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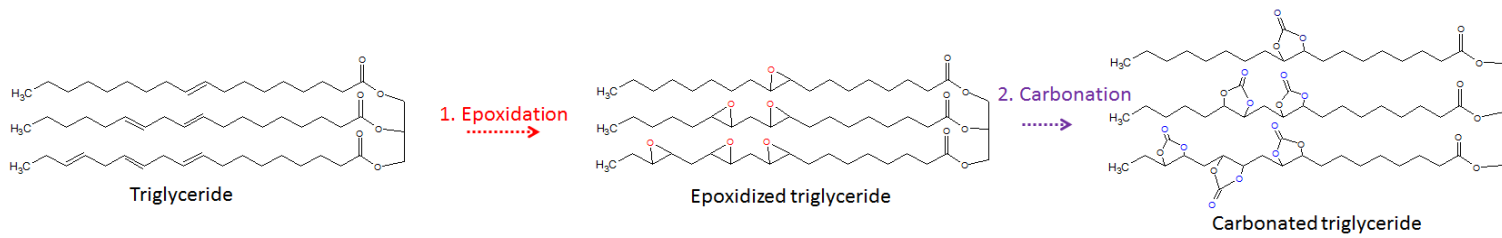
## Thermal stability of epoxidized and carbonated vegetable oils

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## TOC graphic



## **Abstract**

Biomass valorization processes are more and more used in industry. These processes are greener because they use some renewable and biodegradable raw materials, but are they safer? We propose to study the thermal stability of different epoxidized and carbonated vegetable oils. The severity of the thermal risk, i.e., adiabatic temperature rise, was determined by using differential scanning calorimetry tools. The probability of the thermal risk, i.e., Time-to-Maximum Rate under adiabatic conditions, was determined by using accelerating rate calorimeter. By analyzing these safety criteria, we have found that the thermal risk, essentially during the storage and the reactor loading, could be assumed to be negligible.

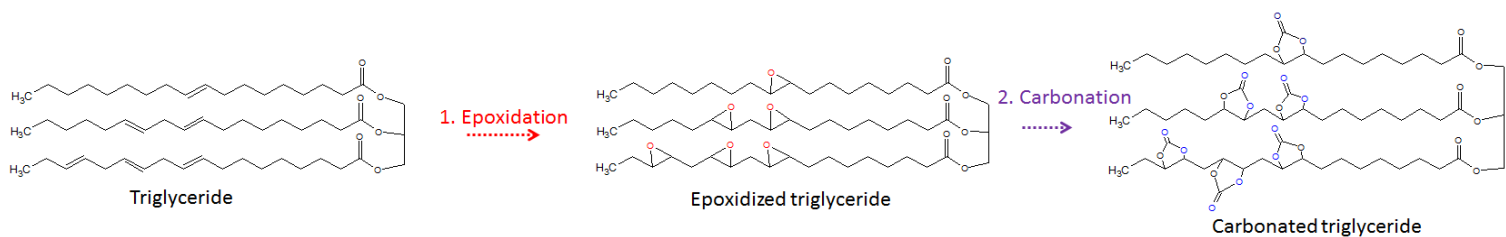
**Keywords:** Vegetable oils, DSC, ARC, thermal risks assessment, Biomass, Thermal analysis.

## 1. Introduction

In recent years, the development of alternative fuels from renewable resources has received considerable attention as sustainable feedstocks that can substitute fossil fuels. The concept of biorefinery has appeared, i.e., chemical process based on the use of renewable raw materials. Several researchers have worked to replace the former petroleum-derived chemical process to biomass one and propose some process flow diagram.<sup>1-3</sup> Academic research makes a huge effort to design some processes based on biomass by including cost and energy constraints.<sup>5-8</sup> The image of biomass plant, bioenergy, biofuel, etc. is not easy to measure on public opinion.<sup>9-12</sup> As chemist or chemical engineers, it is our duty to show that environmental and safety issues are our first priority by developing and studying biomass conversion processes. These processes are greener than their petroleum-derived counterparts but are they safer? To avoid a dramatic perception of people on this plant, risk analysis should be performed. Risk assessments on biomass chemical plant are rare in literature.<sup>13-18</sup>

Vegetable oils are one of the promising renewable resources and their use is nowadays a subject of growing interest. In 2011-2012, about 20 % of the 156 million tons of the major produced vegetable oils were devoted to industrial applications,<sup>19</sup> mainly as sources of energy. However, vegetable oils are also widely used for the manufacture of surfactants, cosmetic products, lubricants, paint formulation, coatings and resins. There are different ways of functionalizing vegetable oils: epoxidation, polyols or polymerization. For example, epoxidized soybean oil or their ring-opening products can be used as lubricant,<sup>20-24</sup> plasticizer<sup>25-26</sup> and for the production of polyurethanes.<sup>27-30</sup>

Carbonation reaction gives a cyclic carbonate with high yield using a more ecofriendly reactant than phosgene. However, this process is mainly studied for short chain molecules such as ethylene oxide, propylene oxide or epichlorohydrin. Carbonated vegetable oils by reacting with different diamines can produce different polyurethanes by nonisocyanate route.<sup>31</sup> And, it can be regarded as a platform molecule for polymer industries. From a process viewpoint, the production of such compounds should include the epoxidation process as illustrated by Scheme 1. Epoxidation reaction is performed at atmospheric pressure by Prileschajew reaction, i.e., 70°C. Carbonation reaction is performed at higher CO<sub>2</sub> pressure (50-70 bar) and higher temperature (140-150°C). Thus, these two steps cannot be performed in one pot. Thus, the thermal risks assessment of such process should be performed on both modified vegetable oils.



Scheme 1. Epoxidation and carbonation of vegetable oils.

The other synthesis route for the production of epoxidized compounds is to use oxygen or hydrogen peroxide as oxidizing agents. These routes are essentially used for short chain molecules, but for fatty acid or vegetable oils the kinetics of epoxidation by hydrogen peroxide or oxygen is slow. Köckritz and Martin have presented different routes for the epoxidation of vegetable oils, and they have underlined that peroxyacetic acid is the most common oxidizing agent.<sup>32</sup>Some studies are still going on to find suitable catalysts for the direct epoxidation of the unsaturated group on vegetable oils or free fatty acids by hydrogen peroxide or oxygen.<sup>33-36</sup>In industry, the epoxidation of soybean oil is performed in batch or semi-batch reactor by using mineral acids and peroxyacetic acid produced *in situ*, namely Prileschajew oxidation route.<sup>36-37</sup>

This reaction system is a liquid-liquid reaction system where several consecutive exothermic reaction steps occur. Some articles have highlighted the strong correlation between mass and energy balances in semi-batch reactor for this system.<sup>38-41</sup>The risk of thermal runaway for this reaction system is not negligible. Furthermore, this reaction system can lead to the formation of non-condensable products leading to a pressure increase. Our group have performed a thermal risk assessment on the epoxidation of oleic acid by peroxyacetic acid produced *in situ*, and the safety criteria determined showed that this process present a risk of thermal runaway.<sup>42</sup>

Valencia-Barragán et al.<sup>43</sup> have performed a quantitative risk analysis on a vegetable oil industry. They have shown that storage represents the highest risk. Thermal assessment for the storage and the loading of the chemicals should be done.<sup>44-46</sup>A thermal accident could occur during the loading of an epoxidized vegetable oil in a reactor for its conversion to carbonated vegetable oils. A fire could also start near to the storage zone for epoxidized or carbonated vegetable oils.

For that reason, we think that one should study the thermal stability of these modified vegetable oils content. Some researchers have studied the thermal stability of epoxidized soybean oil by DSC.<sup>47-49</sup>

To the best of our knowledge, there are not such studies for the carbonated vegetable oils. We have studied the thermal stability of modified vegetable oils to epoxidized and carbonated ones. Three different vegetable oils were used: cottonseed, linseed and soybean oils. This choice was due to the different composition of fatty acids as illustrated by Table 1.

Table 1. Chemical composition of vegetable oils.

	Palmitic C16:0	Palmitoleic C16:1	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Iodine value
Soybean oil	10.6	-	4.8	22.5	52.3	8.2	130
Cottonseed oil	28.7	-	0.9	13	57.4	-	105
Linseed oil	5.1	0.3	2.5	18.9	18.1	55.1	178

In this paper the thermal decomposition of commercial vegetable oils (cottonseed, soybean and linseed oils) and modified vegetable oils was studied by simultaneous differential scanning calorimetric (DSC) and accelerating rate calorimeter (ARC).

## 2. Results and discussion

To determine the stability of these compounds, some safety criteria such as Time-to-Maximum Rate under adiabatic conditions ( $TMR_{ad}$ ), adiabatic temperature rise ( $\Delta T_{ad}$ ),  $T_{D24}$  and  $T_{D8}$  were calculated. Epoxidized vegetable oils and the carbonated vegetable oils were synthesized by the procedures presented in the articles of Zheng et al.<sup>40;50</sup>

### DSC analysis

DSC experiments were performed under dynamic mode until 500°C to determine the presence of exothermic peaks for the vegetable oils (linseed (LSO), cotton seed (CSO) and soy bean oil (SBO)) and their corresponding epoxidized and carbonated forms. Figures 1-3 show the DSC thermogram for the different species with a temperature ramp of 4°C/min.

From Figure 1, one can notice the presence of only one exothermic peak for the pure vegetable oils. This peak is certainly due to the degradation of vegetable oils.

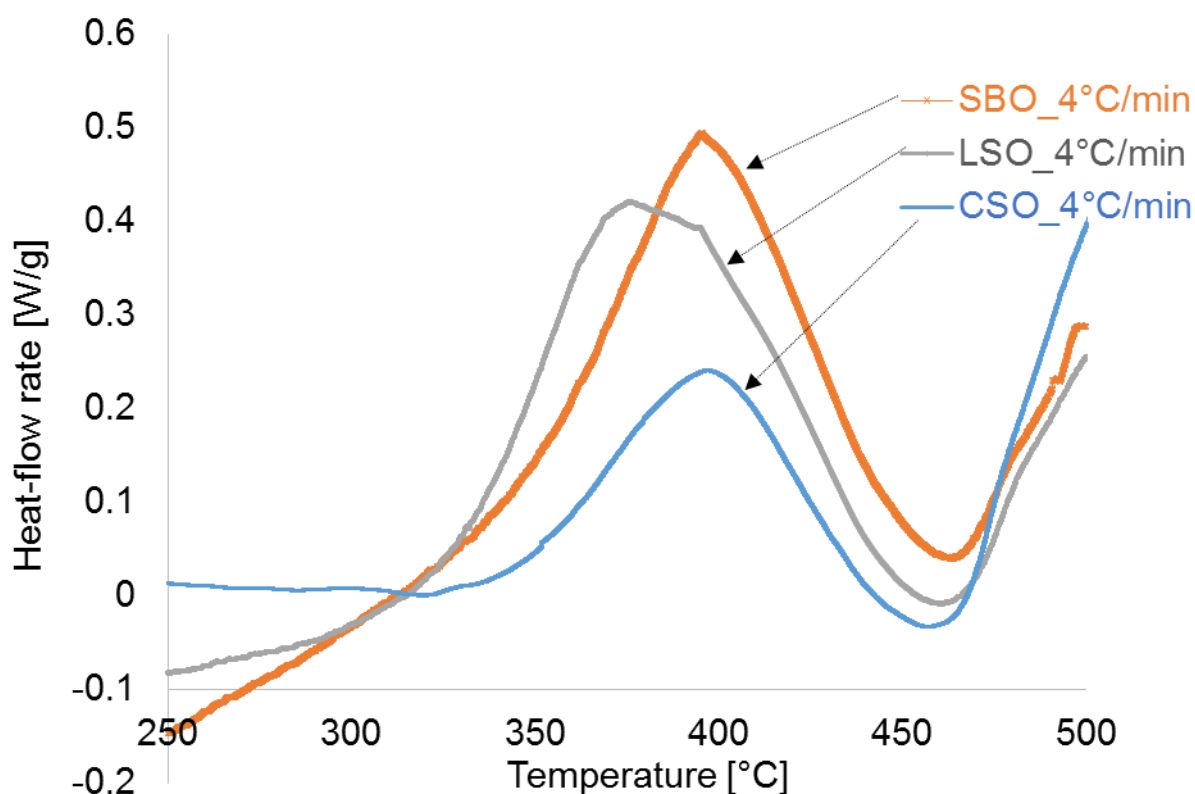


Figure 1. DSC under dynamic mode for SBO, LSO, CSO<sub>2</sub>



Figure 2 shows the thermal stability of epoxidized vegetable oils. During the preparation of the epoxidized cottonseed oil (ECSO), epoxidized linseed oil (ELSO) and epoxidized soybean oil (ESBO), the yield of epoxidized compound was higher than 70 %. One can notice from Figure 2 the presence of two exothermic peaks. According to Howell et al.,<sup>47</sup> the two exothermic peaks observed on the ESBO-DSC-thermogram are due to two different epoxide functional groups. It is difficult to confirm this observation because it is not possible to analyse the DSC samples. By comparing Figure 1 and Figure 2, one can notice that the only exothermic peak for the pure vegetable oils and the second exothermic peak for the epoxidized vegetable oils start approximately at the same temperature. For that reason, we preferred to say that the first peak is due to the ring-opening reactions and the second peak is due to the degradation of the vegetable oils.

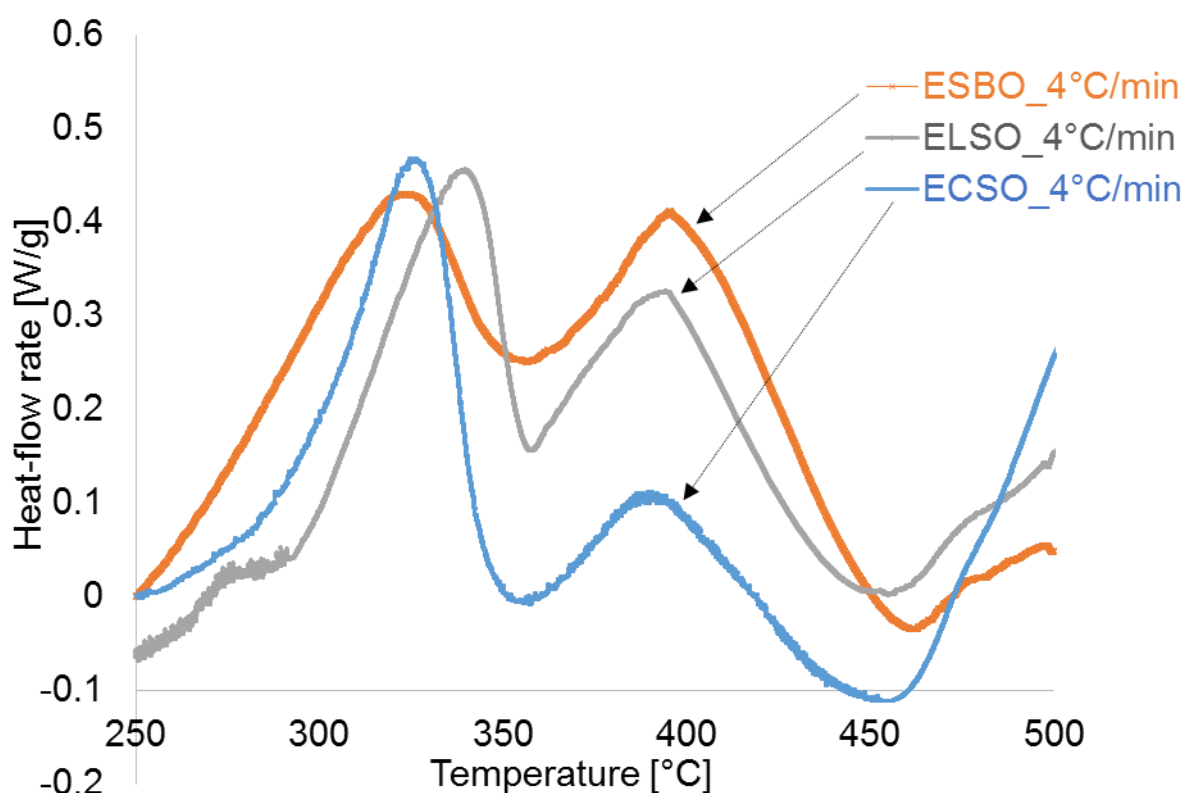


Figure 2. DSC under dynamic mode for ESBO, ELSO, ECSO.

Figure 3 shows the evolution of the heat-flow rate for the carbonated vegetable oils obtained from DSC experiments with a temperature ramp of 4°C/min. One can notice the presence of three exothermic peaks due to the ring-opening of the carbonated and epoxidized groups and the

degradation of the vegetable oils. During the synthesis of carbonated vegetable oils, the final yield of carbonated function was higher than 80 mol.%.

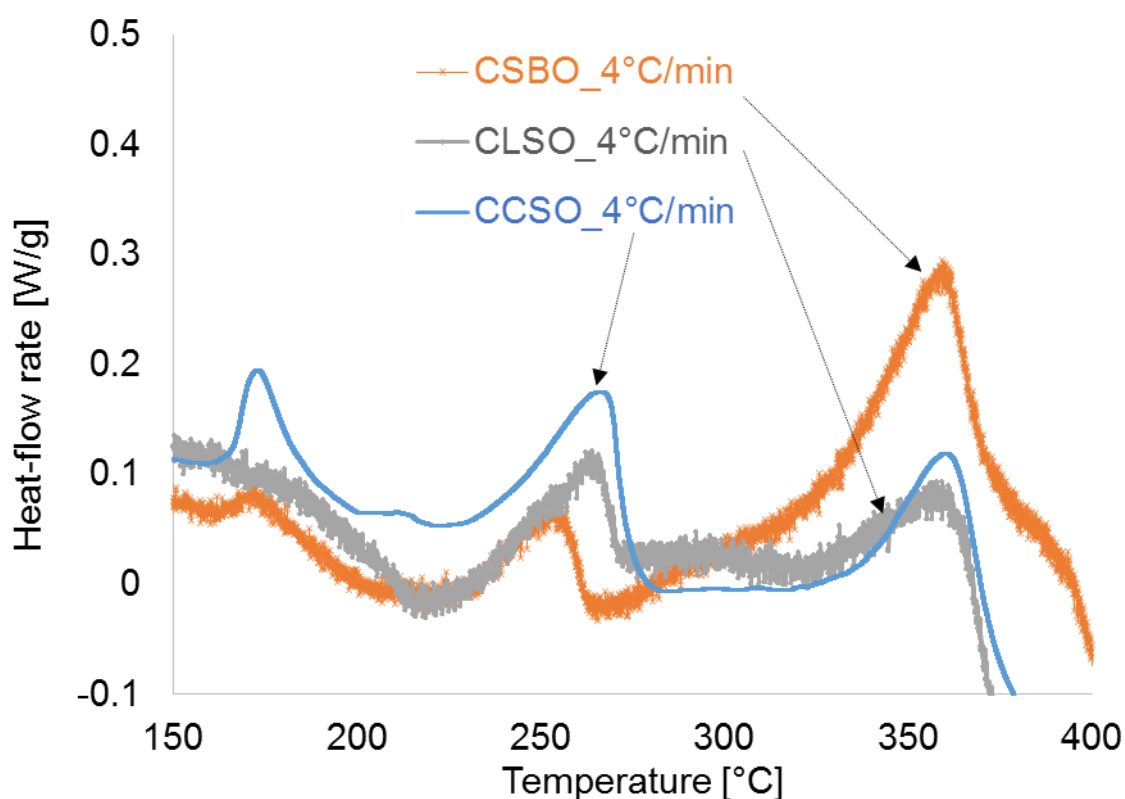


Figure 3. DSC under dynamic mode for CSBO, CLSO, CCSO.

*Calculation of adiabatic temperature rise and the activation energy from DSC measurements*

By integrating the DSC thermogram (Figures. 1-3), it is possible to calculate the total energy released by these compounds during a temperature increase. Thus, it is possible to determine the adiabatic temperature rise  $\Delta T_{ad}$ , which reflects the severity of the thermal risk. The adiabatic temperature rise was determined using the formula:

$$\Delta T_{ad} = \frac{Q_r}{C_{pR}} \quad (1)$$

where  $Q_r$  is the total amount of energy released by the reaction and  $C_{pR}$  is the specific heat capacity of the vegetable oils which can be assumed to be  $2 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ . Table 2 summarizes the value of the adiabatic temperature rise for the different vegetable oils obtained from DSC measurement at different temperature ramp. One can notice that the maximum value of  $\Delta T_{ad}$  is obtained for the epoxidized vegetable oils. Indeed, from a thermodynamic viewpoint, a three-membered ring is less stable than an

unsaturated or a five-membered ring. The total energy released during the degradation of a carbonated vegetable oil is less dramatic than an epoxide compound.

**Table 2.** Adiabatic temperature ( $\Delta T_{ad}$ ) of vegetable oils.

	<b>a (°C/min)</b>			
	4	8	10	
CSO	105	106.5	103.5	Vegetable oils
SBO	166.5	165.5	161.5	
LSO	196	201	199.5	
ECSO	237	232	215	Epoxidized
ESBO	213.5	206	202.5	
ELSO	171.5	189.5	191	
CCSO	103.5	118	125.5	Carbonated
CSBO	187	169.5	202	
CLSO	239	227	225.5	

### ARC experiments

The other safety criterion to determine is the Time-to-Maximum-Rate under adiabatic conditions. As we have illustrated in a previous article of our group,<sup>42</sup> the accelerating rate calorimeter is the most suitable equipment to measure this criterion. Epoxidized and carbonated vegetable oils were tested. The Heat-Wait-and-Search mode was used and the thermal sensitivity was of 0.02 K/min. Figures 4-6 and 7-9 show the evolution of the temperature and pressure for the epoxidized and carbonated vegetable oils, respectively obtained from ARC experiments.

From Figures 4-6, one can notice that the self-heating phenomenon starts at temperature higher than 200°C for any epoxidized vegetable oils. Table 3 summarizes the temperature and pressure rise for the different epoxidized vegetable oils.  $T_0$  is the temperature at which the self-heating phenomenon starts. One can notice that the pressure and temperature rise are similar for the different vegetable oils under adiabatic conditions. The adiabatic temperature rise obtained from ARC experiments was lower than the ones from DSC. In the self-heating zone, there are the different reactions of degradation and ring-opening.

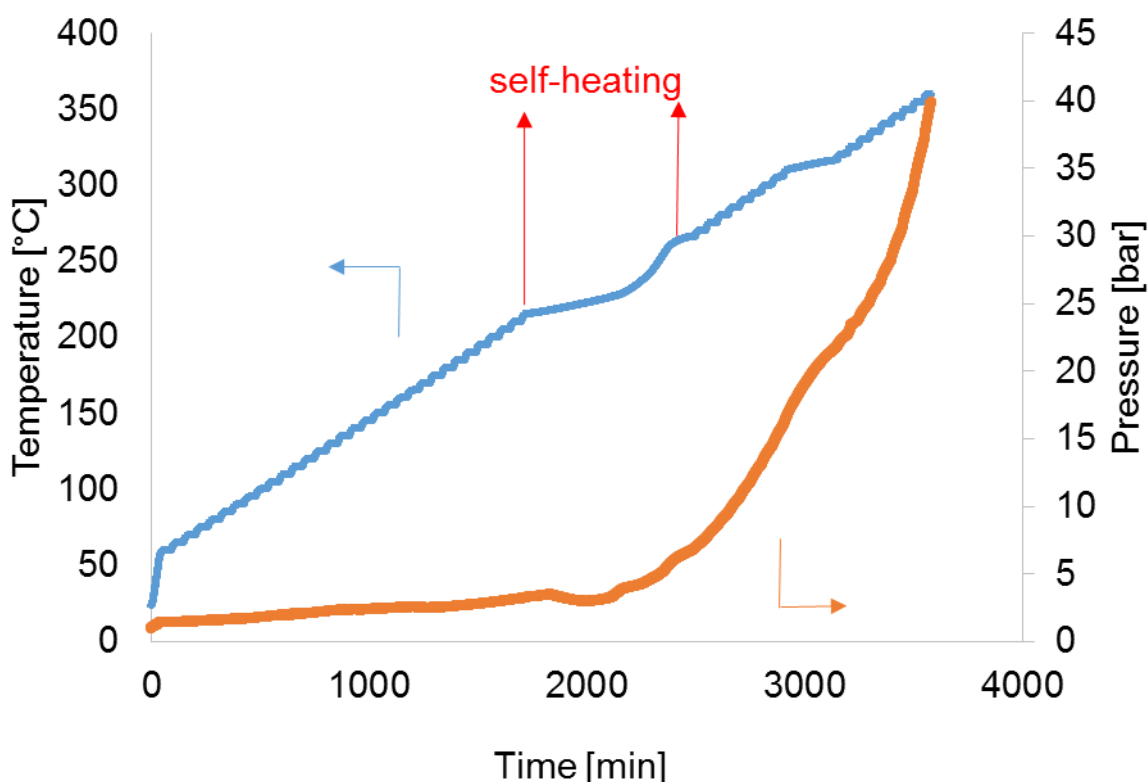


Figure. 4. Evolution of pressure and temperature for ECSO<sub>2</sub>

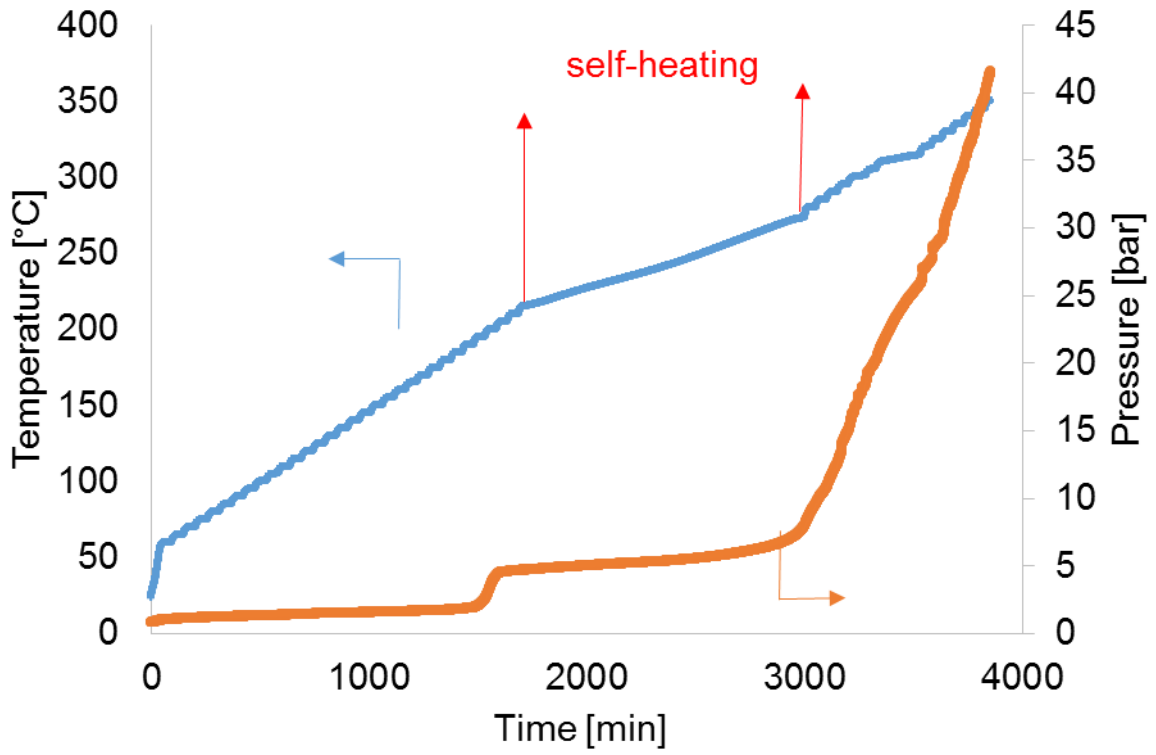


Figure. 5. Evolution of pressure and temperature for ELSO<sub>2</sub>

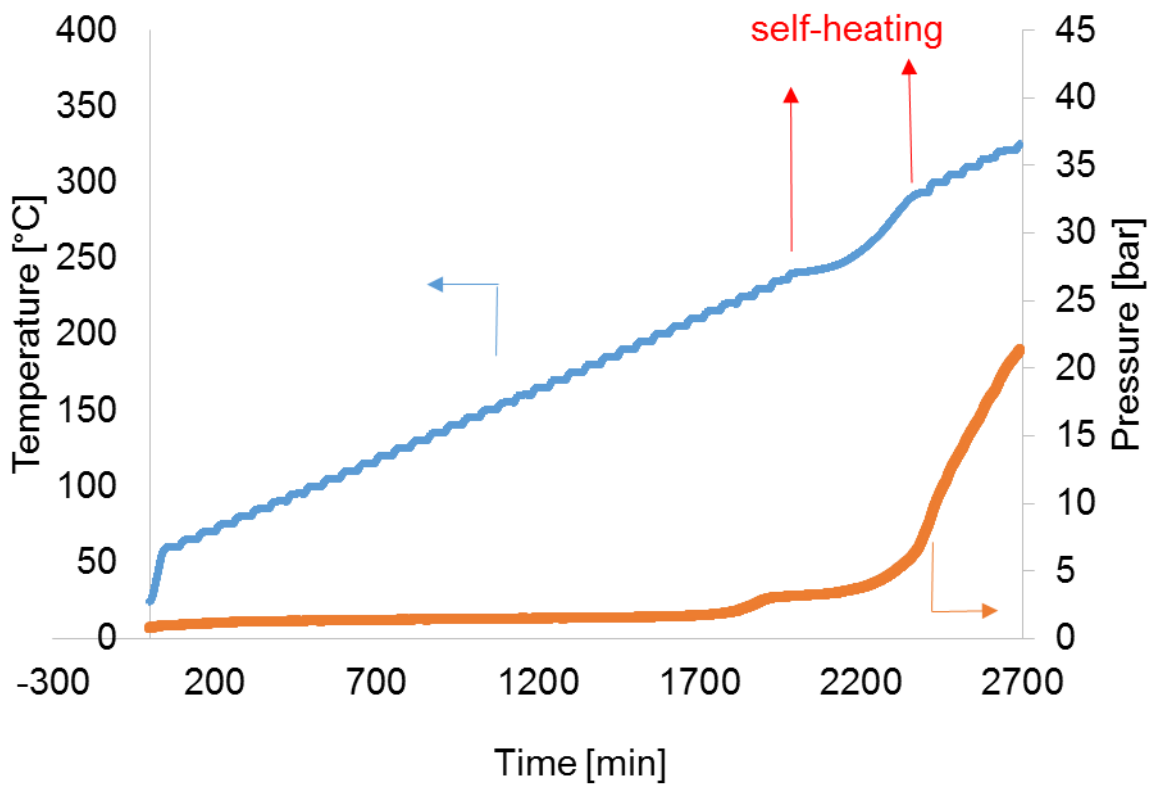


Figure. 6. Evolution of pressure and temperature for ESBO<sub>2</sub>

Table 3. Temperature and pressure rise for epoxidized vegetable oils.

	ECSO	ELSO	ESBO
$T_o$ [°C]	215.65	215.88	240.60
P [bar] at $T_o$	3.29	4.72	3.15
$T_{final}$ [°C]	266.25	273.29	293.18
P [bar] at $T_{final}$	6.88	7.90	8.31
<b><math>\Delta P</math> [bar]</b>	<b>3.59</b>	<b>3.18</b>	<b>5.15</b>
<b><math>\Delta T</math> [°C]</b>	<b>50.60</b>	<b>57.41</b>	<b>52.58</b>

Figures 7-9 show that the kinetic of the temperature rise was slower for the carbonated compounds. The pressure rise (Table 4) was higher due to the release of CO<sub>2</sub> captured by the epoxidized compounds.

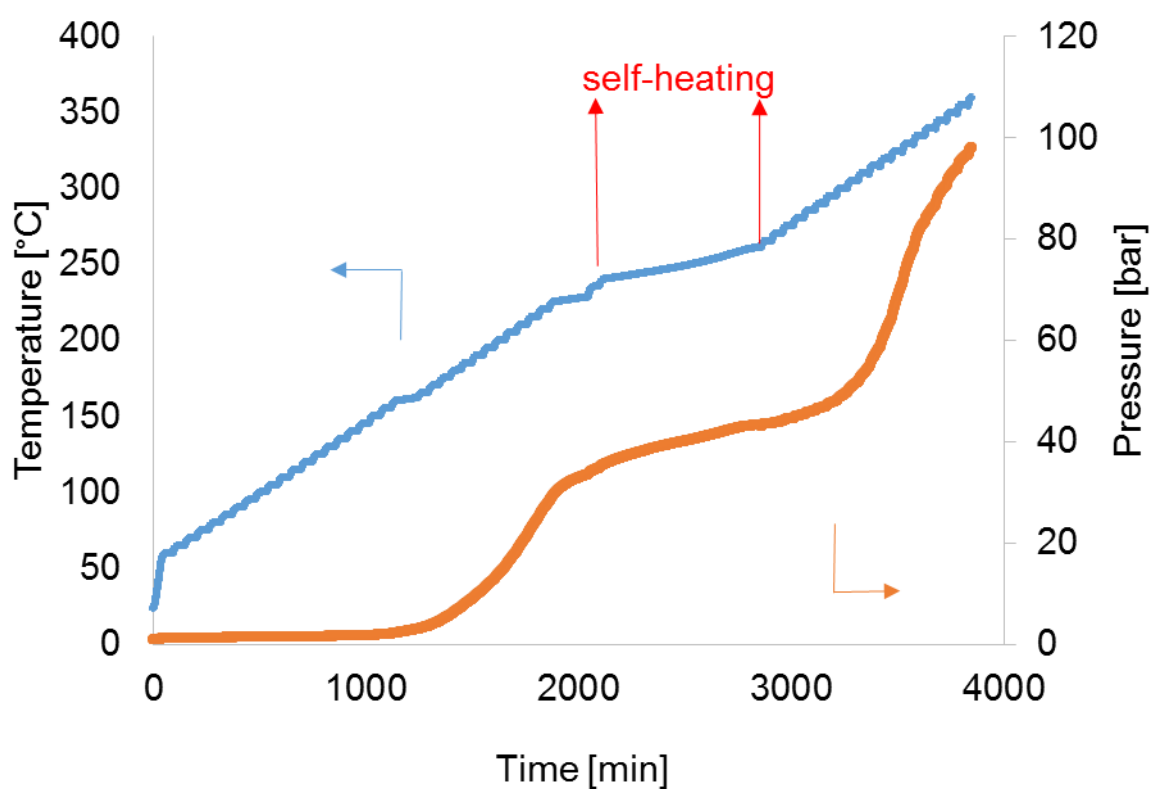


Figure. 7. Evolution of pressure and temperature for CSBO<sub>2</sub>.

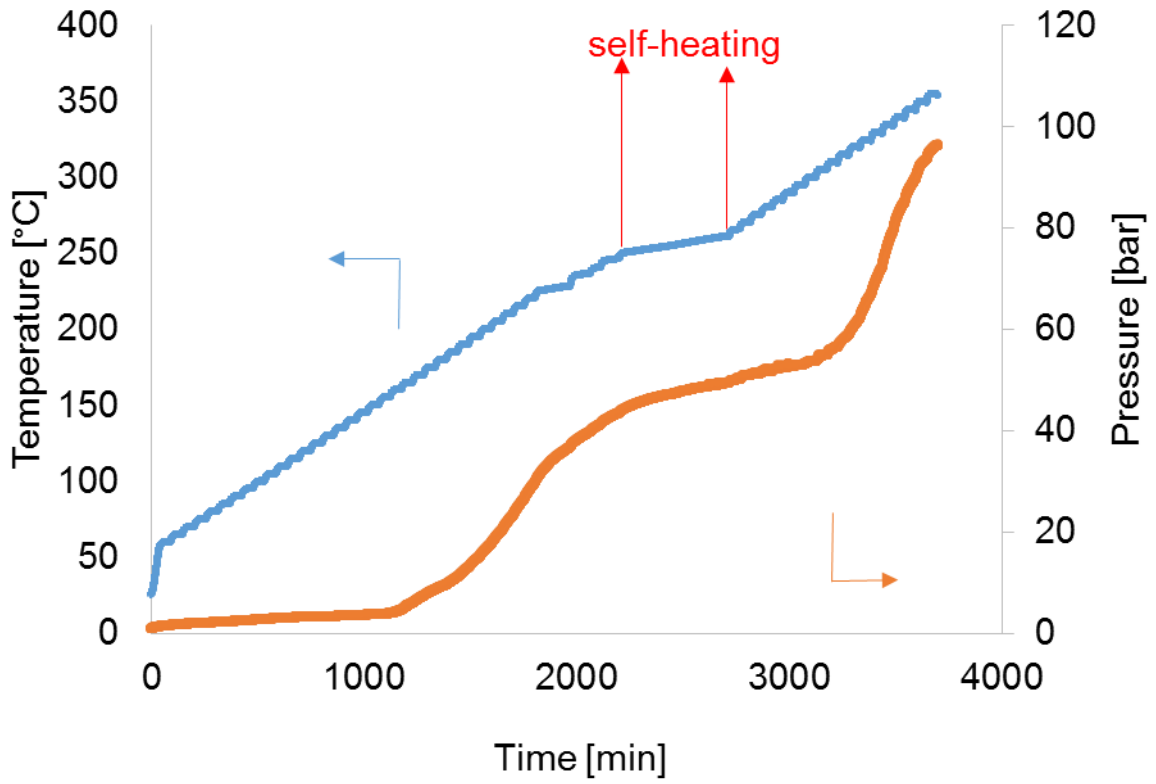


Figure. 8. Evolution of Pressure and Temperature for CLSO<sub>2</sub>

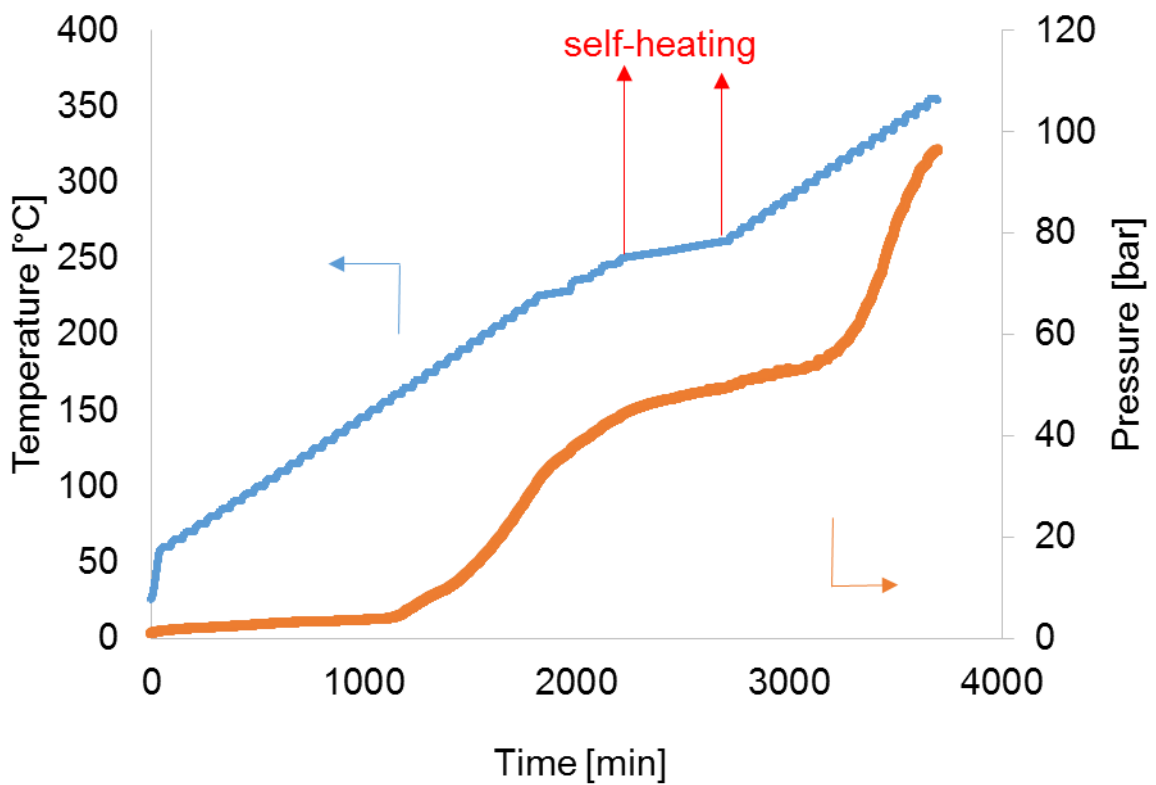


Figure. 9. Evolution of Pressure and Temperature for CCSO<sub>2</sub>

Table 4. Temperature and pressure rise for carbonated vegetable oils

	CCSO	CLSO	CSBO
To [°C]	250.78	250.67	240.65
P [bar] at To	41.25	44.76	36.04
Tfinal [°C]	264.12	261.18	261.16
P [bar] at Tfinal	49.35	49.49	43.16
<b>ΔP [bar]</b>	<b>8.10</b>	<b>4.73</b>	<b>7.12</b>
<b>ΔT [°C]</b>	<b>13.34</b>	<b>10.51</b>	<b>20.51</b>

The temperature evolution obtained from ARC experiment did not take into account the thermal inertia of the system. Thus, to calculate under adiabatic conditions the  $TMR_{ad}$ , one should correct the measured temperature as:

$$T_{i,corrected} = T_o + \varphi.(T_i - T_o) \quad (2)$$

where  $\varphi$  is the thermal inertia of the system.

The other safety criteria are  $T_{D24}$  and  $T_{D8}$  which are the process temperature when  $TMR_{ad}$  is 24 and 8 hours, respectively. These parameters should be extrapolated based on the current measurement. In a previous study of our group,<sup>42</sup> we have detailed the methodology to calculate these parameters.

Figure 10 shows the evolution of  $TMR_{ad}$  with the process temperature for the epoxidized vegetable oils. The  $T_{D24}$  for the different epoxidized vegetable oils is higher than 150°C. One should remember that the carbonation process is usually carried out at temperature lower than 140°C. Thus, the process can be considered thermally safe if the process temperature is lower than  $T_{D24}$ , because in case of cooling failure leading to adiabatic conditions, it will take 24 hours before reaching the maximum temperature.

Figure 11 shows the evolution of  $TMR_{ad}$  with the process temperature for the carbonated vegetable oils. The  $T_{D24}$  for the different carbonated vegetable oils is higher than 220°C.



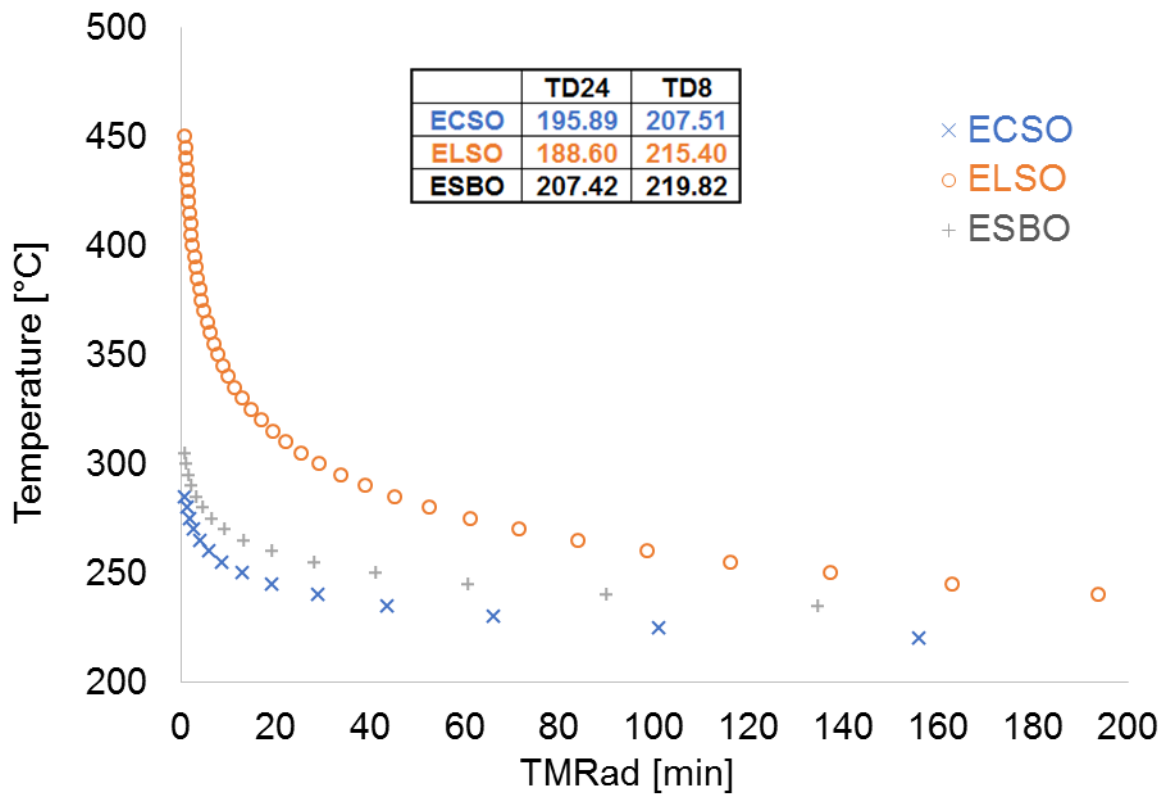


Figure. 10. Evolution of  $TMR_{ad}$  for epoxidized vegetable oils with  $\phi=1$  by using ARC.

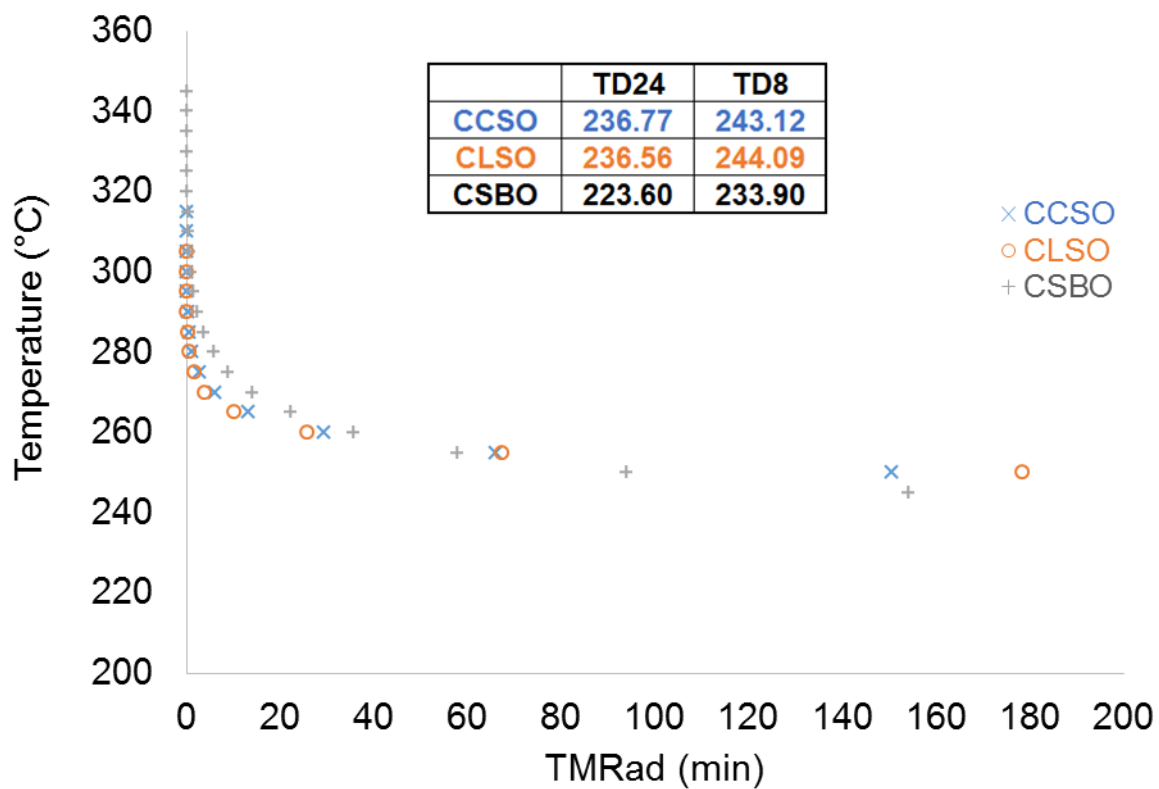


Figure. 11. Evolution of  $TMR_{ad}$  for carbonated vegetable oils with  $\phi=1$  by using ARC.

By assuming that the process temperature used for the different modified vegetable oils is  $140^{\circ}\text{C}$ , which is the maximum temperature for the synthesis of carbonated vegetable oils from the epoxidized one and for the synthesis of polyurethane from carbonated vegetable oils. Thus, from DSC results the final temperature under adiabatic conditions can be calculated. Table 5 summarizes the safety criteria obtained by DSC and ARC.

Table 5. Safety criteria

	$T_P$ [°C]	$T_{D24}$ [°C]	$T_{Final}$ [°C]	
ECSO	140	196	368	Epoxidized
ESBO	140	207	346	
ELSO	140	189	324	
CCSO	140	237	256	Carbonated
CSBO	140	224	335	
CLSO	140	237	371	

One can notice that the process temperature is lower than  $T_{D24}$  which means that the process is safe during the storage of both modified vegetable oils or during the loading of the epoxidized vegetable oils for the carbonation reaction.

Under adiabatic conditions, the final temperature is lower than 380°C for the different system. From Figures 4-6 and 7-9, one can notice that the maximum pressure reached under adiabatic conditions is lower than 40 bar for epoxidized vegetable oils and 120 bar for the carbonated vegetable oils. During the reactor design, the maximum temperature for technical reason should be 400°C and the maximum allowed pressure should be 150 bar.

### 3. Conclusions

Thermal stability of different epoxidized and carbonated vegetable oils were studied by using calorimetry methods. Such study is important for the storage or during the reactant loading. The safety criteria  $T_{D24}$  was lower than the process temperature for the production of carbonated vegetable oils or for the production of nonisocyanate polyurethane. Thus, the probability than a thermal accident occurs during the reactor loading is low.

In case of adiabatic conditions, the final temperature for the epoxidized and carbonated vegetable oils are in the range of 320-370°C and 250-370°C, respectively. The maximum pressure reached for a pressure of 230°C was 120 bar, which represents also a medium severity. The analysis of these different safety criteria shows that these two green processes can be considered as safe from a thermal risk view point during their loading or storage. In the future, some toxicological study and life cycle assessment should complete this study.

## 4. Experimental section

### 4.1. Materials and methods

The thermal decomposition of the following vegetable oils was studied: cottonseed oil (CSO), epoxidized cottonseed oil (ECSO), carbonated cottonseed oil (CCSO), soybean oil (SBO), epoxidized soybean oil (ESBO), carbonated soybean oil (CSBO), linseed oil (LSO), epoxidized linseed oil (ELSO), and carbonated linseed oil (CLSO).

#### *Experimental procedures for epoxidation of vegetable oils*

Experiments were carried out in a glass batch reactor equipped with a glass agitator, a temperature probe and a reflux condenser. The procedure was the same for all the experiments. Firstly, hydrogen peroxide, water and vegetable oil were added into the reactor, and when the desired temperature was reached, the formic acid was added. The experimental details are fully described in previous works.<sup>40</sup>

#### *Experimental procedures for carbonation of epoxidized vegetable oils*

The carbonation of epoxidized vegetable oils were performed in a high-pressure vessel (Parr Instrument Company) with the same procedure developed by our research group.<sup>50</sup>The epoxidized vegetable oil and TBAB (tetrabutylammonium bromide) catalyst were introduced in the reactor. The reaction mixture was heated up to the desired temperature, i.e., 130°C. Then, the headspace of the reactor was purged with CO<sub>2</sub>, and a pressure of 50 bar of CO<sub>2</sub> was adjusted. At this moment of the procedure, the stirring was activated.

#### *Analytical analysis*

Iodine value, as the measure of concentration of double bonds, was determined using the Hanus method.<sup>51</sup>Epoxy oxygen content determination was carried out according to the standard procedure for oils by titration using a standard solution of perchloric acid. Typical chemical data of vegetable oils are shown in Table 6.

Table 6. Physicochemical data of vegetable oils.

Vegetables oils	Parameters		
	Iodine value	Epoxy oxygen content (mol·L <sup>-1</sup> )	Double bounds (mol. L <sup>-1</sup> )
Cottonseed oil (CSO)	106	-	3.9
Epoxidized cottonseed oil (ECSO)	4.6	3.27	0.17
Carbonated cottonseed oil (CCSO)	-	1.02	-
Soybean oil (SBO)	124	-	4.6
Epoxidized soybean oil (ESBO)	7.4	3	0.27
Carbonated soybean oil (CSBO)	-	0.7	-
Linseed oil (LSO)	186	-	6.8
Epoxidized linseed oil (ELSO)	9.7	4.83	0.35
Carbonated linseed oil (CLSO)	-	0.87	-

#### 4.2. Thermal characterization

DSC experiments were performed using a TA Instruments Q1000, utilizing dynamic mode under continuous nitrogen flow (20 L·min<sup>-1</sup>) as purge gas to remove moisture which might damage the cell over time and to avoid the formation of hot-spots. Samples of about 5 ± 0.5 mg in gold pans were analyzed at different heating rates from 1 to 15 °C min<sup>-1</sup>, and at the temperature range between 60 to 550 °C. The high-pressure crucibles were made of gold-plated and they were hermetically sealed (M20 crucible from Swiss Institute for the Promotion of Safety & Security). The heat of the thermal decomposition of each vegetable oils was estimated from the total area of the exothermal DSC peaks which occurs during the analysis.

ARC measurements were performed using a Netzsch ARC® 244 calorimeter. The sample bomb, i.e., a metal sphere in a 9 mm diameter, typically made of stainless steel was used. The sample mass is 1 g. The sample bomb was attached to the lid section on the calorimeter assembly by a swage lock pressure fitting, and a pressure line that led to the pressure transducer. The initial

operating conditions were atmospheric pressure and room temperature. The aim of the Accelerating Rate Calorimeter measurements was to get the time, temperature, and pressure profiles of the exothermic reaction in a safe and controlled manner.

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