} , X_{Carb} and iodine number for the different species.

	X_{DB}	X_{EP}	X_{RO}	X_{Carb}	Iodine value
CSO	1.00	0.00	0.00	0.00	116.88
SBO	1.00	0.00	0.00	0.00	132.16
LSO	1.00	0.00	0.00	0.00	175.18
ECSO	0.04	0.88	0.07	0.00	4.76
ESBO	0.01	0.99	0.00	0.00	3.41
ELSO	0.02	0.98	0.00	0.00	3.58
CCSO	0.04	0.00	0.07	0.88	0.00
CSBO	0.01	0.00	0.00	0.99	8.08
CLSO	0.02	0.00	0.00	0.98	8.71

One can notice that the molar fractions for epoxide and carbonated groups are similar for the different vegetable oils (Table 2). Even if the ring-opening reaction was minimized, the molar fractions of epoxide and carbonated groups were slightly lower than 100 % (Table 2). The standard deviation of the mean for the X_{DB} , X_{EP} , X_{RO} , X_{Carb} and iodine value measurement were 1.16 %, 0.22 %, 2.78 %, 0.20 %, and 1.47 %, respectively, showing the reliability of the measurement.

2.2 Measurements

The epoxide concentration was determined by using the method of Jay⁵⁶, and the concentration of double bond by the method of Hanus.⁵⁷ Based on the concentrations of double bonds and epoxide groups, it was possible to determine the concentrations of ring-opening products and carbonated groups. The Vertex 70 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) equipped with an ATR accessory (ATR MK II Golden Gate, Specac, Eurolabo, France) was also used to confirm the presence of these functional groups.

Refractive indexes were measured by using the Abbemat 300 refractometer (Anton Paar, Austria) with an accuracy of 0.0001 nD according to the manufacturer. Densities were measured by using DMA 4100 M (Anton Paar, Austria) with an accuracy of temperature of 0.02 °C and an accuracy of measurement of 0.05 kg.m⁻³ according to the manufacturer.

The dynamic viscosities were measured by the viscometer Brookfield CAP2000+ (Brookfield Engineering Laboratories, Inc., Stoughton, MA) equipped with a cone plate geometry system and precise temperature control system. CAP spindle 01 was used during the viscosity measurement. The rotational speed of the cone was fixed at 20 RPM under high torque model. The shear rate varied from 133 s^{-1} to 3000 s^{-1} to verify if the vegetable oils are Newtonian or non-Newtonian fluids. For each sample, the value of viscosity was obtained after 60 s of hold time for temperature stabilization and 60 s of recording time for criterion of stability. The accuracy of viscosity is 2 % of Full Scale Range (FSR) and the accuracy of temperature is $2 \text{ }^{\circ}\text{C}$ according to the manufacturer.

The specific heat capacities for vegetable oils and their derivatives were measured by using a Tian-Calvet calorimeter C80 (Setaram Instrumentation, Caluire, France). The accuracy of temperature is $0.1 \text{ }^{\circ}\text{C}$ and the accuracy of enthalpy is 0.1 % according to the manufacturer. Successive heating of $2 \text{ }^{\circ}\text{C}$ was applied to the samples in a hastelloy steel cell. For the sake of clarity, the measurement protocol is described in chapter 3.4.

All the property measurements were performed under atmospheric pressure.

3. Results and discussion

3.1 Refractive index

The use of refractive index for vegetable oil characterization is scarce. One can cite the work of Cho et al.⁵⁸, which has demonstrated that the refractive index is proportional to acid values of vegetable oil. Figure 2 shows the evolution of the refractive index (*RI*) for CSO, ECSO and CCSO. One can notice that the refractive index is linear to the temperature, and this tendency was observed for the different vegetable oils and their corresponding epoxidized and carbonated forms. The coefficients of determination were higher than 95 % for the different vegetable oils and their derivatives by using a linear correlation between refractive index and temperature. The variation of refractive index with temperature can be expressed as:

$$RI = a \times T + b \quad (3)$$

where, *a* and *b* are two constants depending on the nature of the species; *T* is the temperature expressed in kelvin.

This value was measured three times for each sample. The standard deviation of the mean for the refractive index measurement was 0.51 %, showing the reliability of the measurement. Due to space limitation, only the results of cottonseed oil and their corresponding epoxidized and carbonated forms are presented in Figure 2. In general, refractive index linearly decreases when temperature increases. For cottonseed and soybean oils, the refractive index of their epoxidized derivatives is lower than for their vegetable oil and carbonated derivatives. Whereas for linseed oil, the refractive index for their carbonated derivative is lower than for the two other derivatives (Supporting Information Figures S1-S2 and Table S1).

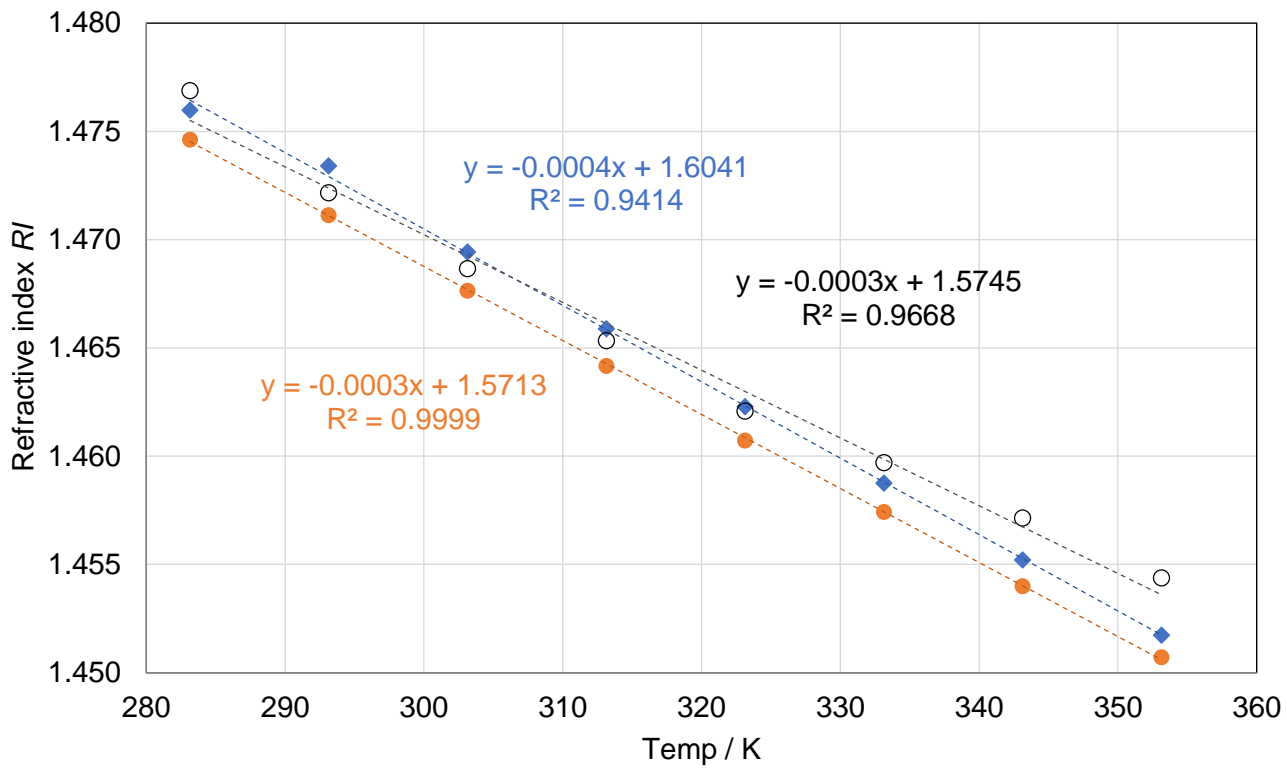


Figure 2. Measured refractive index versus temperature for cottonseed oil, epoxidized cottonseed oil and carbonated cottonseed oil. ♦, CSO; ●, ECSO; ○, CCSO.

Table 3 presents the different values of a and b for the evolution of the refractive index of the different vegetable oils and their derivatives.

Table 3. Evolution of a and b for the refractive index.

Refractive index $RI = a \times T + b$		
	a	b
CSO	-0.0004	1.6041
ECSO	-0.0003	1.5713
CCSO	-0.0003	1.5745
SBO	-0.0004	1.5815
ESBO	-0.0003	1.5696
CSBO	-0.0003	1.5536
LSO	-0.0004	1.5944
ELSO	-0.0003	1.5790
CLSO	-0.0003	1.5570

The values of the refractive index depend on the concentrations of double bond, epoxidized and carbonated groups. Indeed, the refractive indexes of linseed oil and their derivatives are higher than the two other vegetable oils and their derivatives. The concentrations of double bond, epoxidized and carbonated groups are higher for linseed oil and their derivatives.

The differences of refractive index values between the fresh vegetable oils, epoxidized and carbonated forms show that this physical data can be used as an on-line analytical method.

3.2 Density

The evolutions of density (ρ) of CSO, ECSO and CCSO with temperature are displayed in Figure 3.

There is a linear relationship between the density value and the temperature, which can be expressed as:

$$\rho = a' + b' \times T \quad (4)$$

where, a' and b' are two constants depending on the nature of vegetable oil and T is temperature expressed in kelvin. This linear relationship is confirmed by the high values of determination coefficients, i.e., over than 99.9 % for every vegetable oil and their derivatives.

Table 4 shows the values of these constants for the different vegetable oils and their derivatives.

As the temperature increases, the value of density decreases. Density of vegetable oil is lower than their epoxidized derivative than their carbonated derivative.

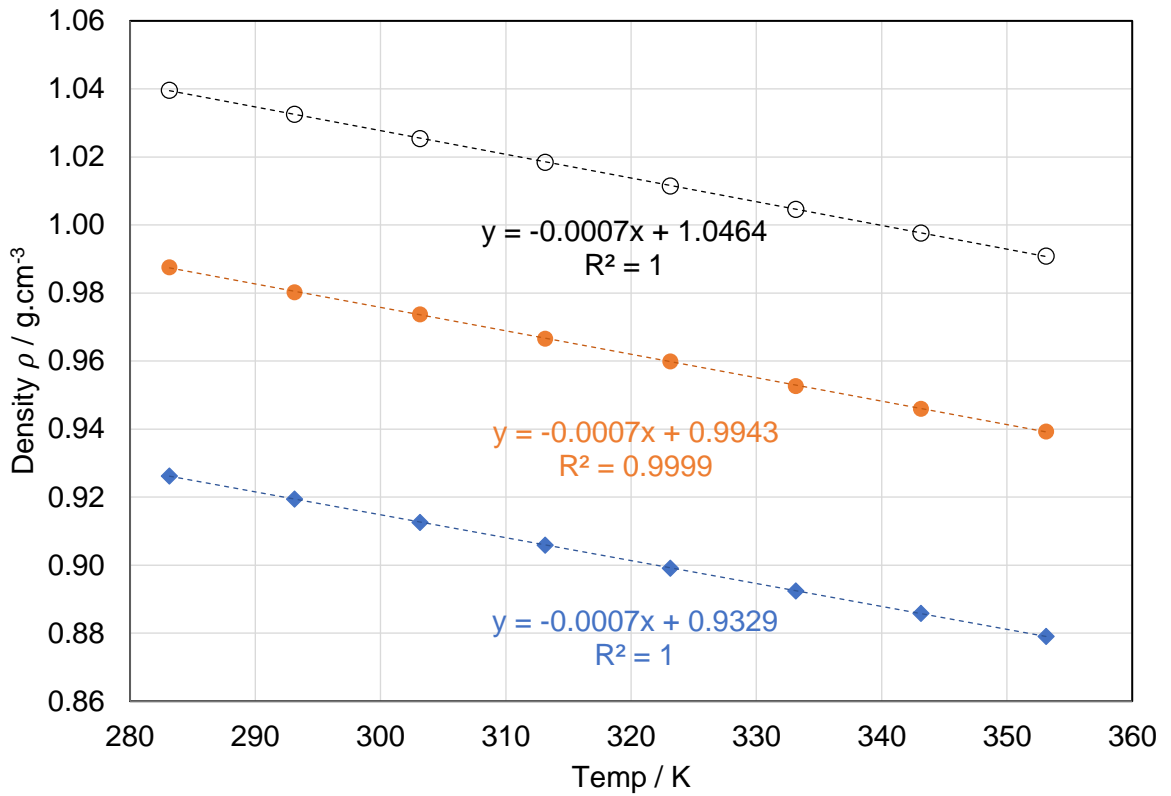


Figure 3. Measured density versus temperature for cottonseed oil, epoxidized cottonseed oil and carbonated cottonseed oil. ♦, CSO; ●, ECSO; ○, CCSO.

Density was measured three times for each sample. The standard deviation of the mean for the measurement of density was 0.07 %. The evolution of soybean oil density with temperature is similar to the ones found by Esteban et al.⁵⁹ with 0.17 % of average relative deviation. The average relative deviation (*RD* %) is calculated as:

$$RD (\%) = \frac{1}{n} \sum_{i=1}^n \frac{|\rho_{\text{literature}^{59}} - \rho_{\text{experiment}}|}{\rho_{\text{literature}^{59}}} \times 100 \quad (5)$$

where, *n* is the number of the data; $\rho_{\text{literature}^{59}}$ is the result from the literature and $\rho_{\text{experiment}}$ is our experiment result.

As the refractive index, density value is also sensitive to the concentrations of double bond, epoxidized and carbonated groups. Density of LSO was found to be higher than CSO and SBO within

the temperature range 283.15-353.15 K. This tendency was also observed for ELSO and CLSO (Supporting Information Figures S3-S4 and Table S2).

Table 4. Evolution of a' and b' for the density.

	$a'/\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$	$b'/\text{g}\cdot\text{cm}^{-3}$
CSO	-0.0007	0.93
ECSO	-0.0007	0.99
CCSO	-0.0007	1.05
SBO	-0.0007	0.94
ESBO	-0.0007	1.01
CSBO	-0.0007	1.09
LSO	-0.0007	0.95
ELSO	-0.0007	1.06
CLSO	-0.0008	1.11

3.3 Viscosity

The CAP2000+ viscometer was chosen because it is suitable for measuring the oil viscosity in a wide applicable temperature (up to 508.30 K) and viscosity range (0.02-1500 Pa.s).

As shown in Supporting Information (Figures S5-S7), all the vegetable oils and the epoxidized, carbonated derivatives were found to be Newtonian fluid at 353.15 K and within shear rate range 133 - 3000 s^{-1} . The influence of temperature was also tested. For example, at 323.15 K, it was also found that CSO, ECSO and CCSO are Newtonian fluids (Figure S8).

This observation was also mentioned by Xu et al.,⁶⁰ where they found that ESBO is Newtonian fluid at 298.15 K. Nevertheless, this observation is different with Campanella et al.,⁵³ who claimed that epoxidized vegetable oils are non-Newtonian fluid at 298.15 K.

Viscosity study of vegetable oils at different temperatures has been done by some research groups.^{59, 61} However, such study is rare for epoxidized and carbonated vegetable oils and sometimes with different values.^{53, 62-66} For instance, viscosity of ESBO at 313.15 K was found to be 0.3 Pa.s by Campanella et al.,⁵³ and 0.036 Pa.s by Poussard et al.⁶⁴

Figure 4 shows the evolution of dynamic viscosity for cottonseed, linseed and soybean oils and their derivatives versus temperature. The shear rate was selected as 267 s^{-1} . One can notice that the viscosity of linseed oil is higher than the other ones. Besides, as the number of carbonated groups increases, the viscosity value increases significantly.

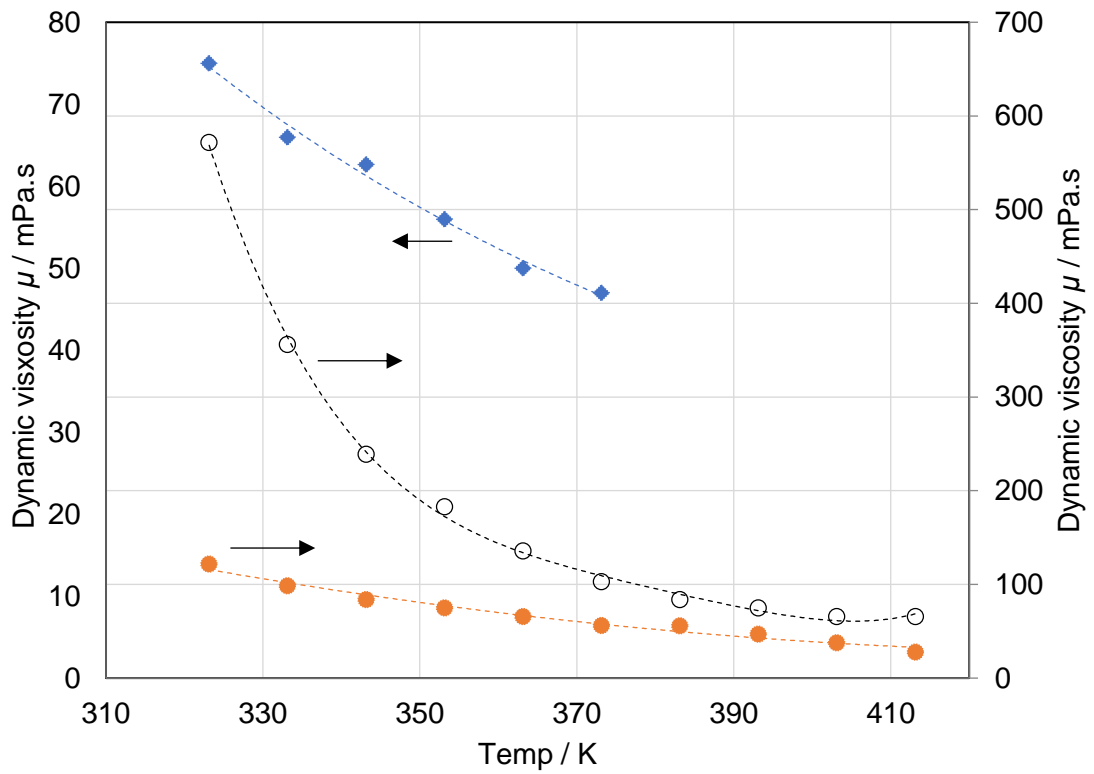


Figure 4. Measured dynamic viscosity versus temperature for cottonseed oil, epoxidized cottonseed oil and carbonated cottonseed oil. ♦, CSO; ●, ECSO; ○, CCSO.

From Figure 4, one can notice that the functional groups have a strong influence on the viscosity value. The evolution of dynamic viscosity is in the order of $\mu(\text{VO}) < \mu(\text{EVO}) < \mu(\text{CVO})$. For instance, at 283.15 K, viscosity of LSO is of 80 mPa.s compared to 100 mPa.s and 120 mPa.s for SBO and CSO, respectively.

Viscosity measurement was done three times for each sample. The standard deviation of the mean for the measurement of viscosity was 1.56 %.

Correlation between viscosity and temperature can be expressed by an Arrhenius law

$$\mu = A \times e^{\frac{-E_a}{RT}} \quad (6)$$

where, μ is the dynamic viscosity, Pa.s; A is the pre-exponential factor; E_a is the activation energy, J.mol⁻¹; R is the universal gas constant; T is temperature, K.

Figure 5 illustrates this correlation, and due to space limitation, only the evolution of cottonseed oil and their derivatives are shown (Supporting Information Figures S11-S12). The coefficients of determination were higher than 95 % for the different vegetable oils showing the exponential relationship between the viscosity and temperature.

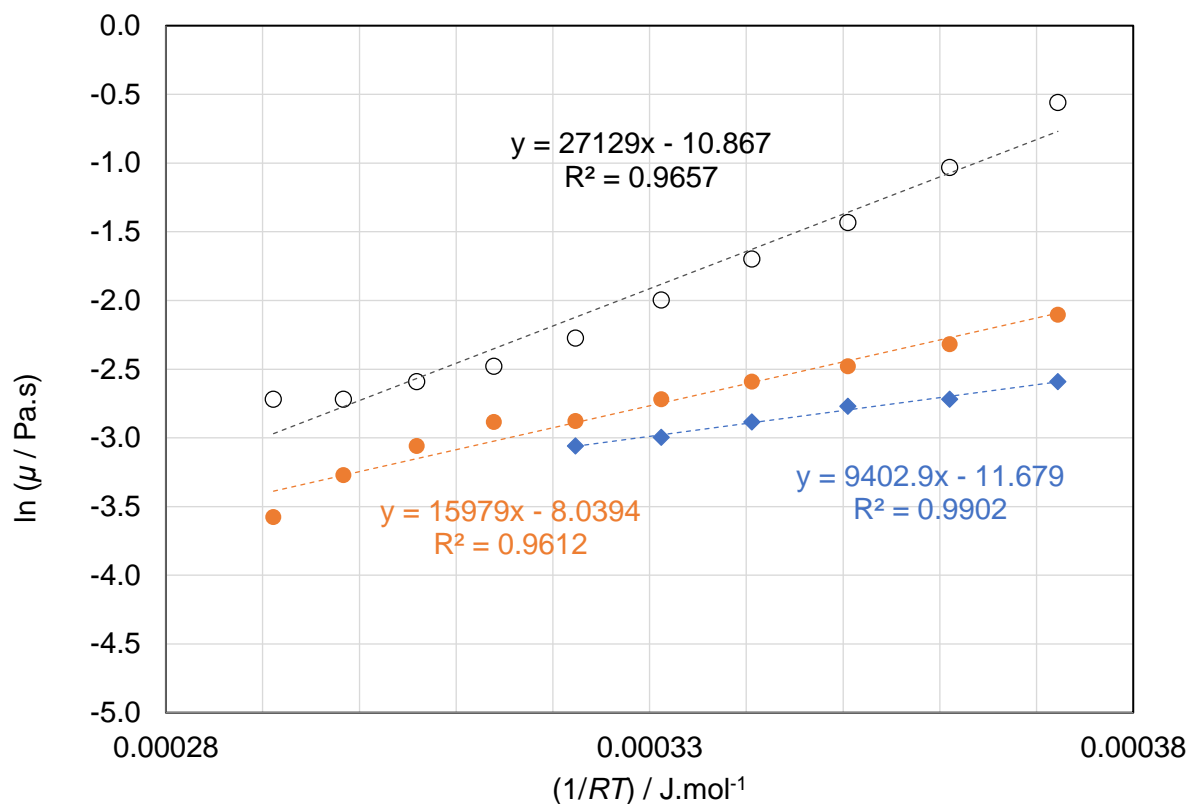


Figure 5. Linear correlation between the logarithm of viscosity and $1/RT$. ♦, CSO; ●, ECSO; ○, CCSO.

Table 5. Arrhenius data for eq 6.

	A / Pa.s	E_a / J.mol ⁻¹
CSO	8.00E-06	-9402.9
ECSO	3.23E-04	-15979
CCSO	1.90E-05	-27129
SBO	2.96E-03	-8688.7
ESBO	7.80E-05	-20308
CSBO	5.00E-06	-31499
LSO	5.34E-03	-6617.7
ELSO	1.00E-04	-21986
CLSO	1.80E-05	-30371

Compared to the literature, the measured viscosities of the fresh vegetable oils might be slightly higher. For example, the viscosity of SBO at 333.15 K was found to be 0.02 Pa.s by Campanella et al.,⁵³ Esteban et al.,⁵⁹ and Fasina et al.,⁶¹ whereas we found 0.07 Pa.s.

Based on eq 6, the viscosity of ELSO was found to be similar to the one measured at 298.15 K by Ishimura et al.⁶⁶ For the ESBO, the viscosity was found to be 0.2 Pa.s in this work which is the same with the one measured by Campanella et al.⁵³ but higher than the one measured by Poussard et al.⁶⁴, i.e., 0.036 Pa.s. The study made by Zhang et al.⁶⁵ shows similar viscosity values for the ECSO compared to our work.

The viscosity data for carbonated vegetable oils in the literature vary. One can cite the following values: CSBO was found to be 2.5 Pa.s at 323.15 K,⁶² 24.4 Pa.s at 313.15 K,⁶⁴ and 30.2 Pa.s at 293.15 K.⁶³ Compared to these values, our data are lower. Nevertheless, for the CCSO we have found similar values than the ones measured by Zhang et al.⁶⁵

3.4 Specific heat capacity

The evolution of specific heat capacity (C_p) of vegetable oils with temperature is relatively rare in the literature.⁶⁷⁻⁶⁸ This lack of data is even more pronounced for the epoxidized and carbonated vegetable oils.

This thermal parameter was measured by using C80-Setaram calorimeter. It is a twin calorimeter where the measuring cell was filled with the oils (ca. 1.0 g \pm 0.0001 g) and the reference cell was kept empty. The cells were kept under isothermal conditions at the desired temperature for 90 minutes. Then, a temperature ramp of 0.5 °C.min⁻¹ was applied to increase the temperature by 2 °C. At that moment, the cells were again kept under isothermal conditions at this new temperature stage for 90 minutes. During the temperature increase, there was an endothermic phenomenon corresponding to the energy absorbed by the oils to increase its temperature by 2 °C.

To determine the C_p values, one needs to take into account the energy absorbed by the system, i.e., with no chemicals in the measuring and reference cells.

Hence, one can determine the values of the C_p at a given temperature by using the following equation:

$$C_p(T) = \frac{Q_r(T) - Q_b(T)}{m \times \Delta T} \quad (7)$$

where, $Q_r(T)$ is the heat absorbed by the oils at the desired temperature; $Q_b(T)$ is the energy absorbed by the system in absence of oils; m is the mass of oils and ΔT is the temperature difference, i.e., 2 °C.

Figure S17 shows an example of measurement by C80-Setaram.

The standard deviation of the mean for the measurement of C_p was 1.06 %. Figure 6 shows the evolution of C_p for LSO, ELSO and CLSO with temperature. One can notice that the values of this parameter are similar for these three compounds within the temperature range 313.15-383.15K. We have also observed this tendency for the other two vegetable oils (Supporting Information Figures S13-S14 and Table S4).

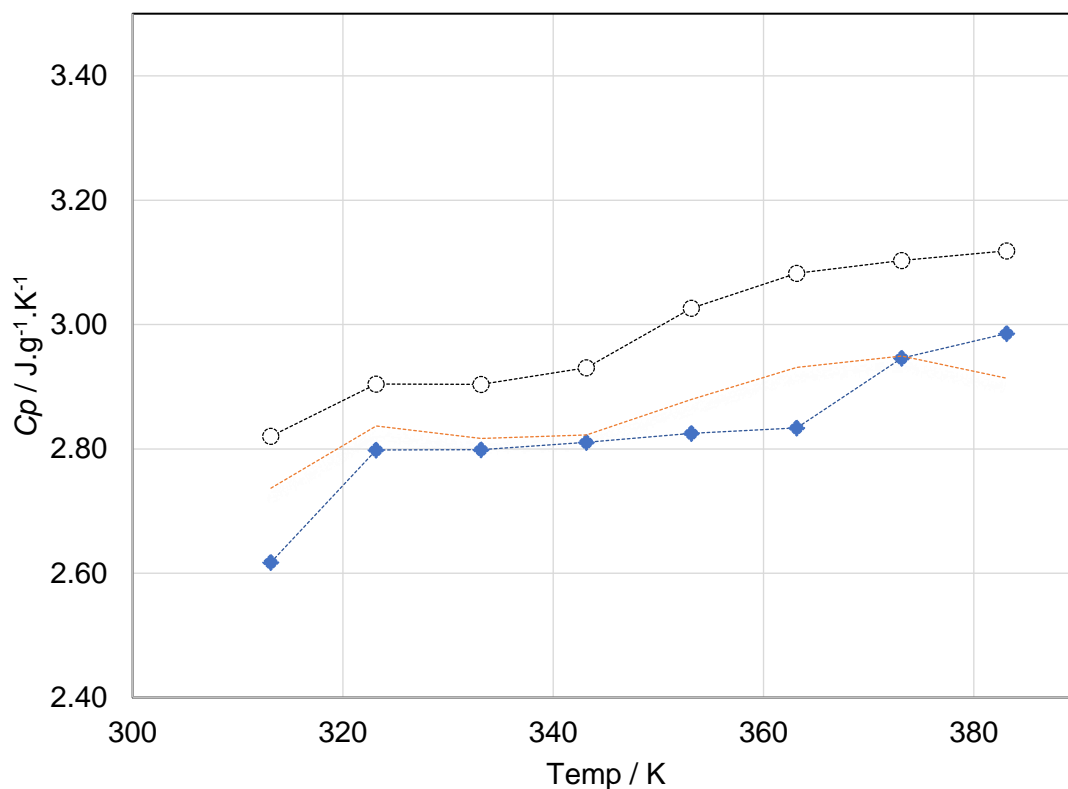


Figure 6. Evolution of specific heat capacity of linseed oil and their derivatives with temperature. ♦, LSO; ●, ELSO; ○, CLSO.

The variation of C_p with temperature can be described by a polynomial equation of second order as: ⁶⁹

$$\frac{C_p(T)}{C_p(T_{ref})} = A \times T^2 + B \times T + C \quad (8)$$

where, T is the temperature and T_{ref} is a reference temperature expressed in kelvin. The coefficient A , B and C are constants. For this study, the reference temperature was fixed at 313.15 K.

Figure 7 shows the fitting of the experimental data, i.e., $\frac{C_p(T)}{C_p(T_{ref}=313.15\text{ K})}$ by using a polynomial equation for LSO, ELSO and CLSO. One can notice that the coefficient of determination was higher than 95 % showing the reliability of this relationship. This observation was the same for CSO, SBO, ECSO, ESBO, CCSO and CSBO. Table 6 gives the values of the coefficients A, B and C for the oils.

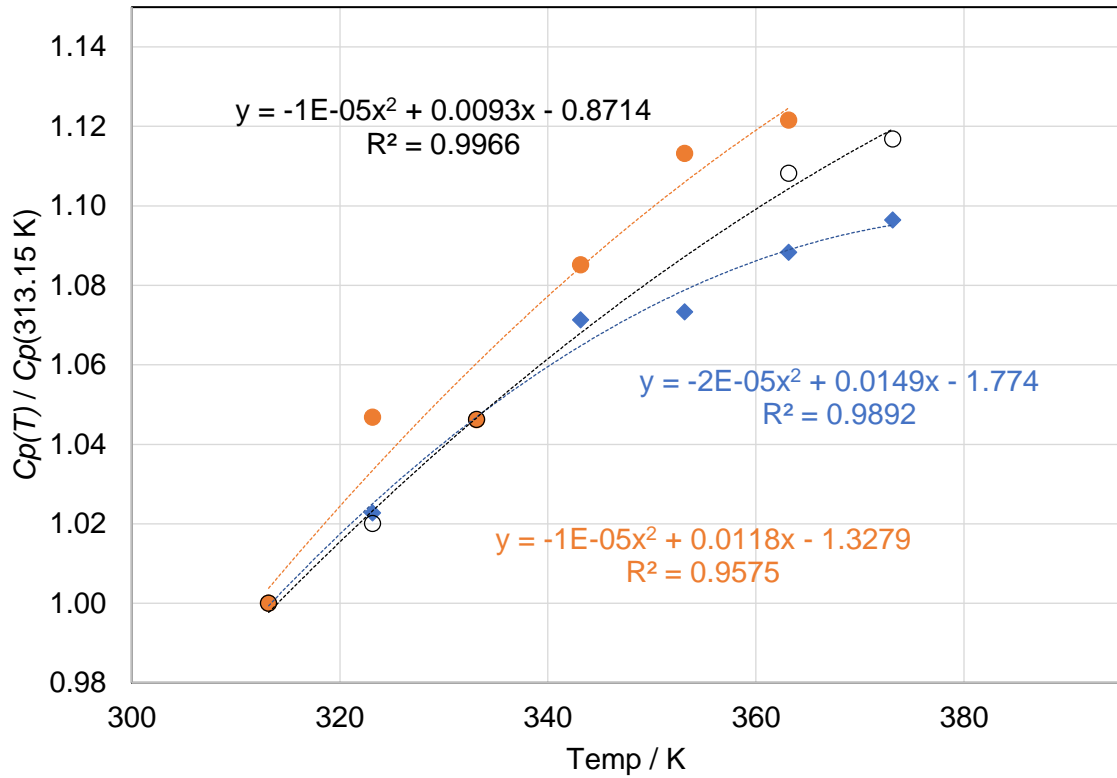


Figure 7. Polynomial fitting for $C_p(T) / C_p(313.15\text{ K})$ for cottonseed oil and their derivatives. ♦,

CSO; ●, ECSO; ○, CCSO.

Table 6. Evolution of the coefficients A, B and C of eq 8 for vegetable oils and their derivatives.

$C_p(T) / C_p(T_{ref}=313.15 \text{ K})=AT^2+BT+C$			
	A / K ⁻²	B / K ⁻¹	C
CSO	-2.00E-05	0.0149	-1.7740
ECSO	-1.00E-05	0.0118	-1.3279
CCSO	-1.00E-05	0.0093	-0.8714
SBO	-1.00E-05	0.0086	-0.6907
ESBO	-3.00E-06	0.0034	0.2521
CSBO	-8.00E-06	0.0066	-0.2973
LSO	-5.00E-06	0.0049	-0.0552
ELSO	-1.00E-05	0.0091	-0.6965
CLSO	-4.00E-06	0.0043	0.0688

3.5 Effects of functional groups in mixing solution

One can notice that the functional groups can have an important effect on refractive index, viscosity and density. Thus, can we predict the evolution of these properties at different concentrations of double bonds, epoxide and carbonated groups?

For that, we have used the solution of fresh vegetable oils, synthesized epoxidized vegetable oils and synthesized carbonated vegetable oils (Table 2). From these solutions, we have prepared different solutions with different weight percentage of SBO, ESBO and CSBO.

Table 7 shows the three different solutions used for these experiments.

Table 7. Solution composition

Solution	Weight percentage w (% in mass fraction)		
	SBO	ESBO	CSBO
S1	49.80	50.20	0.00
S2	19.78	19.98	60.24
S3	39.12	31.41	29.47

The following correlations have been tested:

$$RI(SX) = w(SBO) \times RI(SBO) + w(ESBO) \times RI(ESBO) + w(CSBO) \times RI(CSBO)$$

(9)

$$\rho(SX) = w(SBO) \times \rho(SBO) + w(ESBO) \times \rho(ESBO) + w(CSBO) \times \rho(CSBO)$$

(10)

$$\ln\mu(SX) = w(SBO) \times \ln\mu(SBO) + w(ESBO) \times \ln\mu(ESBO) + w(CSBO) \times \ln\mu(CSBO)$$

(11)

$$Cp(SX) = w(SBO) \times Cp(SBO) + w(ESBO) \times Cp(ESBO) + w(CSBO) \times Cp(CSBO)$$

(12)

where, SX is the solution S1, S2 or S3.

Ramírez Verduzco⁶⁹ has demonstrated that correlations (10) and (11) could be used for a mixture of vegetable oils and fatty acid methyl esters. For the specific heat capacity of a mixture, correlation (12) is widely accepted.⁷⁰

Figures 8-11 show the fittings of the correlation between the experimental data and the model data for refractive index (RI), density (ρ), $\ln\mu$ and specific heat capacity (Cp) for the different solutions

S1, S2 and S3. Due to space limitation, the other fitting curves were put in Supporting Information (Figures S18-S25 and Tables S1-S4).

To evaluate the reliability of these correlations towards experimental data, the overall average relative deviation of determination (*OARD*) was introduced: ⁷¹

$$OARD(\%) = \frac{\sum_{i=0}^N \left| \frac{\theta_e - \hat{\theta}_e}{\theta_e} \right|}{N} \times 100 \quad (13)$$

where, θ_e is the experimental value of the parameter; $\hat{\theta}_e$ is the predicted value given by the correlation and N is experimental data points. The correlation results are shown in Table 8.

Table 8. *OARD* of refractive index, density, $\ln \mu$ and specific heat capacity

	<i>OARD</i> / %
Refractive index	0.14
Density	0.33
$\ln \mu$	16.80
Specific heat capacity	2.37

Generally, one can notice that the experimental data (refractive index, density and specific heat capacity) can be successfully predicted with overall average relative deviation values less than 2.5 %. This result shows that it is possible to sum the contribution of functional group on refractive index, density and specific heat capacity. Interaction between the groups such as the hydrogen bonding or van der Waals force might not affect the value of the physicochemical properties. However, the overall average relative deviation value for $\ln \mu$ is higher due to the fact that eq 11 does not take into account the interaction between the functional groups.

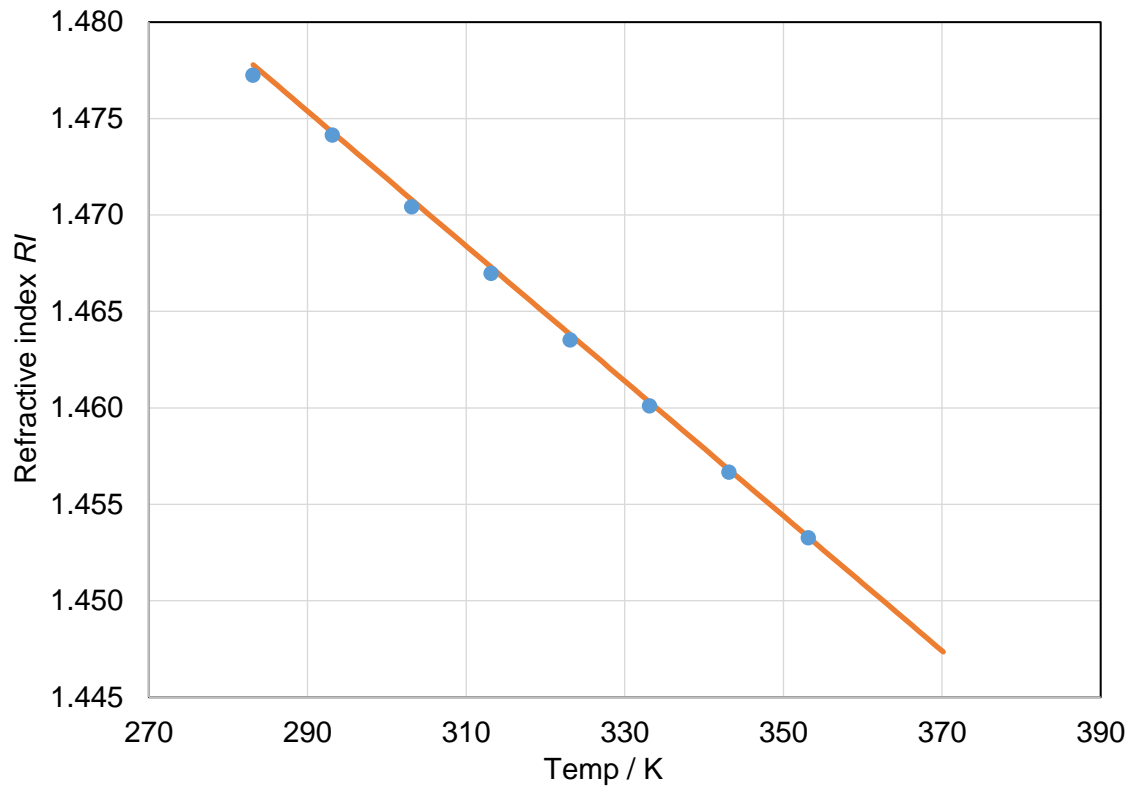


Figure 8. Fit of the model to the refractive index experimental data of solution S1. ●, Experiment data; —, Model data.

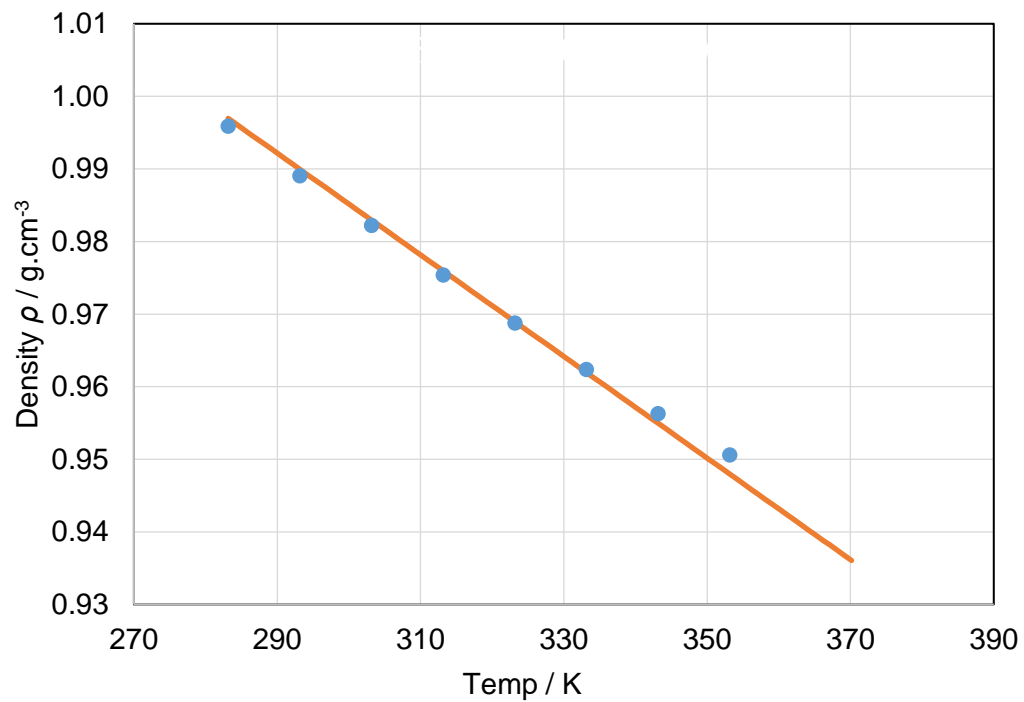


Figure 9. Fit of the model to the density experimental data of solution S3. ●, Experiment data; —, Model data.

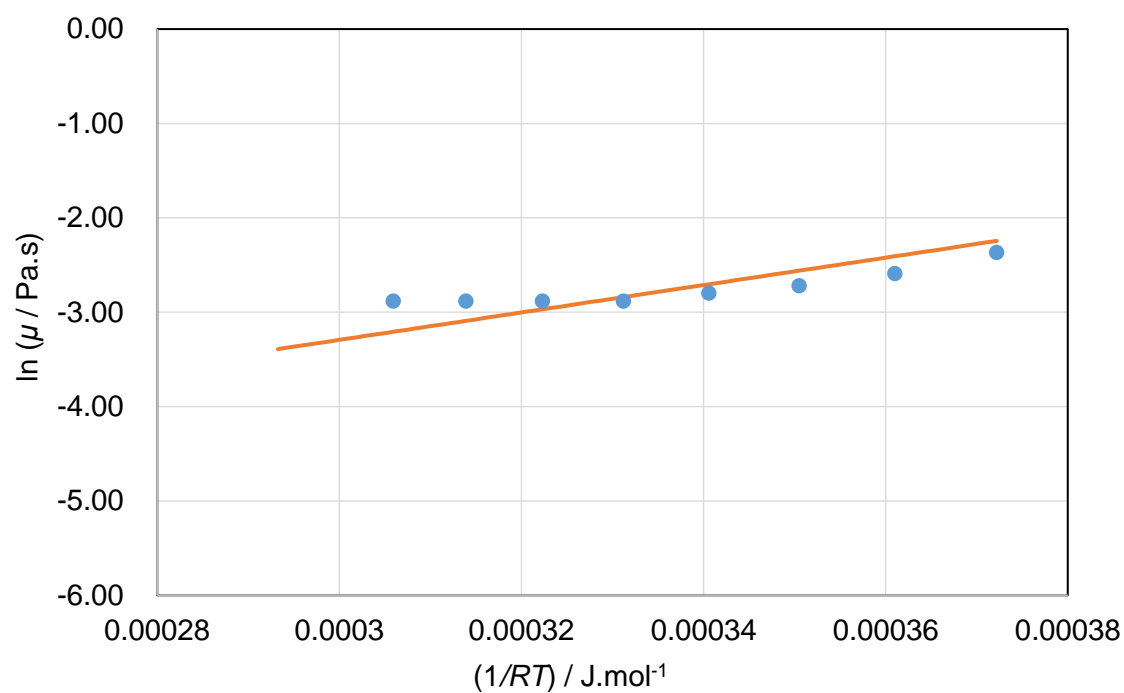


Figure 10. Fit of the model to the viscosity experimental data of solution S1. ●, Experiment data; —, Model data.

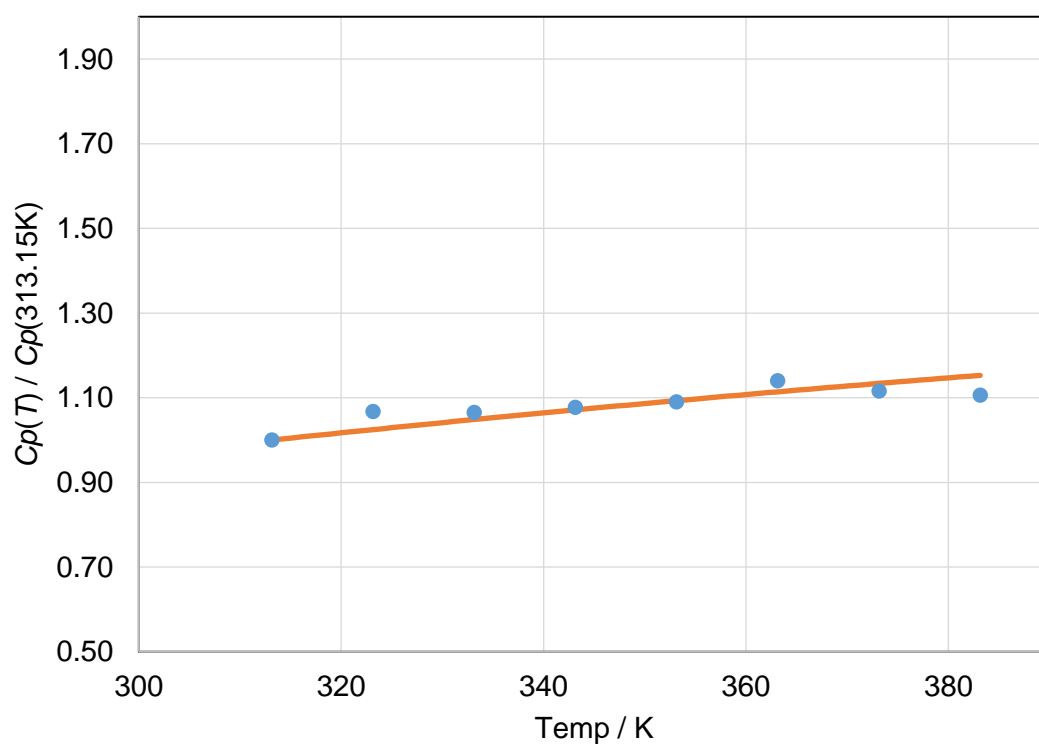


Figure 11. Fit of the model to the specific heat capacity experimental data of solution S2. ●, Experiment data; —, Model data.

4. Conclusion

This article proposed to investigate the influence of temperature on density, refractive index, viscosity and specific heat capacity for vegetable oils and their epoxidized and carbonated derivatives. From a chemical engineering point of view, the knowledge of these properties and the evolutions with temperature and composition are fundamental.

It was demonstrated that refractive index values decrease linearly as the temperature increases. Furthermore, one could use these properties to follow the evolution of vegetable oils and their derivatives. The record of refractive index can be done on-line which is benefit. Density of these oils decreases linearly as temperature increases. It was found that the viscosity of these oils is exponentially proportional to the temperature. The values for the specific heat capacity were found to be relatively constant within temperature range 313.15-383.15K, and did not change significantly between fresh vegetable oils and their derivatives. The ratio $\frac{C_p(T)}{C_p(T_{ref})}$ follows a polynomial of second order with temperature allowing predicting the values of C_p for each oils.

Functional groups have an effect on these physicochemical properties except for C_p . The last part of this study demonstrated that it is possible to predict the values of these physicochemical properties in case of mixture by knowing the evolutions of the pure compounds.

A future investigation could be done to study the evolution of these properties at different degrees of conversion during the course of reactions, namely epoxidation and carbonation.

Associated content

Supporting Information

The Supporting Information is available free of charge: Tables S1-S4 and Figures S1-S25 related to physicochemical properties of different oil species.

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Notes

The authors declare no competing financial interest.

References

- (1) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature*. **2016**, *540*, 354–362.
- (2) Stempfle, F.; Ortmann, P.; Mecking, S. Long-Chain Aliphatic Polymers To Bridge the Gap between Semicrystalline Polyolefins and Traditional Polycondensates. *Chem. Rev.* **2016**, *116*, 4597–4641.
- (3) Islam, M. R.; Beg, M. D. H.; Jamari, S. S. Development of Vegetable-Oil-Based Polymers. *J. Appl. Polym. Sci.* **2014**, *131*, 40787.
- (4) Cai, X.; Zheng, J. L.; Wärnå, J.; Salmi, T.; Taouk, B.; Leveneur, S. Influence of Gas-Liquid Mass Transfer on Kinetic Modeling: Carbonation of Epoxidized Vegetable Oils. *Chem. Eng. J.* **2017**, *313*, 1168–1183.
- (5) Boyer, A.; Cloutet, E.; Tassaing, T.; Gadenne, B.; Alfos, C.; Cramail, H. Solubility in CO₂ and Carbonation Studies of Epoxidized Fatty Acid Diesters: Towards Novel Precursors for Polyurethane Synthesis. *Green Chem.* **2010**, *12*, 2205–2213.
- (6) Jalilian, M.; Yeganeh, H.; Haghighi, M. N. Synthesis and Properties of Polyurethane Networks Derived from New Soybean Oil-Based Polyol and a Bulky Blocked Polyisocyanate. *Polym. Int.* **2008**, *57*, 1385–1394.
- (7) Jalilian, S.; Yeganeh, H. Preparation and Properties of Biodegradable Polyurethane Networks from Carbonated Soybean Oil. *Polym. Bull.* **2015**, *72*, 1379–1392.
- (8) Cuéllar-Franca, R. M.; Azapagic, A. Carbon Capture, Storage and Utilisation Technologies: A Critical Analysis and Comparison of Their Life Cycle Environmental Impacts. *J. CO₂ Util.* **2015**, *9*, 82–102.
- (9) Abraham, M. E.; Benenati, R. F. Kinetics and Mechanism of the Epoxidation of Unsaturated Fatty Acids. *AIChE J.* **1972**, *18*, 807–811.
- (10) Janković M. R., Sinadinović-Fišer S. V.. Kinetic Models of Reaction Systems for the in-Situ Epoxidation of Unsaturated Fatty Acid Esters and Triglycerides. *Hem. Ind.* **2004**, *58*, 569–576.

- (11) Campanella, A.; Fontanini, C.; Baltanás, M. A. High Yield Epoxidation of Fatty Acid Methyl Esters with Performic Acid Generated in Situ. *Chem. Eng. J.* **2008**, *144*, 466–475.
- (12) Leveneur, S.; Zheng, J.; Taouk, B.; Burel, F.; Wärnå, J.; Salmi, T. Interaction of Thermal and Kinetic Parameters for a Liquid–liquid Reaction System: Application to Vegetable Oils Epoxidation by Peroxycarboxylic Acid. *J. Taiwan Inst. Chem. E.* **2014**, *45*, 1449–1458.
- (13) Rangarajan, B.; Havey, A.; Grulke, E. A.; Culnan, P. D. Kinetic Parameters of a Two-Phase Model For in Situ Epoxidation of Soybean Oil. *J. Am. Oil. Chem. Soc.* **1995**, *72*, 1161–1169.
- (14) Beltrán Osuna, Á. A. B.; Mendivelso, L. A. B. Two-phase kinetic model for epoxidation of soybean oil. *Ingeniería e Investigación.* **2010**, *30*, 188–196.
- (15) Santacesaria, E.; Tesser, R.; Di Serio, M.; Turco, R.; Russo, V.; Verde, D. A Biphasic Model Describing Soybean Oil Epoxidation with H₂O₂ in a Fed-Batch Reactor. *Chem. Eng. J.* **2011**, *173*, 198–209.
- (16) Sinadinović-Fišer, S.; Janković, M.; Petrović, Z. S. Kinetics of in Situ Epoxidation of Soybean Oil in Bulk Catalyzed by Ion Exchange Resin. *J. Am. Oil Chem. Soc.* **2001**, *78*, 725–731.
- (17) Goud, V. V.; Patwardhan, A. V.; Dinda, S.; Pradhan, N. C. Kinetics of Epoxidation of Jatropa Oil with Peroxyacetic and Peroxyformic Acid Catalysed by Acidic Ion Exchange Resin. *Chem. Eng. Sci.* **2007**, *62*, 4065–4076.
- (18) Sinadinović-Fišer, S.; Janković, M.; Borota, O. Epoxidation of Castor Oil with Peracetic Acid Formed in Situ in the Presence of an Ion Exchange Resin. *Chem. Eng. Process.: Process Intensification.* **2012**, *62*, 106–113.
- (19) Wisniak, J.; Navarrete, E. Epoxidation of Fish Oil, Kinetic and Optimization Model. *Ind. Eng. Chem. Res.* **1970**, *9*, 33–41.
- (20) Wisniak, J.; Cancino, A.; Vega, J. C. Epoxidation of Anchovy Oils. A Study of Variables. *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, *3*, 306–311.
- (21) Okieimen, F. E.; Bakare, O. I.; Okieimen, C. O. Studies on the Epoxidation of Rubber Seed Oil.

- Ind. Crop. Prod.* **2002**, *15*, 139–144.
- (22) Goud, V. V.; Patwardhan, A. V.; Pradhan, N. C. Studies on the Epoxidation of Mahua Oil (Madhumica Indica) by Hydrogen Peroxide. *Bioresource Techn.* **2006**, *97*, 1365–1371.
- (23) Goud, V. V.; Pradhan, N. C.; Patwardhan, A. V. Epoxidation of Karanja (Pongamia Glabra) Oil by H₂O₂. *J. Am. Oil Chem. Soc.* **2006**, *83*, 635–640.
- (24) Mungroo, R.; Goud, V. V.; Pradhan, N. C.; Dalai, A. K. Modification of Epoxidised Canola Oil. *Asia-Pac. J. Chem. Eng.* **2011**, *6*, 14–22.
- (25) Petrović, Z. S.; Zlatanić, A.; Lava, C. C.; Sinadinović-Fišer, S. Epoxidation of Soybean Oil in Toluene with Peroxoacetic and Peroxoformic Acids — Kinetics and Side Reactions. *Eur. J. Lipid Sci. Tech.* **2002**, *104*, 293–299.
- (26) Dinda, S.; Patwardhan, A. V.; Goud, V. V.; Pradhan, N. C. Epoxidation of Cottonseed Oil by Aqueous Hydrogen Peroxide Catalysed by Liquid Inorganic Acids. *Bioresource Techn.* **2008**, *99*, 3737–3744.
- (27) Zaher, F. A.; El-Mallah, M. H.; El-Hefnawy, M. M. Kinetics of Oxirane Cleavage in Epoxidized Soybean Oil. *J. Am. Oil Chem. Soc.* **1989**, *66*, 698–700.
- (28) Campanella, A.; Baltanás, M. A. Degradation of the Oxirane Ring of Epoxidized Vegetable Oils with Solvated Acetic Acid Using Cation-Exchange Resins. *Eur. J. Lipid Sci. Technol.* **2004**, *106*, 524–530.
- (29) Campanella, A.; Baltanás, M. A. Degradation of the Oxirane Ring of Epoxidized Vegetable Oils with Hydrogen Peroxide Using an Ion Exchange Resin. *Catal. Today.* **2005**, *107*, 208–214.
- (30) Campanella, A.; Baltanás, M. A. Degradation of the Oxirane Ring of Epoxidized Vegetable Oils in Liquid–liquid Heterogeneous Reaction Systems. *Chem. Eng. J.* **2006**, *118*, 141–152.
- (31) Campanella, A.; Baltanás, M. A. Degradation of the Oxirane Ring of Epoxidized Vegetable Oils in a Liquid–liquid–solid Heterogeneous Reaction System. *Chem. Eng. Process.: Process Intensification.* **2007**, *46*, 210–221.
- (32) Zheng, J. L.; Wärnå, J.; Salmi, T.; Burel, F.; Taouk, B.; Leveneur, S. Kinetic Modeling Strategy for an Exothermic Multiphase Reactor System: Application to Vegetable Oils Epoxidation

- Using Prileschajew Method. *AIChE J.* **2016**, *62*, 726–741.
- (33) Zheng, J. L.; Burel, F.; Salmi, T.; Taouk, B.; Leveneur, S. Carbonation of Vegetable Oils: Influence of Mass Transfer on Reaction Kinetics. *Ind. Eng. Chem. Res.* **2015**, *54*, 10935–10944.
- (34) Wentzel, B. B.; Alsters, P. L.; Feiters, M. C.; Nolte, R. J. M. Mechanistic Studies on the Mukaiyama Epoxidation. *J. Org. Chem.* **2004**, *69*, 3453–3464.
- (35) Chou, T. C.; Lee, S. V. Epoxidation of Oleic Acid in the Presence of Benzaldehyde Using Cobalt(II) Tetraphenylporphyrin as Catalyst. *Ind. Eng. Chem. Res.* **1997**, *36*, 1485–1490.
- (36) Aguirre, P.; Zolezzi, S.; Parada, J.; Bunel, E.; Moya, S. A.; Sariego, R. Ruthenium Carbonyl Complexes in Catalytic Epoxidation of Olefins Co-Catalyzed by Isobutyl-Aldehyde. *Appl. Organomet. Chem.* **2006**, *20*, 260–263.
- (37) Di Serio, M.; Turco, R.; Pernice, P.; Aronne, A.; Sannino, F.; Santacesaria, E. Valuation of Nb₂O₅–SiO₂ Catalysts in Soybean Oil Epoxidation. *Catal. Today.* **2012**, *192*, 112–116.
- (38) Arends, I.; Sheldon, R. A. Recent Developments in Selective Catalytic Epoxidations with H₂O₂. *Top. Catal.* **2002**, *19*, 133–141.
- (39) Campanella, A.; Baltanás, M. A.; Capel-Sánchez, M. C.; Campos-Martín, J. M.; Fierro, J. L. G. Soybean Oil Epoxidation with Hydrogen Peroxide Using an Amorphous Ti/SiO₂ Catalyst. *Green Chem.* **2004**, *6*, 330–334.
- (40) Orellana-Coca, C.; Adlercreutz, D.; Andersson, M. M.; Mattiasson, B.; Hatti-Kaul, R. Analysis of Fatty Acid Epoxidation by High Performance Liquid Chromatography Coupled with Evaporative Light Scattering Detection and Mass Spectrometry. *Chem. Phys. Lipids.* **2005**, *135*, 189–199.
- (41) Hilker, I.; Bothe, D.; Prüss, J.; Warnecke, H. J. Chemo-Enzymatic Epoxidation of Unsaturated Plant Oils. *Chem. Eng. Sci.* **2001**, *56*, 427–432.
- (42) Hagström, A. E. V.; Törnvall, U.; Nordblad, M.; Hatti-Kaul, R.; Woodley, J. M. Chemo-Enzymatic Epoxidation-Process Options for Improving Biocatalytic Productivity. *Biotechnol.*

Prog. **2011**, *27*, 67–76.

- (43) Rüschen Klaas, M.; Warwel, S. Complete and partial epoxidation of plant oils by lipase-catalyzed perhydrolysis. *Ind. Crop. Prod.* **1999**, *9*, 125–132.
- (44) Lu, H.; Sun, S.; Bi, Y.; Yang, G.; Ma, R.; Yang, H. Enzymatic Epoxidation of Soybean Oil Methyl Esters in the Presence of Free Fatty Acids. *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 1101–1105.
- (45) Orellana-Coca, C.; Billakanti, J. M.; Mattiasson, B.; Hatti-Kaul, R. Lipase Mediated Simultaneous Esterification and Epoxidation of Oleic Acid for the Production of Alkylepoxyestearates. *J. Mol. Catal. B-Enzym.* **2007**, *44*, 133–137.
- (46) Törnvall, U.; Orellana-Coca, C.; Hatti-Kaul, R.; Adlercreutz, D. Stability of Immobilized *Candida Antarctica* Lipase B during Chemo-Enzymatic Epoxidation of Fatty Acids. *Enzyme Microb. Tech.* **2007**, *40*, 447–451.
- (47) Leveneur, S.; Ledoux, A.; Estel, L.; Taouk, B.; Salmi, T. Epoxidation of Vegetable Oils under Microwave Irradiation. *Chem. Eng. Des.* **2014**, *92*, 1495–1502.
- (48) Aguilera, A. F.; Tolvanen, P.; Eränen, K.; Leveneur, S.; Salmi, T. Epoxidation of Oleic Acid under Conventional Heating and Microwave Radiation. *Chem. Eng. Process.: Process Intensification.* **2016**, *102*, 70–87.
- (49) Leveneur, S. Thermal Safety Assessment through the Concept of Structure–Reactivity: Application to Vegetable Oil Valorization. *Org. Process Res. Dev.* **2017**, *21*, 543–550.
- (50) Rakotondramaro, H.; Wärnå, J.; Estel, L.; Salmi, T.; Leveneur, S. Cooling and Stirring Failure for Semi-Batch Reactor: Application to Exothermic Reactions in Multiphase Reactor. *J. Loss Prevent. Proc.* **2016**, *43*, 147–157.
- (51) Ait Aissa, K.; Zheng, J. L.; Estel, L.; Leveneur, S. Thermal Stability of Epoxidized and Carbonated Vegetable Oils. *Org. Process Res. Dev.* **2016**, *20*, 948–953.
- (52) Leveneur, S.; Estel, L.; Crua, C. Thermal Risk Assessment of Vegetable Oil Epoxidation. *J. Therm. Anal. Calorim.* **2015**, *122*, 795–804.
- (53) Campanella, A.; Rustoy, E.; Baldessari, A.; Baltanás, M. A. Lubricants from Chemically

- Modified Vegetable Oils. *Bioresource Technol.* **2010**, *101*, 245–254.
- (54) Ouboukhlik, M.; Godard, G.; Saengkaew, S.; Fournier-Salaün, M. C.; Estel, L.; Grehan, G. Mass Transfer Evolution in a Reactive Spray during Carbon Dioxide Capture. *Chem. Eng. Technol.* **2015**, *38*, 1154–1164.
- (55) Drapcho C. M.; Nhuan N. P.; Walker T. H. Biofuels engineering process technology[M]. New York: McGraw-Hill, **2008**.
- (56) Maerker, G. Determination of Oxirane Content of Derivatives of Fats. *J. Am. Oil Chem. Soc.* **1965**, *42*, 329–332.
- (57) Paquot, C. *Standard Methods for the Analysis of Oils, Fats and Derivatives (Sixth Edition)*; Elsevier: Pergamon, **1979**.
- (58) Cho, Y. J.; Kim, T. E.; Gil, B. Correlation between refractive index of vegetable oils measured with surface plasmon resonance and acid values determined with the AOCS official method. *LWT - Food Sci. Technol.* **2013**, *53*, 517-521.
- (59) Esteban, B.; Riba, J. R.; Baquero, G.; Rius, A.; Puig, R. Temperature Dependence of Density and Viscosity of Vegetable Oils. *Biomass. Bioenerg.* **2012**, *42*, 164–171.
- (60) Xu, J. Y.; Liu, Z. S.; Erhan, S. Z.; Carriere, C. J. A potential biodegradable rubber—Viscoelastic properties of a soybean oil-based composite. *J. Am. Oil Chem. Soc.* **2002**, *79*, 593–596.
- (61) Fasina, O. O.; Hallman, H.; Craig-Schmidt, M.; Clements, C. Predicting Temperature-Dependence Viscosity of Vegetable Oils from Fatty Acid Composition. *J. Am. Oil Chem. Soc.* **2006**, *83*, 899-903.
- (62) Bähr, M.; Mülhaupt, R. Linseed and Soybean Oil-Based Polyurethanes Prepared via the Non-Isocyanate Route and Catalytic Carbon Dioxide Conversion. *Green Chem.* **2012**, *14*, 483–489.
- (63) Parzuchowski, P. G.; Jurczyk-Kowalska, M.; Ryszkowska, J.; Rokicki, G. Epoxy Resin Modified with Soybean Oil Containing Cyclic Carbonate Groups. *J. Appl. Polym. Sci.* **2006**, *102*, 2904–2914.
- (64) Poussard, L.; Mariage, J.; Grignard, B.; Detrembleur, C.; Jérôme, C.; Calberg, C.; Heinrichs, B.;

- De Winter, J.; Gerboux, P.; Raquez, J.-M.; Bonnaud, L.; Dubois, P. Non-Isocyanate Polyurethanes from Carbonated Soybean Oil Using Monomeric or Oligomeric Diamines To Achieve Thermosets or Thermoplastics. *Macromolecules*. **2016**, *49*, 2162–2171.
- (65) Zhang, L.; Luo, Y.; Hou, Z.; He, Z.; Eli, W. Synthesis of Carbonated Cotton Seed Oil and Its Application as Lubricating Base Oil. *J. Am. Oil. Chem. Soc.* **2014**, *91*, 143–150.
- (66) Ishimura, T.; Yoshida, T. Polymerization of Oriental Lacquer (Urushi) with Epoxidized Linseed Oil as a New Reactive Diluent. *Int. J. polym. Sci.* **2015**, *2015*, 1–7.
- (67) Kowalski, B. Determination of Specific Heats of some Edible Oils and Fats by Differential Scanning Calorimetry. *J. Therm. Anal.* **1988**, *34*, 1321-1326.
- (68) Fasina, O. O.; Z. Colley. Viscosity and specific heat of vegetable oils as a function of temperature: 35 °C to 180 °C. *Int. J. Food Prop.* **2008**, *11*, 738-746.
- (69) Ramírez Verduzco, L. F. Density and viscosity of biodiesel as a function of temperature: empirical models, *Renew. Sust. Rev.* **2013**, *19*, 652–665.
- (70) Stoessel, F. *Thermal Safety of Chemical Processes: risk assessment and process design*; John Wiley & Sons: Weinheim, **2008**.
- (71) Freitas S. V. D.; e Silva F. A.; Pastoriza-Gallego M. J.; Piñeiro M. M.; Lima Á. S.; Coutinho J. A. P. Measurement and Prediction of Densities of Vegetable Oils at Pressures up to 45 MPa. *J. Chem. Eng. Data*. **2013**, *58*, 3046–3053.

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