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.

1. Introduction

Energy sector and chemical industry still depend on the use of fossil raw materials. As example, Speight [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

Nomencature

$\hat{C}_{P_R}$	Specific heat-capacity [J kg^{-1} K^{-1}]
Ea	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
$\overline{T}$	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 [°C min^{-1}]
δ	Parameter taking into account the non-ideality of the solution
φ	Thermal inertia
θ	Objective function

Subscript

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

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.

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.

Perhydrolysis reaction rate can be expressed as [50]:

Table 1
Experimental matrix.

	Initial concentration (mol L^{-1})								
RUN	[DB]$_{org}$	[HP]$_{aq}$	[AA]$_{aq}$	[W]$_{aq}$	[H$_2$SO$_4$]$_{aq}$	V$_{org}$ (L)	V$_{aq}$ (L)	β (°C min^{-1})	Initial T1 (°C)
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