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Safety Criteria for the Epoxydation of Soybean Oil in Fed-Batch Reactor

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The epoxidation of soybean oil is industrially carried out by using peroxyacid generated in situ by reacting concentrated hydrogen peroxide with acetic or formic acid, in the presence of a mineral acid as a catalyst. The reaction is generally highly exothermic and an excessive increase of temperature is proved to occur, with clear safety issue.

This unwanted phenomena is typically prevented by limiting the peroxyacid reactant amount with respect to the stoichiometry, either in semi-continuous fed-batch or in pulse-fed-batch.

In this paper, starting from experiments and given kinetic data, the set of reactions have been analysed in the light of safety, by means of classical runaway criteria.

1. Introduction

In the last years, the epoxidation of vegetable oil has received a great interest from industry. The epoxidized oils are used as plasticizers and stabilizers for polyvinyl chloride (PVC) resins. Moreover, because of the high reactivity of the oxirane ring, epoxides also act as a raw material for a variety of chemicals, such as alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds, and polymers like polyesters, polyurethanes, and epoxy resins (Goud et al., 2007).

One of the most important epoxidized vegetable oil is the soybean oil, with a worldwide production of about 2 10^8 kg per year (Eierdanz, 1993). The most common process is based on epoxidation of unsaturated bonds of oil by peroxy-acids ($R\text{-}CO_3H$), generally peroxy-acetic or peroxy-formic (performic) acid. The peroxy-acid is generally generated in situ by reacting concentrated hydrogen peroxide with acetic or formic acid in the presence of a mineral acid as a catalyst in water phase, according to the following reaction:

$$H_2O_2 + RCOOH \leftrightarrows RCOOOH + H_2O \quad (1)$$

Subsequently, the peroxy-acid migrates into the oil phase and reacts spontaneously, according to the following scheme:

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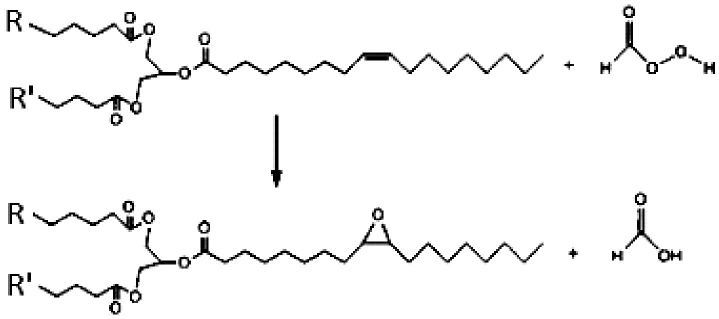

Figure 1. The scheme of epoxydation reaction

This reaction is highly exothermic (ΔH =−230.3 kJ/mol for each double bond) and an excessive increase of the temperature in the industrial reactors is prevented by adding a limited amount of a mixture of H_2O_2 and formic or acetic acid to the mixture of oil and acid catalyst (Santacesaria et al., 2011). In the following this reaction is analysed in terms of safety criteria.

2. Safety criteria

Chemical processes can undergo thermal runaway if the rate of heat generation is faster than the rate of heat removal by cooling system, thus leading to a continuous rise in the reactor temperature and a consequent acceleration of the reactions, leading eventually to explosion. Some measures for improving the safety of chemical processes can be adopted to avoid this unexpected phenomenon. Those measures can be obtained and designed by performing appropriate safety tests (Varma et al., 1999; Zaldivar et al., 2003). The most reliable tests, according to Hub and Jones (1986), are based on the "on-line methods", i.e. performed directly on the process. These methods are built on two typologies of criteria, namely "geometry-based criteria" and "sensitivity-based criteria". The first is based on geometric feature of the profile of a system variable such as temperature or heat-release rate These criteria were first introduced by the pioneering theory of Semenov and were developed later by several authors as Thomas and Bowes (1961), Adler and Enig (1964), Van Welsenaere and Froment (1970) and the same Hub and Jones (1986). On the other hand, sensitivity based criteria are related to the parametric sensitivity concept introduced by Bilous and Amundson (1956) in the context of chemical reactor theory. A reactor exhibits a parametric sensitivity when in some regions of operation a small change in a system parameter produces large changes in the dependent parameters of the system. The criteria of Varma et al. (1999), Strozzi and Zaldívar (1994) own to this class.

In this preliminary work, the geometry based criterion by Hub and Jones (1986), which is based on the increase of heat evolution in the system, is adopted. The method uses the second derivative of the reactor temperature T and the first derivative of the temperature difference between the reactor (T) and the jacket (T_W) for the identification of hazards:

$$\frac{d^2T}{dt^2} > 0 \tag{2}$$

$$\frac{d(T - T_w)}{dt} > 0 \tag{3}$$

If both of these conditions are simultaneously fulfilled, a thermal hazard may be expected and the system may go outside control. In this work, starting from an experimental and modelling study of the epoxidation of soybean oil carried out by Santacesaria et al. (2011), the Hub and Jones criterion has been applied taking into account experimental results and using the developed thermo-kinetic model as a predictive tool to evaluate safety conditions for the process.

3. Reaction scheme of epoxidation process – mass and energy equation

3.1 Reaction scheme

The epoxidation process may be described by considering the mechanism shown by Stepanski et al. (2005). In that work, the process may be sketched in the following steps: i) formation of peroxy-acid in water phase; ii) transfer of both organic and peroxy-acid to organic phase in accordance with the distribution coefficient, iii) epoxidation reaction in organic phase with formation of epoxide and release of organic acid; and iv) decomposition of the obtained epoxide both in oil phase at the phase border.

Following Santacesaria et al. (2011), two specific phases may be considered, the first occuring in acqueous solutions and promoted by an acid catalyst (sulfuric acid), in which formic acid and hydrogen peroxide are involved to give performic acid, and the second occuring in organic phase, that involves performic acid and the double bonds contained in the soybean oil molecules. In this scheme, the mass transfer between the two phases of substances involved in the process is essential.

An overall scheme of the reactions is reported in Table 1, where C=C(n) represents the un-saturated group (double bond) and n (=1,2,3) are mono-enes, di-enes and tri-enes; Epox(n) is the epoxide group deriving from the mono-enes, di-enes and tri-enes, DEG is the decomposed oxirane group obtaining by different compounds: H_2O_2, FA (formic acid), PFA (performic acid), H_2O, or more in general by H_3O^+ group and indicated with H. See Santacesaria et al. (2011) for details.

Table 1: Scheme of the epoxydation reactions.

Aqueous phase
H_2O_2 + HCOOH $\leftrightarrows$ HCOOOH + H_2O
$H_2O_2 \rightarrow H_2O + 0.5\ O_2$
Organic phase
HCOOOH + C=C(n) → Epox(n) + HCOOH
Epox(n) + $H^+ \rightarrow DEG_H$

3.2 Mass and energy equations

The complete system of mass and energy equations may be sketched as in the following:

$$\frac{dn_i^{phase}}{dt} = F_i + \sum_j r_j \cdot V_{phase} + J_i^{phase} \cdot V_{phase} \tag{4}$$

$$\begin{aligned}\bar{c}_p \cdot M_{tot} \cdot \frac{dT}{dt} = & \left(W_{H_2O_2} \cdot c_{p,H_2O_2} + W_{FA} \cdot c_{p,FA} + W_{H_2O} \cdot c_{p,H_2O}\right) \cdot \left(T_{add} - T\right) + \\ & \left[\Delta H_r \cdot \left(-r_c(i)\right) + \Delta H_{deg} \cdot \left(-r_d(i)\right)\right] \cdot V_{org} + \left[\Delta H_{OX} \cdot \left(-r_a\right)\right] \cdot V_{aq} - U \cdot A \cdot \left(T - T_w\right)\end{aligned} \tag{5}$$

where j represents each of reactants or products participating to the overall epoxidation reaction and the term *phase* refers to either aqueous or organic, n_j^{phase} are the moles of the j-th compound in the specified phase, F_j is the molar flow rate, r_j is the reaction rate, V_{phase} is the volume of the phase (V_{org} and V_{aq}), J_i^{phase} are mass transfer rate for the component j in the phase, M_{tot} is the mass of the soybean oil, $c_{p,j}$ is the specific heat capacity at costant pressure of the specie j, W_j is the mass rate of the j-th compound, T_{add} is the inlet flow temperature, ΔH are the reaction heats, U is global thermal exchange coefficients, A is the exchange area, T_w is the temperature of the jacket. This thermo-kinetic model is adopted for the aims of this work.

4. Results

The aim of this work is the analysis of Hub and Jones criteria by varying the process conditions, starting from the experimental results obtained by Santacesaria et al. (2011) in a semi-continuous-fed-batch reactor. In those tests, a continuous flow rate of 0.3 $cm^3.min^{-1}$ of an oxidizing mixture of hydrogen peroxide and formic acid (composition: H_2O_2 = 36.7 g, 60 % w/w; formic acid = 5.38 g, 95 % w/w purity) at the temperature of 10 °C was added to 100 g of well stirred soybean oil containing 0.64 g of catalyst (sulfuric acid) in about 116 minutes. The initial temperature, T_{in}, of the reaction environment was about 65 °C. The system exchanged heat with a thermostatic fluid circulating in a jacket surrounding the reactor and regulated to obtain an approximately constant reaction temperature (~ 65 °C).

The modeling tests have been carried out by assigning different flow rate Q ($cm^3.min^{-1}$) for the mixture of hydrogen peroxide and formic acid and temperature of the jacket T_w (Table 2), keeping all other parameters as in the experimental case. Table 2 reports some main modeling results: the temperature reached after 60 min, the maximum temperature reached in the system T_{MAX} and the yield in epoxide reached after 60 min of the process defined in terms of yield in epoxide :

$$yield(\%) = \frac{n_{e,1,org} + n_{e,2,org} + n_{e,3,org}}{n_d^0} \cdot 100 \tag{6}$$

where $n_{e,1,org}$, $n_{e,2,\ org}$, $n_{e,3,org}$ are the moles of epoxide obtained by mono-enes, di-enes and tri-enes of the molecules of oil and n_d^0 are the moles of double bond of the molecules of oil at the initial time.

Table 2: Test conditions and modeling results for epoxydation reaction in 60 min of process.

Data	Q, flow rate ($cm^3.min^{-1}$)			
	0.3	0.5	1.0	0.5
T_w (°C) (= T_{in})	65	65	65	70
T @ 60 min (°C)	69.96	72.09	69.36	79.10
T_{MAX} (°C) in 60 min	69.96	72.57	127.79	80.49
Yield in epoxide at 60 min (% w/w)	33.7	52.49	87.74	66.24

In Figure 2, the thermal profile of the reaction environment and the yield in epoxide are showed over a range of 60 min.

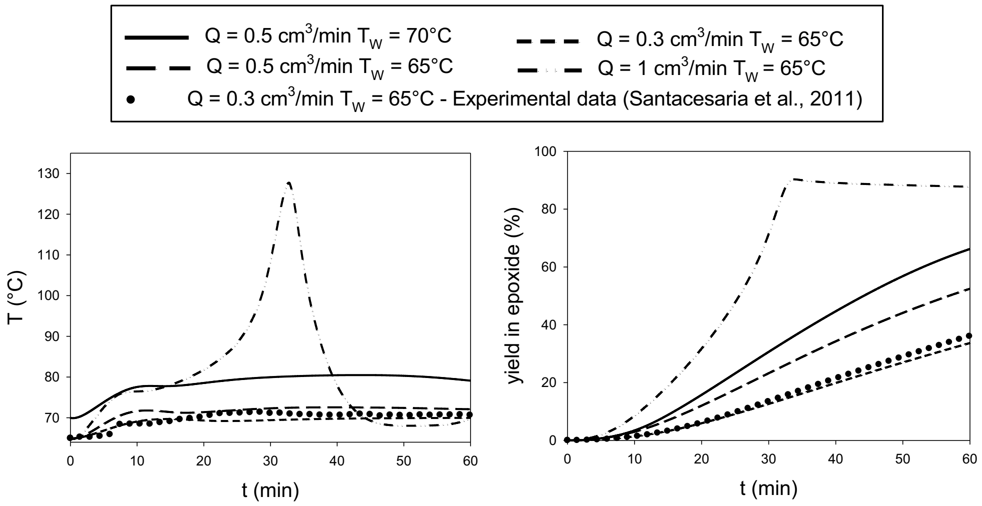

Figure 2: Thermal profile of the reaction environment and yield in epoxide obtained varying the value of the volumetric flow rate. The thermal profile of experimental test is also reported.

For the sake of application of Hub & Jones criterion, Figure 3 shows the prime derivative of the difference between the temperature of reaction environment, T, and the temperature of the jacket, T_W, and the second derivative of the temperature of reaction environment, T.

Following Hub and Jones criterion of positive derivatives, we have recognized the time and process temperature ranges in which process conditions may be considered as hazardous. This means that in those ranges (Table 3) the process may go out of control, possibly leading to runaway reaction.

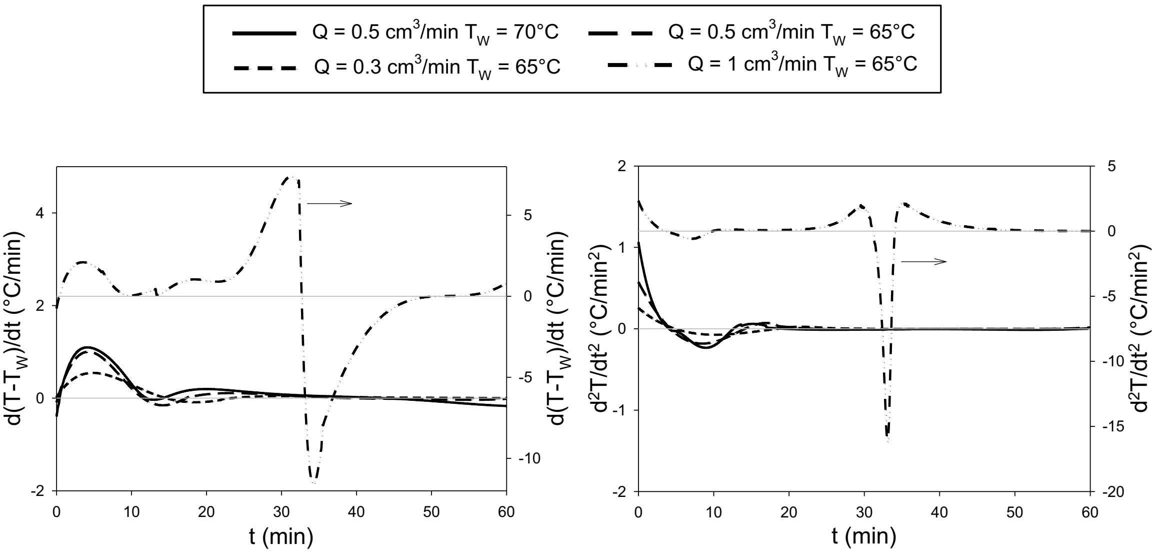

Figure 2: Hub and Jones criteria (Eqs. 2, 3) by varying the value of the volumetric flow rate. The profiles for the case of Q = 1 $cm^3.min^{-1}$ refer to right axis.

Table 3: Ranges of time and initial temperature in which the Hub & Jones criterion is satisfied and hazardous conditions are reached.

Q ($cm^3.min^{-1}$)	0.3	0.3	0.5	0.5	1	1	1	0.5	0.5
T_w=T_{in} (°C)	65		65		65			70	
t (min)	0-5	23-30	0-4	17-23	0-4	10-31	50-60	0-4	14-19
T (°C)	65-66.8	69.2-69.4	65-67.7	71.2-71.7	65-69.6	76.5-117	67.8-69.4	70-72.7	77.8-78.4

5. Discussion

The results shown in Figure 2 and Table 2 show that, quite clearly, the yield increases with the flow rate of reactant and with the temperature of the jacket T_w, because in this case lower heat loss with wall may be predicted, thus promoting the overall rate of reaction. These considerations are related to the process conditions.

As concern safety issues, results shown in Figure 3 and Table 3 demonstrate that in the first four minutes the Hub and Jones criteria are satisfied as concern all the tests for any value of flow rate.

Another region of time such that the criterion is satisfied occurs at longer duration: t > 50 min in the case of Q = 1 $cm^3.min^{-1}$; t > 20 min for T_w = 65 °C; and t > 14 min for Q = 0.5 $cm^3.min^{-1}$ and T_w = 70 °C. There, the rise of temperature is included between a minimum of about 5°C to a maximum of about 8 °C. The maximum temperature obtained is about 80 °C, as showed in Table 2. This value is not a critical value for the process. In the case with Q = 1 $cm^3.min^{-1}$, in addition to the behaviors described for the other cases, a sudden rise of temperature may be observed for 10 min < t < 30 min. In this region the criterion is clearly satisfied and it can be considered as a region of high hazard for thermal runaway. Indeed, due to an higher quantity of inlet flow rate, the higher heat of reaction induces a positive feedback on the reactor temperature, T, thus inducing the possible loss of control of the process.

6. Conclusions

The safety of the process of epoxidation of soybean oil with peroxy-acid in fed-batch reactor has been analysed starting from previous experimental results and adopting thermo-kinetic models developed by Santacesaria et al. (2011), by varying the flow rate of the mixture of hydrogen peroxide and formic acid in order to verify the effects on the yield in epoxide and, at the same time, on process temperature, T. The Hub and Jones criterion has been applied to verify the hazard of runaway reaction. Moreover, the effect of the temperature of the jacket, T_W, has been also analysed with the aims of further increase the yield in epoxide however in safety conditions. This study is a preliminary analysis on the safety of the epoxidation process. Further advances with the application of other criteria will be done in future works to develop some methods and strategies to permit that the epoxidation process may be carried out in safety conditions.

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