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Thermal risk assessment of vegetable oil epoxidation

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Abstract This article describes thermal risk assessment of vegetable oil epoxidation by peroxycarboxylic acid. It is a liquid–liquid system where several exothermic reactions occur. Acetic acid was used as the carboxylic acid, and oleic acid was chosen as a model molecule because it is a common fatty acid in the triglyceride molecule. Differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC) were used to determine safety criteria such as the final temperature (T_{Final}), T_{D24}, and time to maximum rate under adiabatic condition ($\mathrm{TMR}_{\mathrm{ad}}$). We found that the calculation of $\mathrm{TMR}_{\mathrm{ad}}$ based on DSC data could be incorrect when assuming a zero-order kinetic reaction. By using a process temperature of 70 °C, the extrapolated final temperature was found to be 544 °C from DSC experiments, T_{D24} was estimated to 20 °C based on ARC experiment, and $\mathrm{TMR}_{\mathrm{ad}}$ was calculated to 164 min from ARC experiments. These criteria indicate the process can lead to a thermal runaway. Therefore, we recommend that vegetable oil epoxidation by peroxycarboxylic acid should not be performed in batch reactor, but in semi-batch mode.

Keywords Time to maximum rate under adiabatic condition $\mathrm{TMR}_{\mathrm{ad}}$ · MTSR · Adiabatic temperature rise · Thermal risk assessment · Green chemistry

Introduction

Biomass valorization to chemicals or to fuels is the future of chemical industry, i.e., biorefinery. In the 1990s, green chemistry concept appeared [1] and pushed industries to design chemical processes that reduce or eliminate the use or generation of hazardous substances. For example, for oxidation processes, hydrogen peroxide has replaced molecular oxygen or the use of heavy metal oxidants [2]. Even if the use of biomass as feedstock is more sustainable than the use of petroleum-derived feedstock, one should keep in mind that several transformation steps are needed. These steps could involve high-pressure and high-temperature operating conditions, extreme pH, and the use of oxidizing agents. Furthermore, many chemical processes treating biomass valorization occur in batch reactor increasing the risk of thermal accumulation. Thus, the thermal risk of these processes should be evaluated.

Vegetable oils in industry have been widely used as lubricant, as monomer for polymer production, or as biodiesel. From a chemical point of view, a vegetable oil is a triglyceride, which is an ester derived from glycerol and three fatty acids. One of the first steps is the transformation or functionalization of these molecules. For example, biodiesel is produced from the transesterification of vegetable oils by methanol. There are different ways of functionalizing vegetable oils: epoxidation, polyols synthesis, or polymerization. For example, epoxidized soybean oil can be used as lubricant, plasticizer, and hydrolysis of oxirane group is used for the production of polyurethanes. Here, we

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address the epoxidation of vegetable oils [3–5]. Epoxidized vegetable oils can be seen as a platform molecule for the production of polymers, carbonated vegetable oils, or diols. One of the greenest ways to epoxidize such double bonds is the Prileschajew method [6]. It is an exothermic liquid–liquid chemical system where different reactions occur. Figure 1 illustrates the mechanism of epoxidation. Due to the low solubility of hydrogen peroxide in the organic phase, an oxygen carrier is needed. It is the role of peroxycarboxylic acid to carry oxygen from aqueous to organic phase. Usually, peroxyacetic, peroxyformic, and m-chloroperoxybenzoic acids are used and are produced in situ. Growing interest for direct epoxidation by using only hydrogen peroxide was investigated by different research teams [7, 8]. But the heterogeneous catalysts developed for the direct epoxidation by hydrogen peroxide are less efficient than the Prileschajew method.

Bunton et al. [9] have demonstrated that carboxylic acid perhydrolysis was a nucleophilic substitution. Moreover, Shi et al. [10] have demonstrated by quantum chemical calculation that olefin epoxidation by peroxycarboxylic acids is a nucleophilic transfer (π-electrons of alkene) toward the peroxo bond of peroxycarboxylic acids. Thus, perhydrolysis and epoxidation are not occurring through free radical reactions. Under normal process conditions, i.e., atmospheric pressure and temperature range of 60–70 °C, decomposition of hydrogen peroxide and peroxyacetic acid can be neglected in the absence of metal impurities [11]. At higher-temperature process, peroxide species decomposition can occur through free radical reactions, which are no identified. These radicals can interfere with the classical simplified mechanism illustrated in Fig. 1.

The most produced epoxidized vegetable oil is epoxidized soybean oil, with a production of around 200,000 tons in 2011 [12]. The unit process is batch or semi-batch operation with a risk of thermal accumulation. The worst-case scenario is a thermal runaway leading to a pressure increase due to the non-condensable products and vapor pressure of the liquid components. It is essential to discriminate synthesis reactions occurring at normal process temperature, and secondary reactions occurring at higher temperature. Secondary reactions are more temperature sensitive than synthesis reactions due to their higher activation energies and lead to the formation of non-condensable gaseous products. In the epoxidation process, synthesis reactions are carboxylic acid perhydrolysis, epoxidation, and ring-opening reactions. Decomposition reactions are peroxycarboxylic acid and hydrogen peroxide decompositions.

The consecutive and parallel kinetic reactions (Fig. 1) make the risk assessment rather complex, especially when synthesis and decomposition reactions can occur at same temperature range due to the presence of peroxyformic acid. Peroxyformic acid is more reactive and unstable than peroxyacetic acid [13], and thus epoxidation reaction is faster and more exothermic. Due to its instability, the spontaneous decomposition of peroxyformic acid occurs at process temperature [14]. Furthermore, formic acid is a stronger carboxylic acid than acetic acid, thus favoring ring-opening reactions. For these reasons, we used acetic acid in this study.

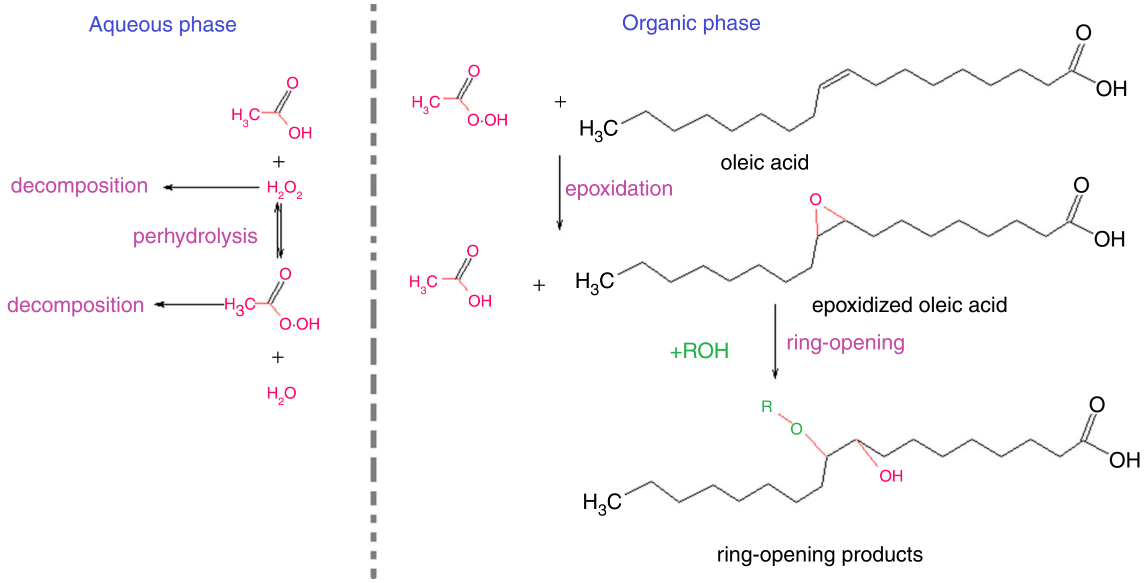

Fig. 1 Simplified mechanism of the of oleic acid epoxidation by peroxyacetic acid

Stoessel [15] summarized the different thermal analysis methods to make a thermal safety assessment. But how to interpret the safety criteria obtained by these methods for multiphase reactions system?

Several articles address the safety assessment of pure peroxide compounds for storage [16–19]. In 2010, Wu et al. [20] studied the decomposition of hydrogen peroxide with different solvents. You et al. [21] studied the decomposition of lauroyl peroxide with different nitric acid concentrations. Chi et al. [22] studied the effect of propanone on hydrogen peroxide stability by using different calorimetric methods.

To the best of our knowledge, few articles have investigated multiphase composite reactions system in microcalorimetry, and fewer still have considered vegetable oil epoxidation by peroxycarboxylic acid [23, 24]. The first goal of our approach was to identify the thermal risk of a chemical process through the product of its probability and severity, without requiring detailed kinetic and thermodynamic studies. Our approach was to use classical microcalorimetry devices as several environmental and safety agencies or industries do for their safety assessments. It was in that logic that thermal risk assessment of vegetable oils by peroxycarboxylic acid was performed in this article.

The goal of this article was to compare the safety criteria obtained by differential scanning calorimetry and accelerating rate calorimetry. Oleic acid was chosen as a model molecule, and acetic acid was used as carboxylic acid.

Experimental

Differential scanning calorimetry (DSC)

DSC, TA Q1000 with purge using extra pure nitrogen (50 L min^{-1}) was used during the experiments. Samples mass comprised between 4 and 10 mg, and gold-plated high-pressure crucibles (M20 crucible from Swiss Institute for the Promotion of Safety & Security) were used. Table 1 shows the experimental matrix.

Table 1 Experimental matrix

Acetic acid	0–30	mass/%
H_2O_2	14–20	mass/%
H_2O	28–55	mass/%
Oleic acid	31–34	mass/%
Sample mass	5–8	mg
Temperature ramp	0–5	°C min^{-1}
Temperature	60–250	°C min^{-1}

Accelerating rate calorimeter (ARC)

Netzsch MMC 274 Nexus® was used during the adiabatic experiment. Sample mass was around 1 g and was introduced into a stainless steel tube-shaped container. Initial reaction temperature and pressure were room temperature (ca. 20 °C) and atmospheric pressure, respectively. The mode Heat-Wait-and-Search was used with a thermal sensitivity of 0.02 K min^{-1}. According to the ARC manufacturer, the protocol ASTM E 1981 has been used.

Theoretical section

The purpose of this section is to present the different safety criteria used in this manuscript and how they were derived. By considering a batch reactor operating under isothermal mode, in case of cooling failure, the system can move from isothermal to adiabatic mode. Figure 2 illustrates this shift, and the safety criteria are defined.

MTSR stands for maximum temperature of the synthesis reactions and corresponds to:

$$\mathrm{MTSR} = T_\mathrm{p} + \Delta T_\mathrm{ad,synthesis} \tag{1}$$

where $\Delta T_\mathrm{ad,synthesis}$ is defined as the adiabatic temperature rise for synthesis reactions:

$$\Delta T_\mathrm{ad,synthesis} = \frac{Q_\mathrm{r,synthesis}}{m_\mathrm{r} \cdot \hat{C}_{\mathrm{P}_\mathrm{R}}} \tag{2}$$

where $Q_\mathrm{r,synthesis}$ (J) is the total amount of energy released by the reactions, m_r (kg) is the mass of reaction mixture, and $\hat{C}_{\mathrm{P}_\mathrm{R}}$ is the specific heat capacity of the reaction mixture in J kg^{-1} K^{-1}.

In case of secondary reactions, final temperature T_Final can be calculated as:

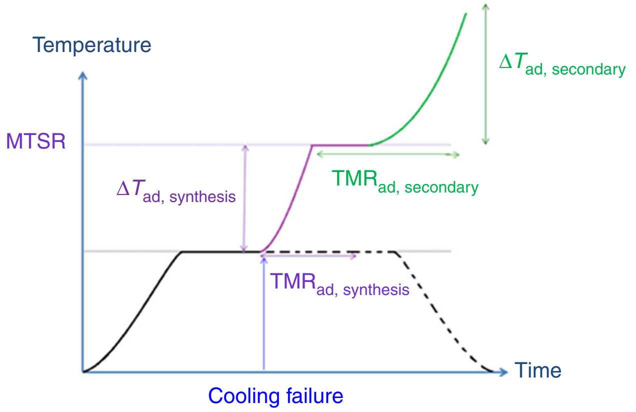

Fig. 2 Cooling failure scenario accident

$$T_{\mathrm{Final}} = \mathrm{MTSR} + \Delta T_{\mathrm{ad,decomposition}} \tag{3}$$

where $\Delta T_{\mathrm{ad,decomposition}}$ stands for the adiabatic temperature rise for decomposition reactions:

$$\Delta T_{\mathrm{ad,decomposition}} = \frac{Q_{\mathrm{r,decomposition}}}{m'_{\mathrm{r}} \cdot \hat{C}_{\mathrm{P_R}}} \tag{4}$$

In the literature, single irreversible reaction of first order is presented and the total energy released is $Q_{\mathrm{r,synthesis}} = \mathrm{n}_0 \cdot \Delta H_{\mathrm{r}}$. However, in case of composite reactions, this definition is not valid anymore. The presence of decomposition reactions is difficult to take into account because kinetic data are usually not known as well as initial conditions.

The probability criterion which is time to maximum rate under adiabatic conditions ($\mathrm{TMR_{ad}}$) can be difficult to estimate without kinetic data. The general consensus is to assume a zero-order reaction to calculate that criterion. Then, the following equation [25] is used:

$$\mathrm{TMR_{ad}}(T_{\mathrm{P}}) = \frac{m_{\mathrm{R}} \cdot \hat{C}_{\mathrm{PR}} \cdot R \cdot T_{\mathrm{P}}^2}{q_{\mathrm{P}} \cdot (T_{\mathrm{P}}) \cdot E_{\mathrm{a}}} \tag{5}$$

The derivation of this equation is detailed as follows. The power released q_{p} (W) by a chemical reaction is

$$q_{\mathrm{P}} = r \cdot \Delta \mathrm{H_r} \cdot V \tag{6}$$

where r (mol L^{-1} s^{-1}) is the reaction rate, ΔH_{r} (J mol^{-1}) is the enthalpy associated with the reaction, and V (L) is the reaction volume. For a zero-order reaction, $r = k$, where k (mol L^{-1} s^{-1}) is the kinetic rate constant. Thus, Eq. (6) becomes:

$$q_{\mathrm{P}} = k \cdot \Delta \mathrm{H_r} \cdot V \tag{7}$$

The kinetic rate constant follows a modified Arrhenius equation such as:

$$k = k_{\mathrm{ref}} \exp\left(\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \tag{8}$$

where $k_{\mathrm{ref}} = Ae^{-\left(\frac{-\mathrm{E_a}}{\mathrm{RT_{ref}}}\right)}$, with T_{ref} being a reference temperature.

Thus, Eq. (7) becomes:

$$\begin{aligned} q_{\mathrm{p}} &= k_{\mathrm{ref}} \exp\left(\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \cdot \Delta H_{\mathrm{r}} \cdot V \\ &= q_{\mathrm{p,ref}} \exp\left(\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \end{aligned} \tag{9}$$

where, $q_{\mathrm{p,ref}} = k_{\mathrm{ref}} \cdot \Delta H_{\mathrm{r}} \cdot V$.

$q_{\mathrm{p,ref}}$ is the power at a reference temperature for a zero-order reaction. Under adiabatic condition and with no phase change, the energy balance is simplified to:

$$m_{\mathrm{r}} \cdot \hat{C}_{\mathrm{PR}} \cdot \frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}t} = q_{\mathrm{P}}(T_{\mathrm{r}}) \tag{10}$$

where T_{r} is the reaction temperature and $q_{\mathrm{p}}(T_{\mathrm{r}})$ is the power released by the reaction at T_{r}.

By adding Eqs. (9) and (10), one gets:

$$\frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}t} = \frac{q_{\mathrm{p,ref}}}{m_{\mathrm{r}} \cdot \hat{C}_{\mathrm{PR}}} \cdot \exp\left(\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \tag{11}$$

By integrating Eq. (11) from process temperature to the maximum temperature of synthesis reactions, one gets:

$$\begin{aligned} &\left[\frac{-1}{\frac{E_{\mathrm{a}}}{R}\frac{1}{T^2}} \cdot \exp\left(\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right)\right]_{\mathrm{T_p}}^{\mathrm{MTSR}} \\ &\quad = \frac{q_{\mathrm{p,ref}}}{m_{\mathrm{r}} \cdot \hat{C}_{\mathrm{PR}}} \cdot \left(t_{\mathrm{MTSR}} - t_{\mathrm{T_p}}\right) \end{aligned} \tag{12}$$

After some simplifications, Eq. (12) becomes

$$\begin{aligned} t_{\mathrm{MTSR}} = \mathrm{TMR_{ad,synthesis}} &= \frac{m_{\mathrm{r}} \cdot \hat{C}_{\mathrm{PR}} \cdot R \cdot T_{\mathrm{P}}^2}{q_{\mathrm{p,ref}} \cdot E_{\mathrm{a}} \cdot \exp\left(\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T_{\mathrm{ref}}} - \frac{1}{T_{\mathrm{P}}}\right)\right)} \\ &= \frac{m_{\mathrm{r}} \cdot \hat{C}_{\mathrm{PR}} \cdot R \cdot T_{\mathrm{P}}^2}{q_{\mathrm{p}}(T_{\mathrm{P}}) \cdot E_{\mathrm{a}}} \end{aligned} \tag{13}$$

Using the same reasoning, one can calculate time to maximum rate under adiabatic condition for decomposition reactions as:

$$\begin{aligned} t_{\mathrm{final}} &= \mathrm{TMR_{ad,decomposition}} \\ &= \frac{m_{\mathrm{r}} \cdot \hat{C}_{\mathrm{PR}} \cdot R \cdot \mathrm{MTSR}^2}{q_{\mathrm{p,ref}} \cdot E_{\mathrm{a}} \cdot \exp\left(\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{T_{\mathrm{ref}}} - \frac{1}{\mathrm{MTSR}}\right)\right)} \\ &= \frac{m'_{\mathrm{r}} \cdot \hat{C}_{\mathrm{PR}} \cdot R \cdot \mathrm{MTSR}^2}{q_{\mathrm{p}}(\mathrm{MTSR}) \cdot E'_{\mathrm{a}}} \end{aligned} \tag{14}$$

One should keep in mind that Eqs. (13) and (14) are correct for zero-order reaction. These equations are often used in case of single reaction with complex kinetics or even in case of composite reactions. Indeed, one cannot know the intrinsic kinetics and by assuming a zero order for a safety assessment the worst-case scenario is taken into account. However, are not there any risks of overestimating the probability? A comparison between $\mathrm{TMR_{ad}}$ obtained from DSC results and ARC was made in that manuscript.

In case of composite reactions, one should determine which activation energy to use for Eqs. (13) and (14). It is a typical problem in thermal safety assessment for complex reaction system. One method to calculate the activation energies for the synthesis and decomposition parts is the Kissinger Ozawa method [26]. It is based on the use of DSC under dynamic mode, and it could be possible to discriminate between both mechanisms [24].

Concentration evolution can be described by the following equations:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k \cdot f(C) \tag{15}$$

Indeed, a reaction is function of the rate constant and reactant concentrations. Equation (15) is equivalent to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k \cdot (1-\alpha)^{\mathrm{n}} \tag{16}$$

where α represents the chemical advancement of a reaction.

By using Arrhenius law, the above equation becomes:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \cdot \exp\left(\frac{-E_\mathrm{a}}{R \cdot T}\right)(1-\alpha)^n \tag{17}$$

There is an extremum at this function at:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = 0 \tag{18}$$

which is equivalent to

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = 0 \\
&\Leftrightarrow \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = (1-\alpha)^{\mathrm{n}} \cdot \frac{\mathrm{d}}{\mathrm{d}t}\left(A \cdot \exp\left(\frac{-E_\mathrm{a}}{RT}\right)\right) \\
&\quad + A \cdot \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \cdot \frac{\mathrm{d}(1-\alpha)^{\mathrm{n}}}{\mathrm{d}t} \\
&\Leftrightarrow \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = (1-\alpha)^{\mathrm{n}} \cdot \frac{\mathrm{d}}{\mathrm{d}T} \cdot \frac{\mathrm{d}T}{\mathrm{d}t}\left(A \cdot \exp\left(\frac{-E_\mathrm{a}}{RT}\right)\right) \\
&\quad + A \cdot \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \cdot \frac{\mathrm{d}}{\mathrm{d}\alpha}\frac{\mathrm{d}\alpha(1-\alpha)^{\mathrm{n}}}{\mathrm{d}t} = 0 \\
&\Leftrightarrow \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = (1-\alpha)^{\mathrm{n}} \cdot \frac{A \cdot E_\mathrm{a}}{RT^2} \cdot \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \cdot \frac{\mathrm{d}}{\mathrm{d}T} \\
&\quad - A \cdot \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \cdot n(1-\alpha)^{\mathrm{n}-1} \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}t} = 0
\end{aligned} \tag{19}$$

when $T = T_\mathrm{m}$ (temperature at the maximum heat flow);

$$\begin{aligned}
&(1-\alpha)^{\mathrm{n}} \cdot \frac{A.E_\mathrm{a}}{RT_\mathrm{m}^2} \cdot \exp\left(\frac{-E\mathrm{a}}{RT_\mathrm{m}}\right) \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = A \cdot \exp\left(\frac{-E_\mathrm{a}}{RT_\mathrm{m}}\right) \cdot n \\
&\quad \cdot (1-\alpha)^{\mathrm{n}-1} \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}t} \\
&\Leftrightarrow (1-\alpha) \cdot \frac{E_\mathrm{a}}{RT_\mathrm{m}^2} \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = n \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}t} = n \cdot k \cdot (1-\alpha)^{\mathrm{n}} \\
&\Leftrightarrow \frac{E_\mathrm{a}}{RT_\mathrm{m}^2} \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = n \cdot A \cdot \exp\left(\frac{-E_\mathrm{a}}{RT_\mathrm{m}}\right) \cdot (1-\alpha)^{\mathrm{n}-1}
\end{aligned} \tag{20}$$

By introducing the following notation, $\beta = \frac{\mathrm{d}T}{\mathrm{d}t}$ which represents the temperature ramp, then:

$$\begin{aligned}
&\frac{\beta}{T_\mathrm{m}^2} = \frac{R \cdot A}{E_\mathrm{a}} \cdot n \cdot (1-\alpha)^{\mathrm{n}-1} \cdot \exp\left(\frac{-E_\mathrm{a}}{RT_\mathrm{m}}\right) \\
&\Leftrightarrow \ln\left(\frac{\beta}{T_\mathrm{m}^2}\right) = \ln(\text{constant}) - \frac{E_\mathrm{a}}{RT_\mathrm{m}}
\end{aligned} \tag{21}$$

The Kissinger approach was used in this study.

In order to measure the TMR_ad, the adiabatic reactor was used.

Results and discussion

Results obtained by differential scanning calorimeter

In order to determine the effect of H_2O_2 on total energy released by the system, we conducted an experiment with an excess of hydrogen peroxide. Figure 3 shows two DSC experiments performed under dynamic mode with different hydrogen peroxide concentrations (Table 2).

When there is an excess of hydrogen peroxide (Case 2), the total energy released by the system is higher, i.e., 2091 J g^{-1}. One can notice the presence of two different peaks in case of excess of hydrogen peroxide. As said in the "Introduction", the mechanism of vegetable oil epoxidation is complex, and decomposition reactions can be the decomposition of hydrogen peroxide into oxygen and water and the different decomposition routes of peroxyacetic acid [27, 28]. Thus, the second peak can be assumed to be the decomposition of the excess of hydrogen peroxide and decomposition of peroxyacetic acid into non-condensable gaseous products.

The adiabatic temperature rise can be calculated from both experimental conditions,

$$\begin{aligned}
&\Delta T_\mathrm{ad} = \frac{Q_\mathrm{r,total}}{m'_\mathrm{r} \cdot \hat{C}_{\mathrm{P_R}}} = 816\,\mathrm{K} \quad \text{for} \quad \frac{\text{mass/\% (AA)}}{\text{mass/\% }(\mathrm{H_2O_2})} = 0.5 \\
&\Delta T_\mathrm{ad} = \frac{Q_\mathrm{r,total}}{m'_\mathrm{r} \cdot \hat{C}_{\mathrm{P_R}}} = 474\,\mathrm{K} \quad \text{for} \quad \frac{\text{mass/\% (AA)}}{\text{mass/\% }(\mathrm{H_2O_2})} = 2.0
\end{aligned} \tag{22}$$

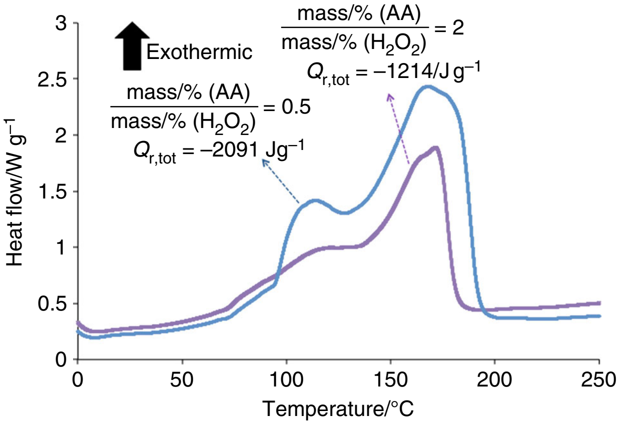

Fig. 3 DSC experiment at 4 °C min^{-1} at different ratio of acetic acid on hydrogen peroxide

Table 2 Experimental conditions for DSC under dynamic mode

	Case 1	Case 2	
Acetic acid	30.04	10.51	mass/%
H_2O_2	14.86	19.30	mass/%
H_2O	32.82	42.04	mass/%
Oleic acid	22.28	28.15	mass/%
Sample mass	5.57	5.33	mg
Temperature ramp	4	4	°C min^{-1}

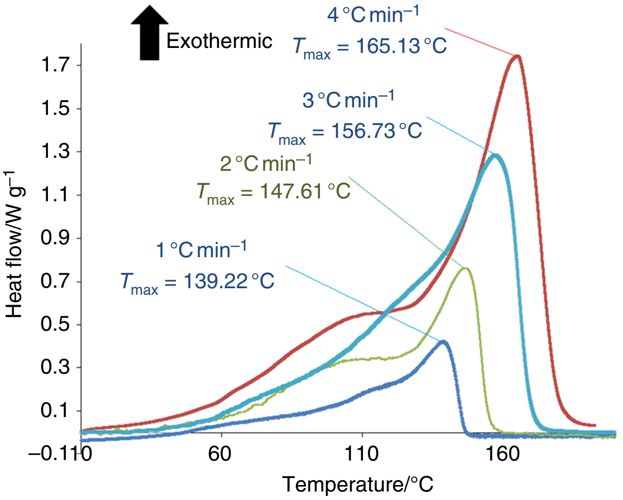

Fig. 4 DSC under dynamic mode

One can notice that in case of excess of hydrogen peroxide, the severity of the accident is higher. The objective of this article was to make the safety assessment under normal condition, and for that reason it was decided to take into consideration only the case 1, i.e., mass ratio of acetic acid on hydrogen peroxide equal to 0.5. The following experiments were performed by using similar concentrations as case 1.

Different temperature ramps are used as illustrated on Fig. 4.

We applied the Kissinger methodology and generated the correlation in Fig. 5.

The value of the activation energy is equal to 72,090 J mol^{-1}. To determine TMR_{ad} from Eq. (5) at process temperature, one should determine the power released by the chemical system q_p and the activation energy. The power released can be determined by using DSC under isothermal condition (Fig. 6a, b). The maximal power released $q_{p,max}$ was chosen to calculate the TMR_{ad} at different process temperatures.

By using Eq. (9), it is possible to determine an average activation energy, i.e., covering synthesis and decomposition part. Figure 7 illustrates the Eq. (9).

Figure 8 shows the evolution of TMR_{ad} with the temperature process based on $q_{p,max}$. TMR_{ad} calculated with activation energy equal to 48,590 or 72,090 J mol^{-1} gives similar results. On Fig. 8, prevision values correspond to the value of TMR_{ad} calculated with a $q_{p,max}$ belonging to temperature range 60–250 °C, and prediction values are obtained by using a $q_{p,max}$ which is outside of this range.

The safety criteria for this system by using DSC experiment are displayed in Table 3.

One can notice that the difference between both systems is small. One should observe that T_{D24} was determined by using the following assumptions:

- Equation (5) is based on a zero-order reaction,
- by using the maximum power released $q_{p,max}$.

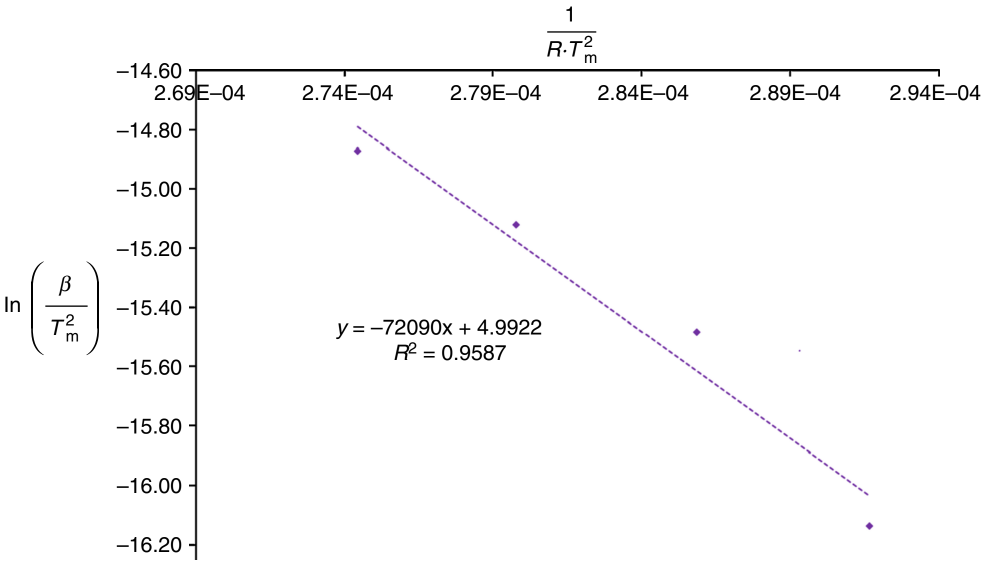

Fig. 5 Kissinger plot for oleic acid epoxidation by peroxyacetic acid

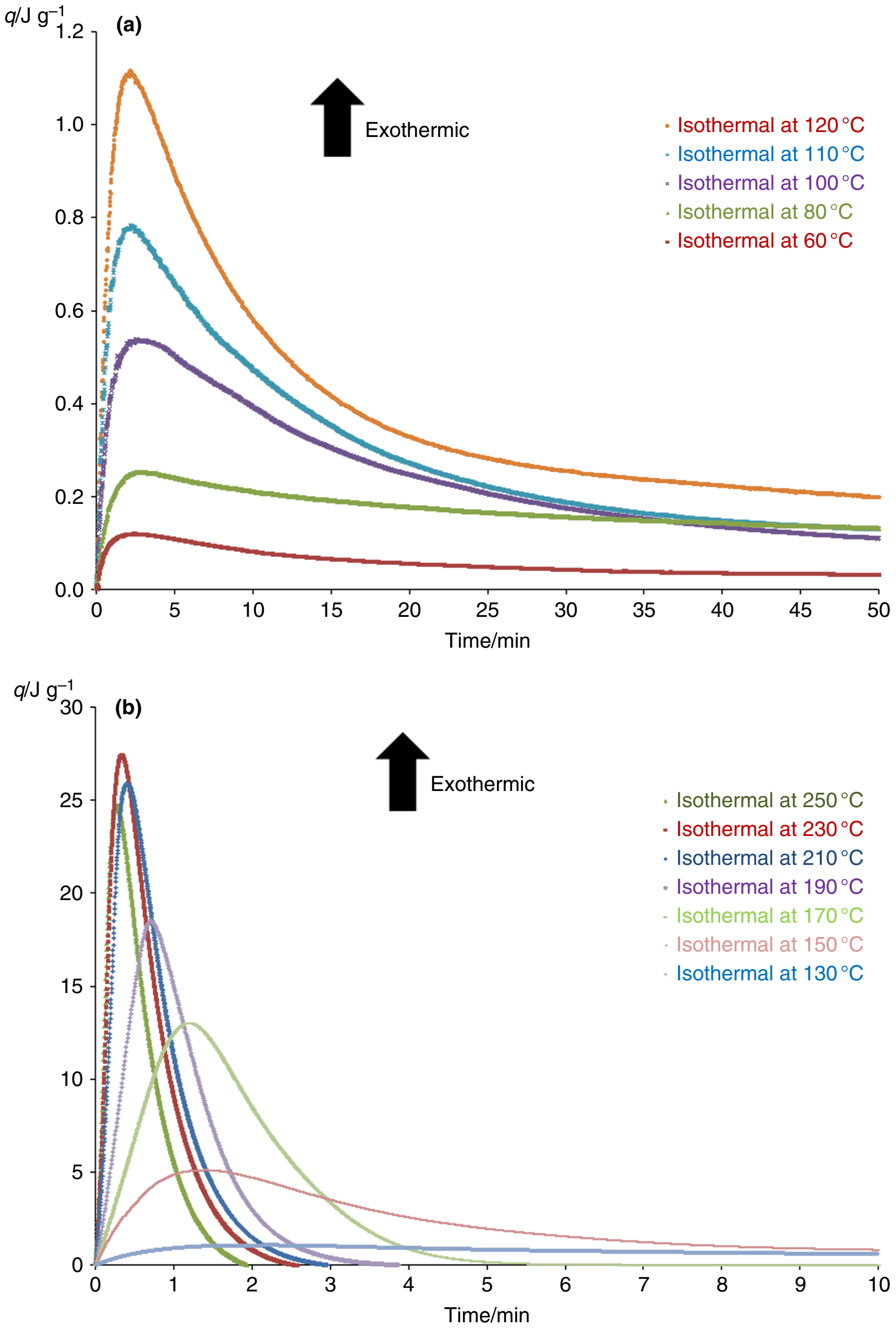

Fig. 6 **a** DSC under isothermal condition for the epoxidation of oleic acid by peroxyacetic acid within temperature range of 60–120 °C. **b** DSC under isothermal condition for the epoxidation of oleic acid by peroxyacetic acid within temperature range of 130–250 °C

Furthermore, the obtained value of T_{D24} is far from the experimental temperature range, i.e., −24 °C.

Results obtained by accelerating reaction calorimeter

By using Eq. (5), the user should be aware that it was derived for a zero-order reaction. In order to check whether this assumption was correct, an adiabatic reactor was used. Figure 9 shows the evolution of temperature and pressure with a φ-factor equal to 1.87.

The measured temperature should be corrected with the thermal inertia of the system as:

$$T_{i,corr} = T_0 + \varphi \cdot (T_i - T_0) \tag{23}$$

where φ is defined as:

$$\varphi = \frac{m_R \cdot \hat{C}_{P_R} + m_{cellule} \cdot \hat{C}_{P_{cellule}}}{m_R \cdot \hat{C}_{P_R}} \tag{24}$$

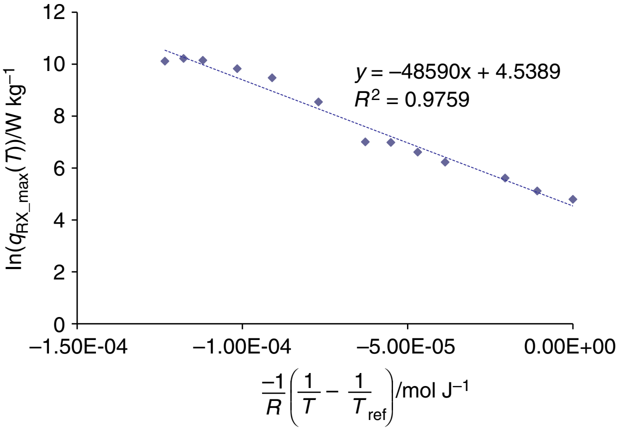

Fig. 7 Evolution of $\ln(q_{\mathrm{RX\_max}})$ versus $\frac{-1}{R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{ref}}}\right)$

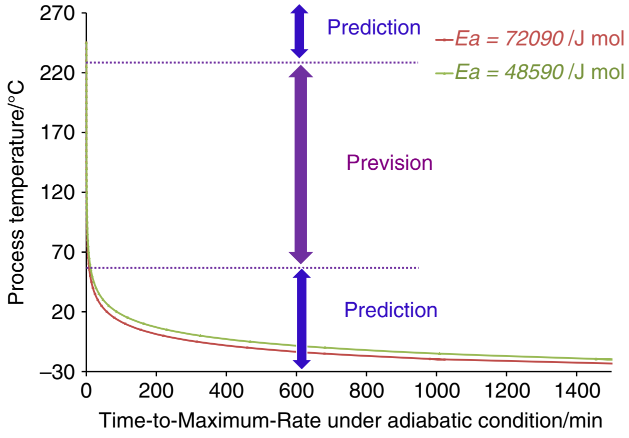

Fig. 8 $\mathrm{TMR}_{\mathrm{ad}}$ from DSC data

Table 3 Safety criteria from DSC results

	$E_a = 72{,}090/\mathrm{J\ mol}^{-1}$	$E_a = 48{,}590/\mathrm{J\ mol}^{-1}$
T_{final}/°C	544.00	544.00
MTT/°C	100.00	100.00
T_p/°C	70.00	70.00
T_{D24}/°C	−24.00	−19.50

when the system is completely adiabatic then $\varphi = 1$.

Figure 10 shows the corrected value in function of the $\mathrm{TMR}_{\mathrm{ad}}$.

The final extrapolated temperature for $\varphi = 1$ was 401.9 °C. It was not possible in our experiment to reach T_{D24}, i.e., process temperature when $\mathrm{TMR}_{\mathrm{ad}}$ is 24 h. It is compulsory to extrapolate that value by using Eq. (5) representing the worst-case scenario. Figure 11 shows $\ln(\mathrm{TMR}_{\mathrm{ad}})$ versus the inverse of the temperature process.

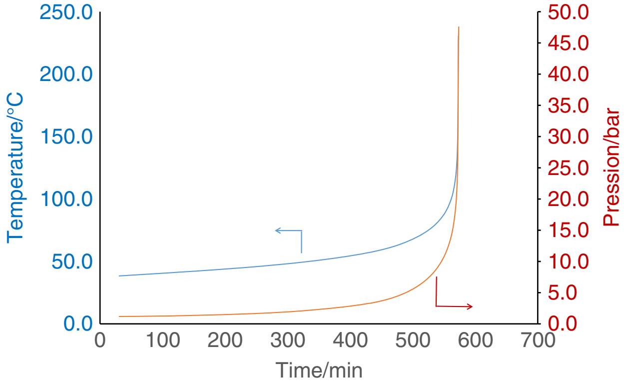

Fig. 9 Evolution of temperature and pressure in the ARC

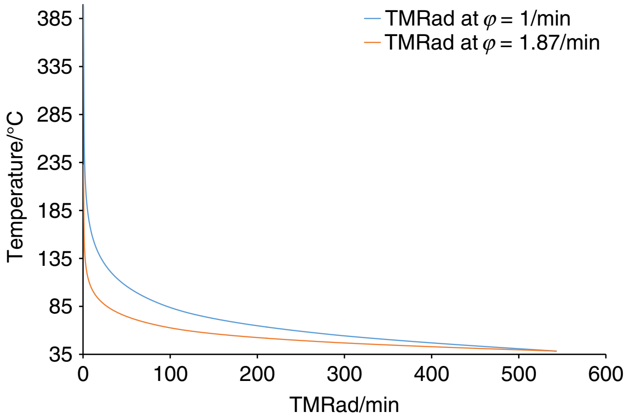

Fig. 10 Evolution of $\mathrm{TMR}_{\mathrm{ad}}$ with φ-factor

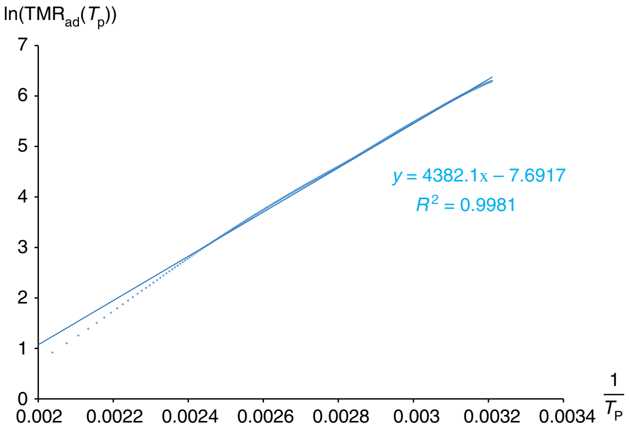

Fig. 11 $\ln(\mathrm{TMR}_{\mathrm{ad}})$ versus T_P^{-1}/K^{-1}

The value of the activation energy was of 36,431 J mol^{-1}, thus by extrapolation $T_{D24} = 19.69$ °C. The value of T_{D24} was closer to the experimental temperature interval than the one obtained from DSC experiments.

Table 4 Comparison between DSC and ARC

	DSC	ARC
T_{final}/°C	544.00	401.94
MTT/°C	100	100
MTSR/°C	x	x
T_{p}/°C	70	70
T_{D24}/°C	−24	19.7
$\Delta T_{\mathrm{ad,total}}$/°C	474	331.94
$\mathrm{TMR}_{\mathrm{ad,total}}$(70 °C)/min	4.41	164

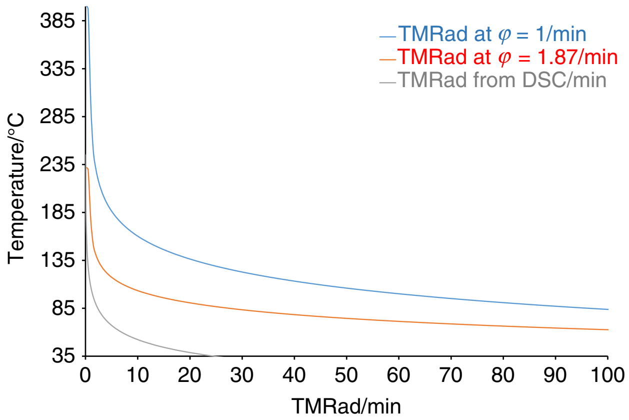

Fig. 12 Evolution of $\mathrm{TMR}_{\mathrm{ad}}$ at different process temperatures

Comparison between DSC and ARC

The safety criteria obtained by DSC and ARC are compared. From DSC, by using the dynamic mode, it was possible to notice the presence of secondary reactions and to calculate the total energy released by a chemical system. Furthermore, it is possible to determine the maximum power released by a chemical system by using the isothermal mode, which is essential for the heat exchanger scale-up. However, $\mathrm{TMR}_{\mathrm{ad}}$ obtained by DSC was overestimated due to the use of $q_{\mathrm{p,max}}$ in Eq. (5) and the fact that $q_{\mathrm{p,max}}$ was not obtained at −20 °C (Table 4; Fig. 12). ARC is an excellent complementary calorimetry tool to estimate $\mathrm{TMR}_{\mathrm{ad}}$. In this system, it was not possible to measure directly that value, and an extrapolation should have been done. The final temperature was lower with ARC because the hydrogen peroxide decomposition reaction was not triggered.

Conclusions

We assessed the thermal safety of oleic acid epoxidation by peroxyacetic acid using ARC and DSC under both dynamic and isothermal modes. The reaction composition was similar to those used in industry, i.e., 25 mass/% of acetic acid, 15 mass/% of hydrogen peroxide, and 30 mass/%of oleic acid. In case of excess of hydrogen peroxide, the total energy released by the chemical system was higher, and we observed synthesis and decomposition reactions.

We found that the $\mathrm{TMR}_{\mathrm{ad}}$ calculated from DSC data was higher than the $\mathrm{TMR}_{\mathrm{ad}}$ calculated from ARC data. The widely used Eq. (5) is derived based on zero-order kinetic reactions and leads to an overestimate of the risk probability. Furthermore, it was calculated by using the maximum power released. In the case of ARC, by taking into account the thermal inertia of the system, the $\mathrm{TMR}_{\mathrm{ad}}$ calculated can be assumed closer to the one in case of cooling failure.

In such system, the user should use DSC under dynamic mode to observe the presence of secondary reactions and DSC under isothermal mode to calculate the adiabatic temperature rise from the total energy released, and ARC should be used to approach the value of T_{D24}.

We estimated the adiabatic temperature rise to be 544 °C from DSC data and the value of T_{D24} from ARC to be 20 °C, which is higher than the normal temperature process, i.e., 60–70 °C. Thus we recommend operating under semi-batch mode to limit the accumulation of reactant inside the reactor.

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