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Parameters affecting thermal risk through a kinetic model under adiabatic condition

: Application to liquid-liquid reaction system

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ABSTRACT

Risk of thermal runaway for epoxidation is not negligible and should be analyzed and assessed. In industry, epoxidation of vegetable oils is carried out by the oxidation of Prileschajew, involving the in situ production of percarboxylic acid from hydrogen peroxide and the corresponding carboxylic acid. Different research groups have developed kinetic models under isothermal or isoperibolic mode for this liquid-liquid reaction system. Nevertheless, none of them have built a kinetic model under adiabatic mode. Such kinetic model under adiabatic condition is important to evaluate the thermal risk of a process.

During this study, a kinetic model was built for the epoxidation of cottonseed oil by peracetic acid by using ARSST system, which works under near-adiabatic condition. This kinetic model can fit the experimental reaction temperature. Then, based on this model, the influence of different inlet parameters (i.e. initial temperature and concentrations) on safety parameters, i.e., Time-to-Maximum rate under adiabatic conditions and adiabatic temperature rise was investigated.

KEYWORDS: kinetic modeling, liquid-liquid reactions, adiabatic calorimeter, thermal risk assessment, epoxidation.

HIGHLIGHTS

A kinetic model for complex chemical system under adiabatic condition was developed

ΔT_{ad} and TMR_{ad} in presence of several exothermic reactions were determined

Thermal risk assessment for the epoxidation of vegetable oil were performed

1. INTRODUCTION

Energy sector and chemical industry still depend on the use of fossil raw materials. As example, Speight (2016) [1] reported that 90 % of organic chemicals are produced from natural gas or petroleum. Recently, academies, industries and public authorities have put a great effort to develop new processes and new chemicals using renewable feedstock.

The use of vegetable oils, as a renewable feedstock, for the production of chemicals or biofuels is a good illustration of this effort. The worldwide production of vegetable oil is increasing since 1975 [2]. The part of production for industrial uses also increases and not only for biodiesels [3]. Vegetable oils can be considered as platform molecules [4-6].

Among the different functionalization of vegetable oils, there is the epoxidation of vegetable oils. Epoxidized vegetable oils are important chemicals for the production of non-isocyanate polyurethanes [7-13], biolubricants [14-18], plasticizers [19-20] or stabilizers for polymers. Several routes for the production of epoxidized vegetable oils exist. One of the more eco-friendly methods is the use of oxygen or hydrogen peroxide [21], however, the research on catalyst is still ongoing [22-28]. The use of enzymes is an alternative that is being more and more applied [29-36].

For these reasons, at the industrial scale, the Prileschajew oxidation is the most used process [37-41]. Prileschajew oxidation is a liquid-liquid process where a percarboxylic acid is produced in situ in the aqueous phase from the perhydrolysis reaction, and diffused into the organic phase to epoxide the unsaturated groups of the vegetable oils. Solubility in the organic phase and reactivity of percarboxylic acid are higher compared to hydrogen peroxide. However, one of the main drawbacks of this reaction system is the risk of thermal runaway induced by several consecutive exothermic reactions [42-48].

The aforementioned articles have studied thermal risks and/or thermal instabilities of this chemical system. Nevertheless, none of them has built a kinetic model under adiabatic conditions, including secondary reactions as the decomposition of peroxide species. This work proposes to fill this gap by building a kinetic model for the epoxidation of cottonseed oil by peracetic acid produced in situ. The benefit of such model compared to the zero-order approach [49] is that one can estimate the safety parameters at different initial operating conditions.

Based on this model, safety parameters such as the time to maximum rate under adiabatic conditions, TMR_{ad} , and the adiabatic temperature rise, ΔT_{ad} , are estimated. These safety parameters are necessary to make a thermal risk assessment because while the latter represents the severity of a thermal risk, the former signifies its probability. The influence of reactant, catalyst concentrations and the initial temperature on these safety parameters are studied in the current work.

2. EXPERIMENTAL SECTION

2.1 Chemicals

To perform the experiments in the Advanced Reactive System Screening Tool (ARSST) system, the following chemicals were used: distilled water, hydrogen peroxide (33 wt %, VWR International), acetic acid (>99%, Alfa Aesar GmbH & Co.) and cottonseed oil (ThermoFisher Scientific GmbH).

2.2 Experiments performed in ARSST

ARSST system is a calorimeter which can work under near-adiabatic conditions by using the principle of heat loss compensation [7-10, 17, 42, 49]. It yields critical experimental knowledge of the rates of temperature and pressure rise during a runaway reaction. The detailed description of the ARSST equipment can be found in our previous articles [42, 49].

The system consists of an open glass cell reactor surrounded by a heater belt. This glass cell reactor is put in an insulation sheath, which is put in a pressurized vessel. The vessel is pressurized under 35 bar of nitrogen to limit the evaporation of the liquid phase. Through the heater belt, a background heating rate β is applied to the reaction mixture.

In order to build a kinetic model, taking into account different inlet parameters such as reactant and catalyst concentrations or background heating rate, Table 1 shows the experimental matrix.

Table 1: Experimental matrix

RUN	Initial concentration (mol.L ⁻¹)					V _{org} (L)	V _{aq} (L)	β (°C.min ⁻¹)	Initial T1 (°C)
	[DB] _{org}	[HP] _{aq}	[AA] _{aq}	[W] _{aq}	[H ₂ SO ₄] _{aq}				
1	3.9	4.75	4.15	35.95	0	0.0036	0.0057	4.04	22.58
2	3.9	5.12	4.47	34.11	0.11	0.0034	0.0053	0.89	22.58
3	3.9	4.45	4.02	35.25	0.52	0.0035	0.0058	2.12	20.23
4	3.9	4.7	3.51	36.41	0.56	0.0034	0.0057	0.9	27.37
5	3.9	5.37	4.14	33.57	0.53	0.0034	0.0057	1.83	24.08

3. RESULTS AND DISCUSSION

3.1 Kinetics, mass and energy balances

3.1.1 Kinetics

Epoxidation of vegetable oils by Prileschajew oxidation is a liquid-liquid reaction system, where peracetic acid (PAA) is produced in the aqueous phase from the perhydrolysis reaction. Then, PAA diffuses to the organic phase to epoxidize the unsaturated groups.

Different side reactions, such as decomposition of peroxide species (hydrogen peroxide and PAA) or ring-opening reactions by different nucleophiles, can occur. Fig. 1 shows the different reactions occurring in the aqueous phase. As shown in previous papers [42, 47], the decomposition of hydrogen peroxide during this process can be neglected.

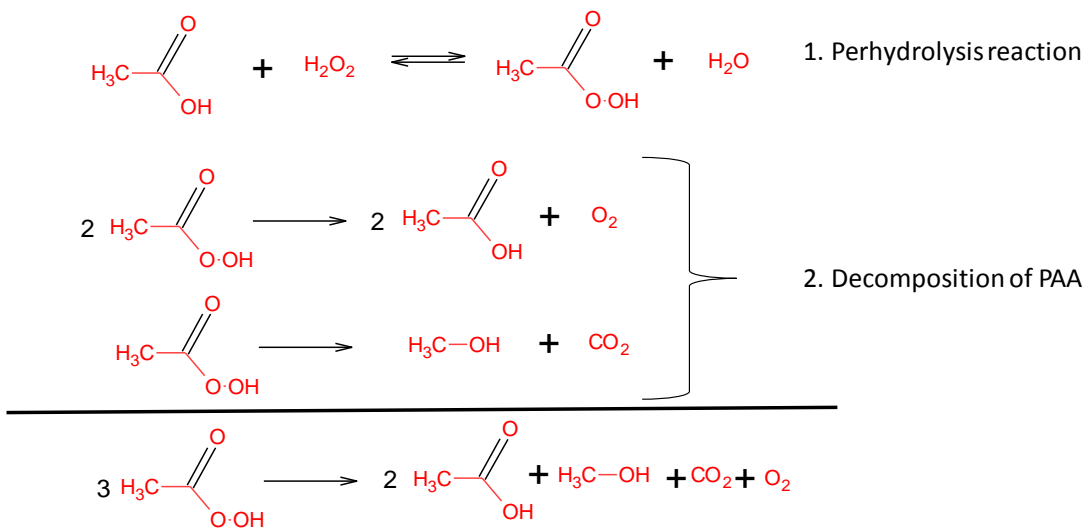


Figure 1: Reactions in the aqueous phase.

Perhydrolysis reaction rate can be expressed as [50]:

$$r_{perh} = k_{perh} \cdot \frac{[H_3O^+]_{aq}}{[H_2O]_{aq}} ([AA]_{aq} \cdot [H_2O_2]_{aq} - \frac{1}{K^C} \cdot [PAA]_{aq} \cdot [H_2O]_{aq}) \quad (1)$$

where, K^C is the equilibrium constant based on the concentrations and can be expressed as:

$$K^C = \delta \cdot [H_2SO_4]_{aq} + K^T \quad (2)$$

Here, the parameter δ takes into account the non-ideality of the reaction mixture, and K^T is the true thermodynamic constants, which can be expressed by a law of van't Hoff. To determine the value of K^C with temperature and sulfuric acid concentration, the parameters from the work of Leveneur et al. [50] were used.

The concentration of hydroxonium ions in the aqueous phase can be derived by taking into account the electroneutrality of the reaction mixture and the mass balance of sulfuric and acetic acids:

$$[H_3O^+]_{aq} = \frac{1}{2} [H_2SO_4]_{aq} + \sqrt{\frac{[H_2SO_4]_{aq}^2}{4} + 2 \cdot K_{II}^C \cdot [H_2SO_4]_{aq} \cdot [H_2O]_{aq} + K_{III}^C \cdot [H_2O]_{aq} \cdot [AA]_{aq}} \quad (3)$$

where, K_{II}^C and K_{III}^C are the dissociations constants for the second dissociation of sulfuric acid and acetic acid, respectively [51-52].

As described by Musakka et al. [53] and Leveneur et al. [54], the decomposition of percarboxylic acid can follow two reaction pathways (also illustrated in Fig. 1). To minimize the number of parameters to estimate, these two decomposition reactions were represented in one reaction. The kinetic expression for the decomposition of PAA can be expressed as:

$$r_{decomp_PAA} = k_{decomp_PAA} \cdot [PAA]_{aq} \cdot [H_3O^+]_{aq} \quad (4)$$

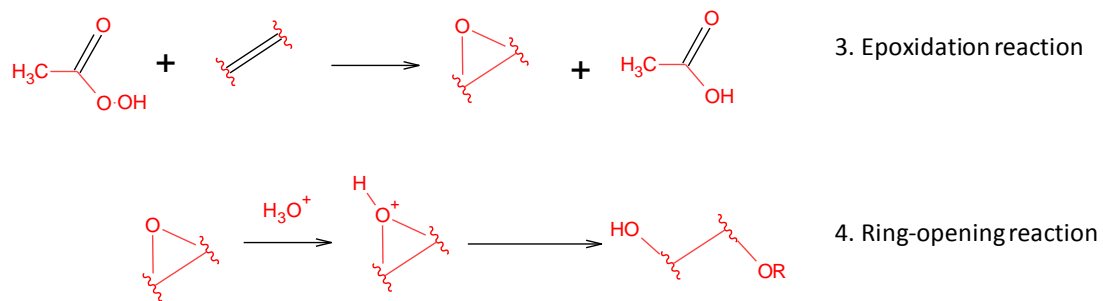


Figure 2: Reactions in aqueous phase.

Fig. 2 exhibits the reactions in the organic phase. In the organic phase, two main reactions occur, namely, epoxidation reaction and ring-opening reactions. For the ring-opening reaction, several nucleophile agents can open the oxirane ring: water, acetic and peracetic acid or hydrogen peroxide. In our earlier work [37], we have demonstrated that ring-opening by percarboxylic acid is the fastest one. For that reason, here, we have only considered the ring-opening by percarboxylic acid.

The kinetics of epoxidation and ring-opening by peracetic acid can be expressed to

$$r_{Ep} = k_{Ep} \times [PAA]_{aq} \times [DB]_{org} \quad (5)$$

$$r_{RO} = k_{RO} \times [Ep]_{org} \times [PAA]_{aq} \times [H_3O^+]_{aq} \quad (6)$$

3.1.2 Mass balance

This section consists in describing the mass balance of the different compounds in aqueous and organic phases. By assuming that interfacial mass transfer is faster than chemical reaction [37-38, 44], mass balance in the organic and aqueous phases can be expressed as:

$$\frac{dC_{i,org}}{dt} = (\alpha \cdot K_i + 1 - \alpha)^{-1} \cdot [\alpha \sum v_{ij} \cdot r_{aq,j} + (1 - \alpha) \sum v_{ij} \cdot r_{org,j}] \quad (7)$$

$$\frac{dC_{i,aq}}{dt} = \left(\alpha + \frac{1 - \alpha}{K_i} \right)^{-1} \cdot [\alpha \sum v_{ij} \cdot r_{aq,j} + (1 - \alpha) \sum v_{ij} \cdot r_{org,j}] \quad (8)$$

where, $\alpha^{-1} = \frac{V_{aq}}{V_T}$ and $K_i = \left(\frac{C_{i,aq}}{C_{i,org}} \right)_{equilibrium}$.

Here, the solubilities of water and hydrogen peroxide in the organic phase were assumed to be negligible, i.e., K_W, K_{AA}, K_{PAA} and $K_{HP} \rightarrow \infty$. Additionally, the solubilities of vegetables and their derivatives in the aqueous phase were assumed to be negligible, i.e., $K_{cotton}, K_{Ep}, K_{RO} \rightarrow 0$ [38]. Thus, mass balance for each compound can be expressed as:

$$\frac{dC_{AA,aq}}{dt} = (-r_{perh} + 2 * r_{decomp_PAA}) + \frac{(1 - \alpha)}{\alpha} * r_{Ep} \quad (9)$$

$$\frac{dC_{W,aq}}{dt} = r_{perh} \quad (10)$$

$$\frac{dC_{HP,aq}}{dt} = -r_{perh} \quad (11)$$

$$\frac{dC_{PAA,aq}}{dt} = (r_{perh} - 3 * r_{decomp_PAA}) - \frac{(1 - \alpha)}{\alpha} * r_{Ep} \quad (12)$$

$$\frac{dC_{DB,org}}{dt} = -r_{Ep} \quad (13)$$

$$\frac{dC_{Ep,org}}{dt} = r_{Ep} - r_{RO} \quad (14)$$

$$\frac{dC_{RO}}{dt} = r_{RO} \quad (15)$$

3.1.3 Heat balance

Heat balance in the liquid phase can be expressed as [42, 49, 55]:

$$\varphi \cdot m_R \cdot \hat{C}_{PR} \cdot \frac{dT_R}{dt} = q_{rx} + q_{elec}. \quad (16)$$

where, φ is the thermal inertia factor, and is expressed as $\varphi = \frac{m_R \cdot \hat{C}_{PR} + m_{ins} \cdot C_{P_{ins}}}{m_R \cdot \hat{C}_{PR}}$. The term q_{elec} is the electrical power provided to the reaction mixture through the heater belt. By dividing this term by $\varphi \cdot m_R \cdot \hat{C}_{PR}$, one gets the electrical heating background β .

The heat-flow rate due to the chemical reactions can be expressed as

$$q_{rx} = -(r_{perh} \cdot \Delta H_{R,perh} + r_{decomp_PAA} \cdot \Delta H_{R,decomp_PAA}) \cdot V_{aq} - (r_{Ep} \cdot \Delta H_{R,Ep} + r_{RO} \cdot \Delta H_{R,RO}) \cdot V_{org} \quad (17)$$

The reaction enthalpy for acetic perhydrolysis is $-5.66 \text{ kJ}\cdot\text{mol}^{-1}$ [50], epoxidation of unsaturated groups by percarboxylic acid is $-230 \text{ kJ}\cdot\text{mol}^{-1}$ [37] and for the ring-opening reactions is $-77 \text{ kJ}\cdot\text{mol}^{-1}$ [37]. Furthermore, reaction enthalpy for the decomposition of PAA can be estimated from the heat of formation (see Table 2) as

$$\Delta H_{R,decomp_PAA} = 2 * \Delta H_{f,AA} + \Delta H_{f,MeOH} + \Delta H_{f,CO_2} + \Delta H_{f,O_2} - 3 * \Delta H_{f,PAA} \quad (18)$$

Thus, the reaction enthalpy of PAA decomposition can be estimated to be $-450.3 \text{ kJ}\cdot\text{mol}^{-1}$.

Table 2: Heat of formation.

	ΔH_f (kJ/mol)	References
Acetic acid	-484.5	[56]
Peracetic acid	-390.1	[57]
Carbon dioxide in aqueous solution	-413.25	[58]
Methanol	-283.4	[59]
Oxygen	0.0	

3.2 Kinetic modeling

ModEst software [60] is used during the modeling stage. The set of ordinary differential equations (Eqs. (9) to (15)) were solved using the ODESSA algorithm. Reaction temperature was an observable. The objective function θ was defined as:

$$\theta = \sum (T_i - \hat{T}_i)^2 \quad (19)$$

where, T_i is the experimental temperature and \hat{T}_i is the temperature obtained from the model. The goal of this stage was to estimate the kinetic constants for the decomposition of PAA, the ring-opening reaction and epoxidation reaction. To decrease the correlation between the rate constant at one temperature and the activation energy, a modified Arrhenius equation was used:

$$k_j(T_R) = k_j(T_{Ref}) * \exp\left(\frac{-E_{a_j}}{R} \left(\frac{1}{T_R} - \frac{1}{T_{Ref}}\right)\right) \quad (20)$$

where, T_{ref} is a reference temperature which was fixed to 90°C in this study.

The objective function was firstly minimized by the Simplex algorithm then by the Levenberg-Marquardt algorithm.

To evaluate the fitting of the model to the experimental data, a coefficient of determination was calculated as

$$R^2 = 1 - \frac{\sum (T_i - \hat{T}_i)^2}{\sum (T_i - \bar{T})^2} \quad (21)$$

where, \bar{T} is the mean value of the experimental temperatures.

The value of R^2 was found to be 96% revealing that the model fits correctly the experimental data, see also Figs 3. A-C, where one can notice a good correlation between observations and modeling.

Table 3 shows the values of the kinetic constants. One can notice the standard errors are significantly low.

Table 3: Kinetic constants estimated at 90°C and statistical data.

		Estimated parameters	Standard error (%)
$k_{Decomp_PAA}(90^{\circ}C)$	[L.mol ⁻¹ .s ⁻¹]	1.62E-07	6.4
Ea_{Decomp_PAA}	[kJ.mol ⁻¹]	180.00	0.0
$k_{RO}(90^{\circ}C)$	[L.mol ⁻¹ .s ⁻¹]	1.30E-05	28.0
Ea_{RO}	[kJ.mol ⁻¹]	147.0	4.7
$k_{Ep}(90^{\circ}C)$	[L.mol ⁻¹ .s ⁻¹]	4.13E-05	0.6
Ea_{Ep}	[kJ.mol ⁻¹]	79.2	0.4

From the work of Leveneur et al. [50], the kinetic constant of acetic acid perhydrolysis (k_{perh}) at 90°C is equal to 0.058 L.mol⁻¹.s⁻¹ and the activation energy (Ea_{perh}) is equal to 75.58 kJ.mol⁻¹. From Table 3, when the reaction temperature is lower than 109°C, then the kinetics of epoxidation is faster than the ring-opening or decomposition of PAA. For higher reaction temperature, the kinetics of ring-opening by peracetic acid is faster than epoxidation.

Figs 3. A-C show some fittings of the model to the experimental data. Fig 3A shows that the model can fit experiment performed in the absence of sulfuric acid. Experiments illustrated by Figs 3B and 3C were performed at different concentration of sulfuric acid. Nevertheless, one can notice that the model slightly overestimates the experimental temperature in the presence of sulfuric acid. This deviation might be due to the fact that the effect of protons on the kinetics is more complex.

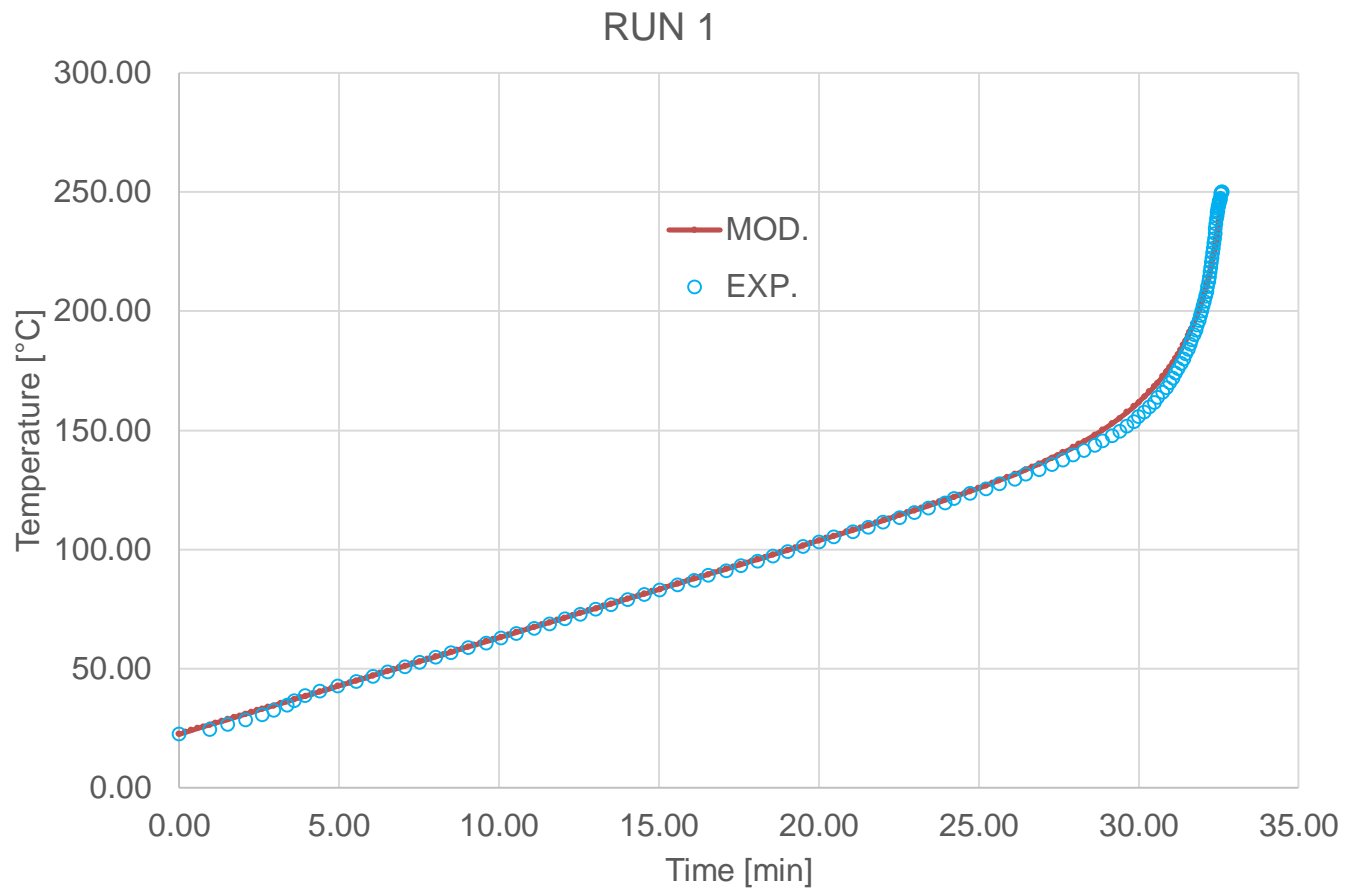


Figure 3.A: Fit of the model to the experimental data for Run 1.

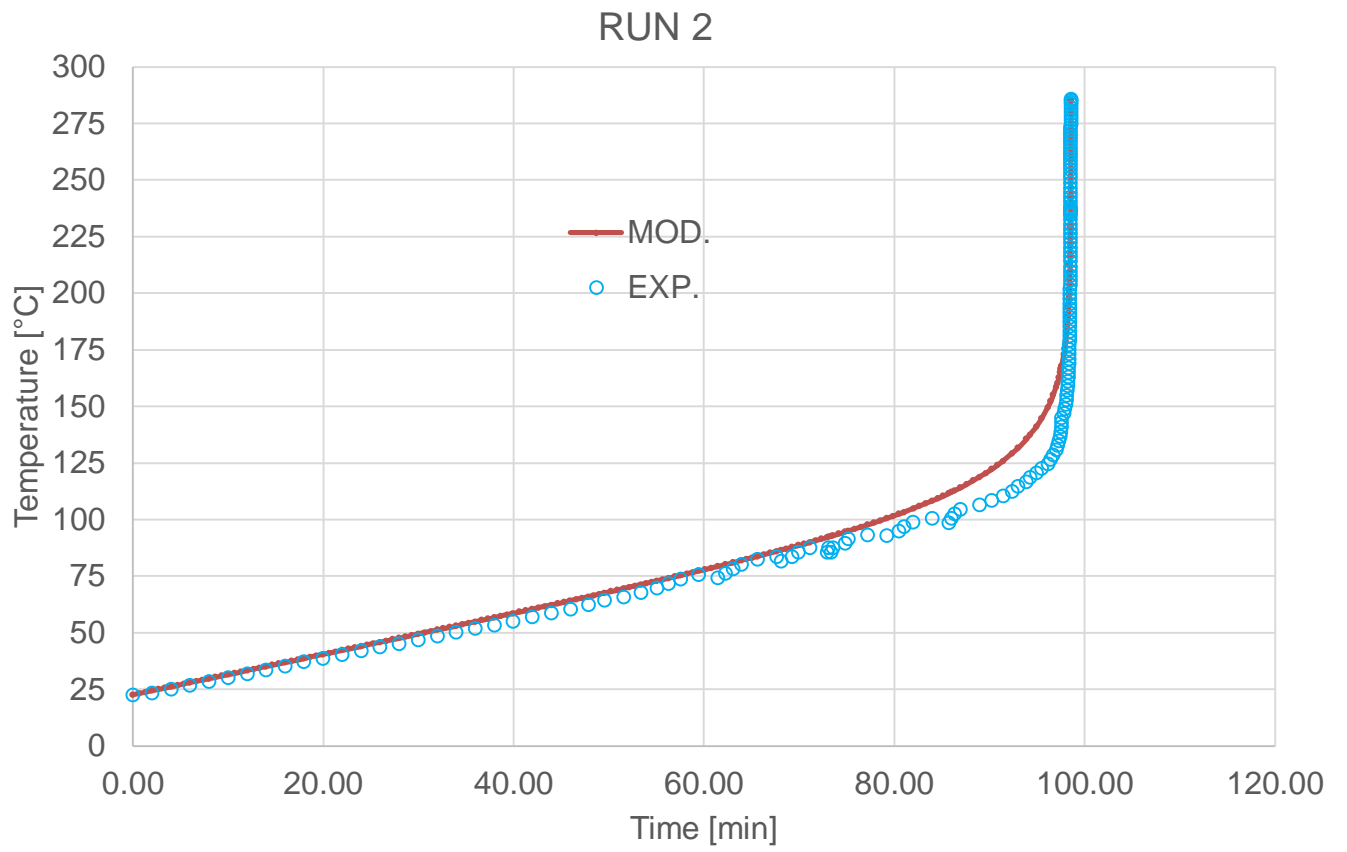


Figure 3.B: Fit of the model to the experimental data for Run 2.

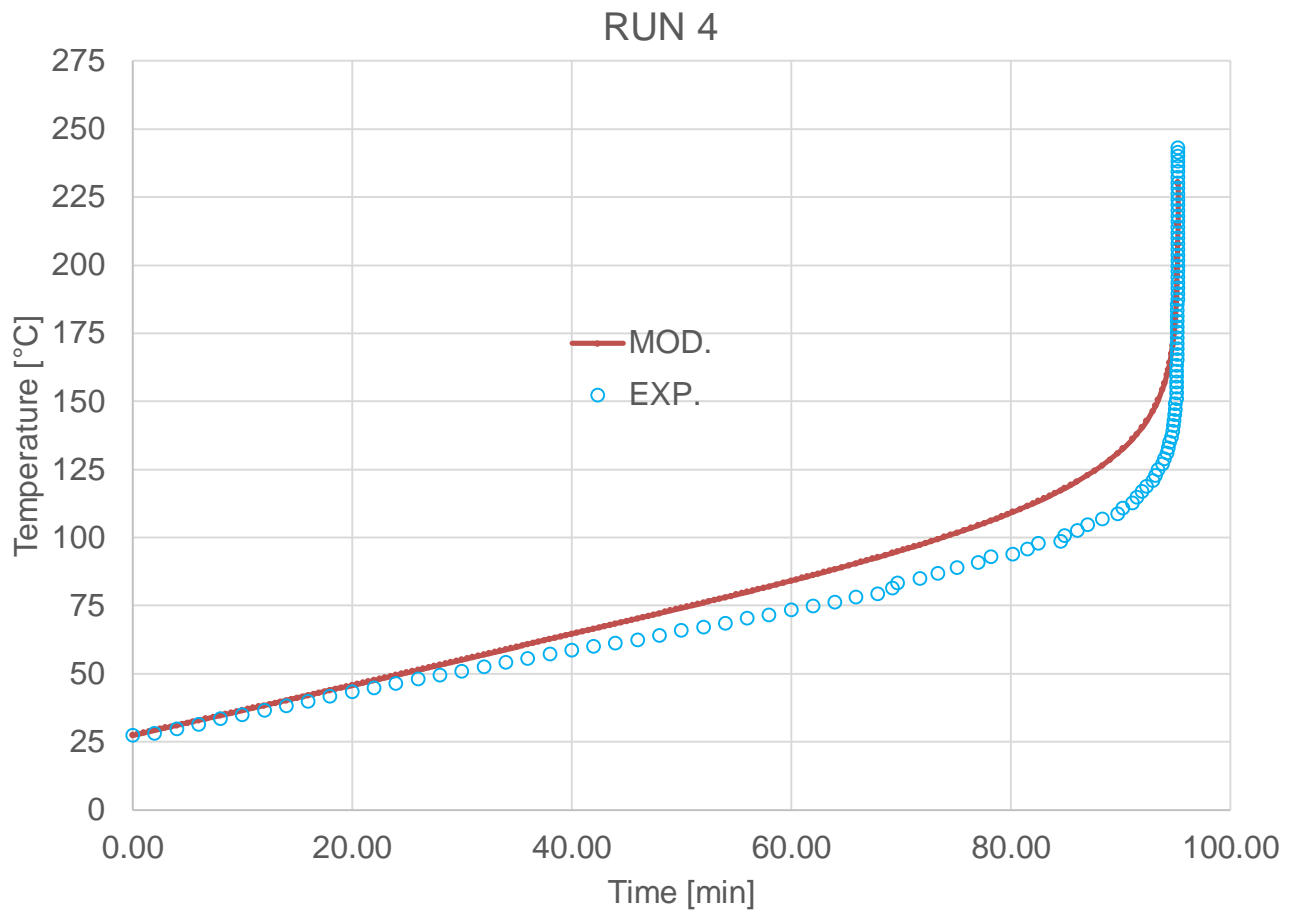


Figure 3.C: Fit of the model to the experimental data for Run 4.

3.3 Safety parameters.

Thermal risk is defined by the product of the probability represented by TMR_{ad} and severity represented by ΔT_{ad} [61]. Based on the kinetic model, the influence of sulfuric acid, hydrogen peroxide, acetic acid concentrations and initial temperature on the safety parameters: TMR_{ad} and ΔT_{ad} . The parameter TMR_{ad} represents the time it takes for a reaction mass to reach the maximum rate of heat release for a given starting temperature under adiabatic condition and the parameter ΔT_{ad} is the difference between the initial and the final temperatures.

These parameters were studied for the epoxidation of cottonseed oil under adiabatic condition in a batch reactor. Figs 4 to 7 illustrate the influence of these parameters. Fig. 4 shows that the increase of sulfuric acid concentration does not have a significant effect on ΔT_{ad} . However, the increase of sulfuric acid concentration accelerates the kinetics of reaction, thus decreases the value of TMR_{ad} .

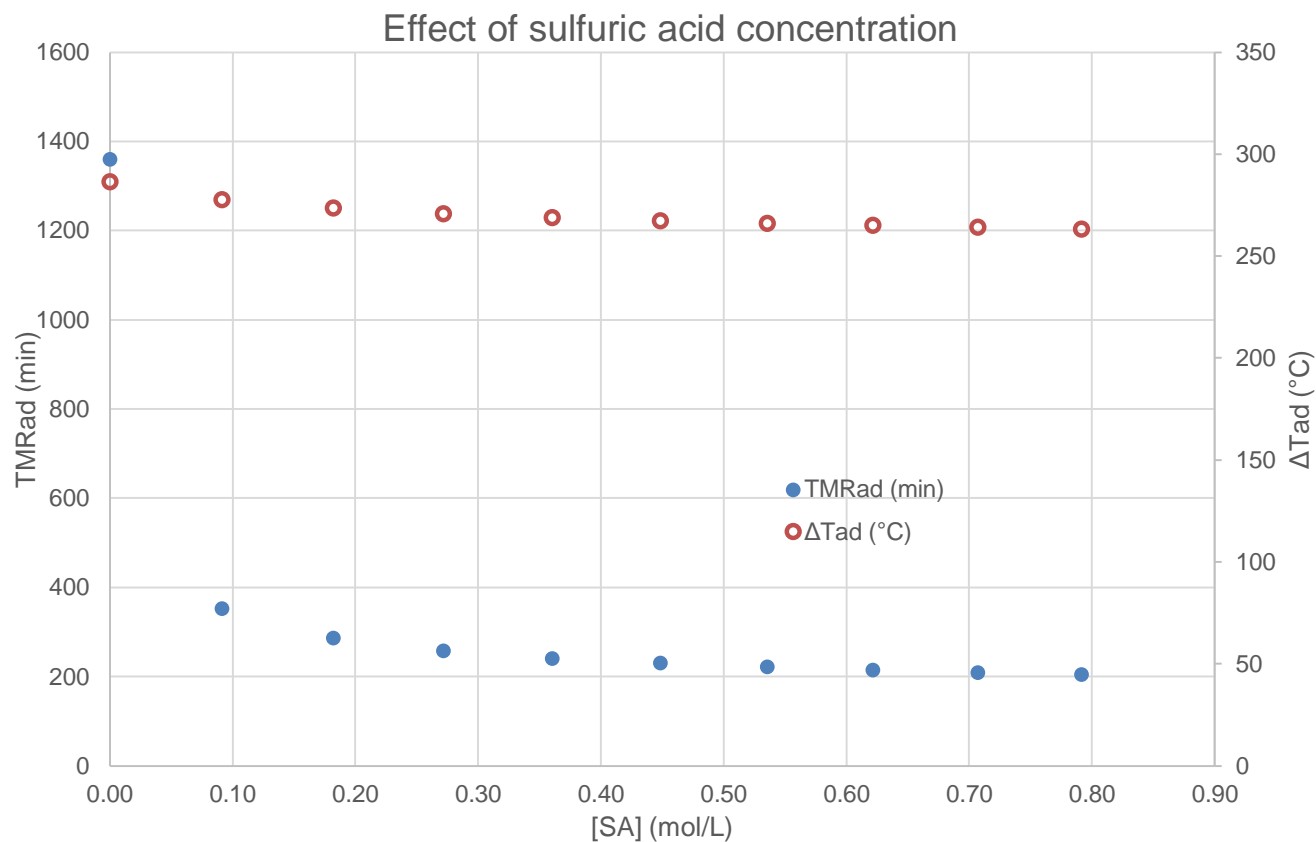


Figure 4: Effect of sulfuric acid concentration on TMR_{ad} and ΔT_{ad} with the following operating conditions: [H₂O₂]_{aq,0} = 5.81-5.56 mol.L⁻¹, [AA]_{aq,0} = 6.11-5.85 mol.L⁻¹, [W]_{aq,0} = 28.74-27.59 mol.L⁻¹ and initial temperature of 70°C.

Fig. 5 shows that the increase of the initial reaction temperature does not have a significant effect on the value of ΔT_{ad}. By increasing the initial temperature, the kinetics is faster, thus the TMR_{ad} is shorter.

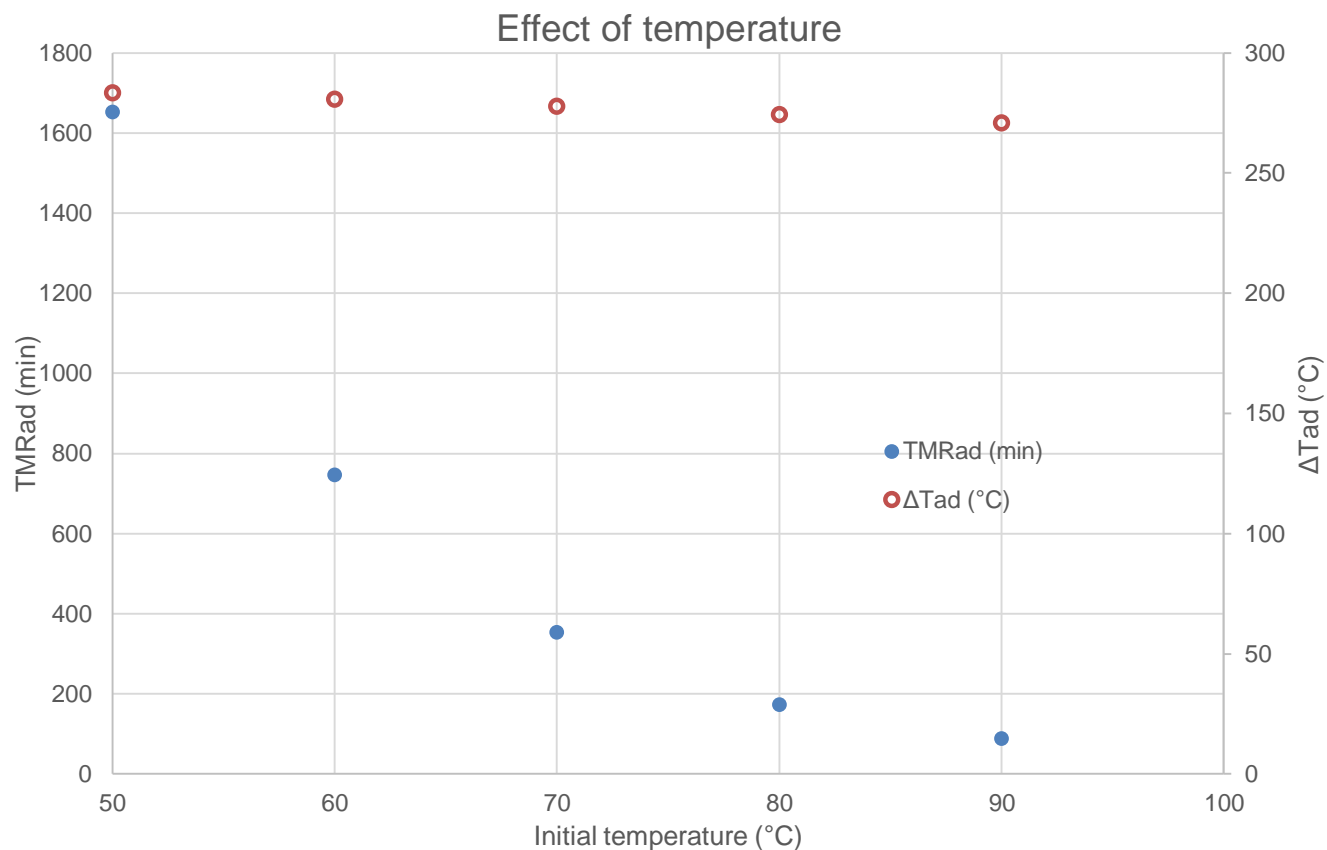


Figure 5: Effect of initial temperature on TMR_{ad} and ΔT_{ad} with the following operating conditions: $[H_2O_2]_{aq,0} = 5.79 \text{ mol.L}^{-1}$, $[AA]_{aq,0} = 6.08 \text{ mol.L}^{-1}$, $[W]_{aq,0} = 28.60 \text{ mol.L}^{-1}$ and initial $[H_2SO_4]_{aq,0} = 0.09 \text{ mol.L}^{-1}$.

The increase of hydrogen peroxide concentration increases the adiabatic temperature rise and the values of TMR_{ad} , as depicted in Fig. 6. By increasing the concentration of hydrogen peroxide, the kinetics of peracetic acid production and epoxidation are faster leading to shorten TMR_{ad} . In addition, the increase of hydrogen peroxide concentration leads to increase the production of peracetic acid and its decomposition involving an increase of ΔT_{ad} .

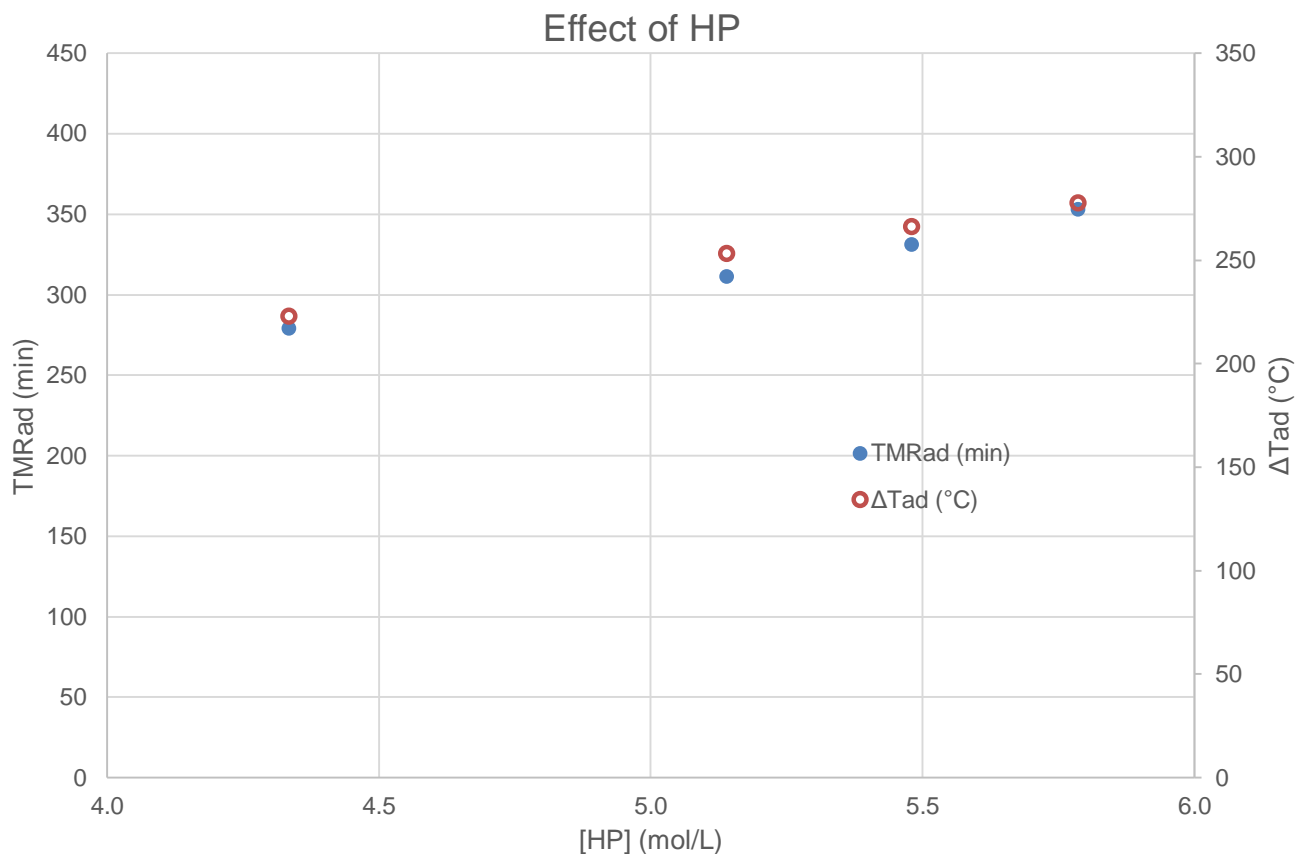


Figure 6: Effect of hydrogen peroxide concentration on TMR_{ad} and ΔT_{ad} with the following operating conditions: [AA]_{aq,0}= 5.53-7.60 mol.L⁻¹, [W]_{aq,0}= 29.71-25.57 mol.L⁻¹, [H₂SO₄]_{aq,0}= 0.08-0.11 mol.L⁻¹ and initial temperature of 70°C.

Inversely to the behavior of hydrogen peroxide, the increase of acetic acid concentration decreases the adiabatic temperature rise and the values of TMR_{ad} as expressed in Fig. 7. Indeed, by increasing the concentration of acetic acid compared to hydrogen peroxide, thus hydrogen peroxide is the limiting reactant which leads to decrease the production of PAA.

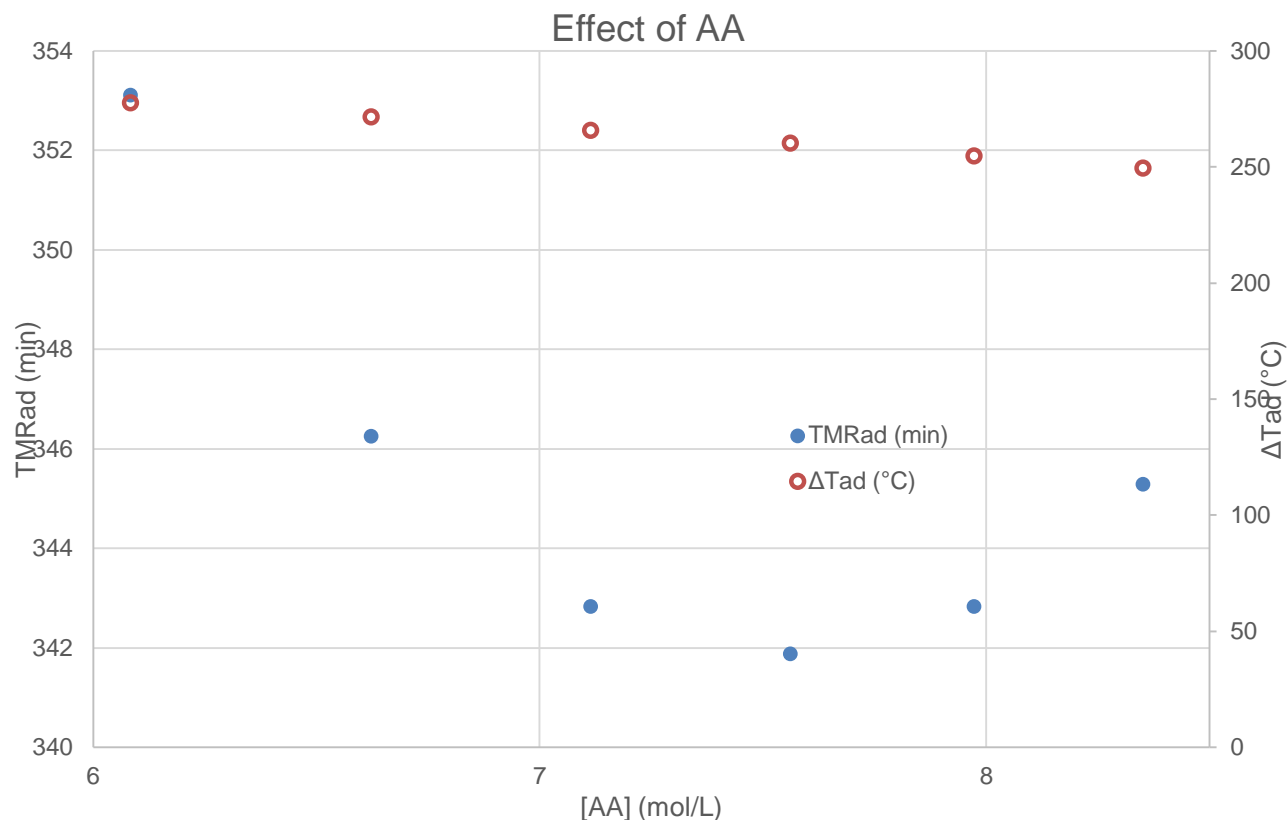


Figure 7: Effect of acetic acid concentration on TMR_{ad} and ΔT_{ad} with the following operating conditions: $[H_2O_2]_{aq,0} = 5.79-4.63 \text{ mol.L}^{-1}$, $[W]_{aq,0} = 28.60-22.91 \text{ mol.L}^{-1}$, $[H_2SO_4]_{aq,0} = 0.09-0.07 \text{ mol.L}^{-1}$ and initial temperature of 70°C .

The observation made from Figs 4 to 7, indicates that concentrations of acetic acid and hydrogen peroxide have an important impact on safety parameters. Concentration of double bond could also have an impact on these parameters, but at time zero fresh vegetable oils were used.

Furthermore, one can notice that the adiabatic temperature rise is critical because it is higher than 200°C and TMR_{ad} is frequent or critical because the values are lower than 8 hours [61]. The time to react is then not enough.

4. CONCLUSIONS

Epoxidation of vegetable oils is an important process for polymer industries, because epoxidized vegetable oils can be seen as platform molecules. In industry, Prileschajew oxidation is used, which consists of the in situ production of a percarboxylic acid in the aqueous phase. This percarboxylic acid diffuses to the organic phase to epoxidize the unsaturated groups. Several studies have built kinetic model under isothermal or isoperibolic conditions, and other studies have stressed their effort on the thermal risk of this reaction system. Nevertheless, no research work so far, to our best knowledge, have proposed a kinetic model under adiabatic condition.

In this study, we have built a kinetic model for the epoxidation of cottonseed oil by peracetic acid under near-adiabatic condition. The following reactions were considered: perhydrolysis of acetic acid, decomposition of peracetic acid, epoxidation of unsaturated groups and ring-opening reaction by peracetic acid. Mass transfer was assumed to be faster than chemical reactions allowing to simplify the model. The model fits the experimental reaction temperature correctly.

The chosen safety parameters, time-to-maximum rate under adiabatic condition and adiabatic temperature rise, were estimated by this model under different operating conditions. The benefit of such model is to avoid the use of a zero-order kinetic model which cannot describe a system at different operating conditions. It was found that these two parameters were sensitive to the concentrations of acetic acid and hydrogen peroxide.

It is noted that the kinetic model developed in this study was built based on the evolution of the experimental temperature under adiabatic condition and not based on the evolution of the species concentrations. A further work could be the use of an online analytical method to follow the concentration of double bonds, epoxide, PAA or ring-opening group under adiabatic conditions to improve the model.

ACKNOWLEDGEMENTS

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NOMENCLATURE

\hat{C}_{pR}	Specific heat-capacity [J.kg ⁻¹ .K ⁻¹]
E _a	Activation energy [J.mol ⁻¹]
ΔH	Reaction enthalpy [J.mol ⁻¹]
k	Rate constant
K	Equilibrium constant
K _i =	Distribution coefficient $\left(\frac{C_{i,aq}}{C_{i,org}}\right)_{equilibrium}$
m _{ins}	Insert mass [kg]
m _R	Mass of reaction mixture [kg]
q _{el}	Electrical heating-rate [°C.min ⁻¹]
q _{rx}	Heat-flow rate due to chemical reactions [J.s ⁻¹]
R	Gas constant [J.K ⁻¹ .mol ⁻¹]
R ²	Coefficient of determination [%]
ΔT _{ad}	Adiabatic temperature rise [°C]
T ₁	Temperature of the reaction mixture [°C]
T _{Ref}	Reference temperature [°C]
T _i	Experimental temperature
T _p	Process temperature
\bar{T}	Mean value of the experimental temperatures
\hat{T}_i	Simulated temperature
V	Volume [L]

Greek letters

α	$\frac{V_{aq}}{V_T}$
β	Background heating rate [$^{\circ}\text{C}\cdot\text{min}^{-1}$]
δ	Parameter taking into account the non-ideality of the solution
φ	Thermal inertia
θ	Objective function

Abbreviations

AA	Acetic acid
ARSST	Advanced Reactive System Screening Tool
DB	Double bond
HP	Hydrogen peroxide
PAA	Peracetic acid
RO	Ring-opening
$\text{TMR}_{ad}(T_P)$	Time-to-maximum rate under adiabatic conditions at T_P [min]
W	Water

Subscript

aq	Aqueous
decompo_PAA	Decomposition of PAA
Ep	Epoxidation
ins	Insert
j	Reaction
org	Organic
perh	Perhydrolysis
T	Total
0	Initial

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