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Performance of Runaway Detection in a Batch Reactor using Thermal Runaway Criteria

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Thermal runaway is a serious problem in the chemical industry from a safety point of view. Among the measures that must be taken into consideration to avoid it, is the set of the optimal operating conditions. However, reactors are never safe from failure events despite the choice of optimal operating conditions. In the present work, the fault detection was studied and discussed by using two different thermal runaway criteria. The performances of detection when a faulty situation occurred, were compared using the chosen thermal runaway criteria. These faulty operations are the results of faults on the cooling system. The chosen reaction for this study is the perhydrolysis of formic acid to peroxyformic acid by hydrogen peroxide. The reaction was studied in a batch reactor under isoperibolic normal mode.

From the results obtained, the studied criteria can provide good prediction of unsafe operation of reactors when a fault on the operating parameters occurred. The performance of detection of thermal runaway situation differs between the criteria. However, the criteria can be used as helpful tools for online reactor operations.

1. Introduction

Thermal runaway is one of the biggest issues in chemical reaction engineering. Prevention, detection and control of that event is crucial in order to maintain safety operations in chemical industries. Thermal runaway has been identified for many years as the main cause of accidents in chemical industries. In China, the thermal runaway accidents have mainly occurred in organic and inorganic chemical industry (Zhang et al., 2021). Moreover, 25% of accidents that occurred in the French chemical industry were caused by thermal runaway (Dakkoune et al., 2019). Loss of temperature control is the main cause of thermal runaway (Casson et al., 2012), it mainly occurs during the operation of chemical reactors under exothermic reactions that release huge amount of heat, in which the cooling capacity of the reactor is lower than the heat generation rate of the reaction. Disastrous consequences can then be feared, the most dramatic example of which is certainly the Bhopal gas tragedy; this disaster resulted in the greatest loss of life and also property damage (Palazzi et al., 2015).

It seems obvious that such an event should be avoided. That is why, in the last decades, various methodologies have been developed to mitigate the consequences of accidents (Gygax, 1988) (Stoessel, 2009). One of those strategies, is the use of thermal runaway criteria in the design phase capable of predicting the thermal runaway in a system, therefore the safe and non-safe regions can be conducted for a specific initial and operating conditions of a chemical reaction process. They can be applied in order to specify the range of stability related to the operating conditions (Casson et al., 2012), but also for early warning detection in case of unexpected situations leading to a thermal runaway (Westerterp and Molga, 2006). Consequently, in the case of a faulty situation in the system, the monitoring is possible by alerting the user, which allows the early detection of the problem in order to avoid thermal runaway.

Thermal runaway has been studied extensively in recent years. In their review papier, (Kummer and Varga, 2021) present an excellent understanding of the thermal runaway. They discussed the possible cause and consequences of this phenomenon, the main runaway criteria in the literature and application examples of some criteria. In addition, many studies on thermal runaway in chemical reactors have been conducted (Zang et al., 2021); (Guo et al., 2016); (Westerterp et al., 2014); (Casson et al., 2012).

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A general criterion based on the calculation of the divergence was established and applied in a series of papers (J. M. Zaldívar et al., 2003); (Zaldívar et al., 2005); (Bosch et al., 2004). The criteria states that the reactor operates safely when the divergence of a function that describes the reacting system is positive on a segment of reaction path. Based on the divergence criterion of Strozzi and Zaldivar, (Guo et al., 2016) developed a new criterion to distinguish between runaway and non-runaway situations and determine the acceptable accumulation for the case of reactions carried out in semi-batch reactors. Numerous papers have been written about the concept of safety boundary diagram for reactions carried out in semi-batch and batch reactors (Westerterp et al., 2014); (Westerterp and Molga, 2004); (Molga et al., 2007). According to this concept, the runaway and non-runaway areas can be easily illustrated. Moreover, the diagram presents a rapid procedure to predict the inherently safe operating conditions (Molga et al., 2007). There are some several studies that aim to compare runaway criteria (Casson et al., 2012); (Ampelli and Maschio, 2012). However, (Casson et al., 2012) applied some thermal runaway criteria in a batch isoperibolic operating mode for the detection of runaway and to distinguish between safe operating conditions. Then a comparison of the criteria was made based on the experimental and simulated data. In a study of (Ampelli and Maschio, 2012), an investigation of thermal runaway in semibatch reactor using the divergence criterion was conducted when failures or malfunctions occur.

The aim of the present paper is to study the detection of thermal runaway for a reacting system under batch operating mode by applying two of the thermal runaway criteria reported in the literature. The goal is to use these criteria for the detection of thermal runaway situations in the case of errors that may occur in the cooling system. These criteria should also allow an on-line detection with corrective actions in a sufficiently short time.

2. Reaction model

The reaction of perhydrolysis of formic acid to peroxyformic acid by hydrogen peroxide was chosen as a test for safety studies under isoperiodic mode in a batch reactor. The reaction is illustrated in Eq (1) and the kinetic expression of the formation of the peroxyformic acid was determined by (Zheng et al., 2016) in Eq (2).

The main reaction is characterized by the presence of two parallel secondary reactions of decomposition of formed peroxyformic acid according to Eq (3) and Eq (4). The first decomposition leads to the formation of carbon dioxide and water, regarding the second decomposition it forms the formic acid and oxygen. The kinetics of decompositions are illustrated in Eq (5) and Eq (6).

$$HCOOH + H_2O_2 \rightleftharpoons HCOOOH + H_2O \tag{1}$$

$$R_{r,perh} = k_{0,perh}\, exp\left(\frac{-E_{a,perh}}{R}\left(\frac{1}{T_r} - \frac{1}{T_{ref}}\right)\right)\sqrt{K_{FAD}^{C}\frac{[HCOOH]}{[H_2O]}}\left([HCOOH][H_2O_2] - \frac{1}{K^C}[HCOOOH][H_2O]\right) \tag{2}$$

$$HCOOOH \longrightarrow CO_2 + H_2O \tag{3}$$

$$HCOOOH \longrightarrow HCOOH + \frac{1}{2}O_2 \tag{4}$$

$$R_{r,decomp1} = k_{0,decomp1} \exp\left(\frac{-E_{a,decomp1}}{R}\left(\frac{1}{T_r} - \frac{1}{T_{ref}}\right)\right)[HCOOOH]) \tag{5}$$

$$R_{r,decomp2} = k_{0,decomp2} \exp\left(\frac{-E_{a,decomp2}}{R}\left(\frac{1}{T_r} - \frac{1}{T_{ref}}\right)\right)[HCOOOH]) \tag{6}$$

Where $k_{0,y}$ and $E_{a,y}$ are respectively the pre-exponential factor and the activation energy of the reaction y for y ϵ {perh, decomp1, decomp2}. T_r is the reaction temperature. $T_{ref} = 67\ °C$. $\mathrm{K}_{\mathrm{FAD}}^{\mathrm{C}}$ is the parameter of association of the formic acid. K^{C} is the equilibrium parameter of the reaction of perhydrolysis. The kinetic parameters and thermodynamic constants of the two reactions of decomposition are listed in Table 1.

Under the influence of temperature, hydrogen peroxide can decompose spontaneously or due to the presence of catalyst. In the present work, only the spontaneous mechanism has been considered. The kinetic equation was determined by (Vernières-Hassimi et al., 2017). The rate of the reaction can be expressed as follow:

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2 \tag{7}$$

$$R_{r,spont} = k_{0,spont} \exp\left(\frac{-E_{a,spont}}{R}\left(\frac{1}{T_r} - \frac{1}{T_{ref}}\right)\right)[H_2O_2] \tag{8}$$

Where $k_{0,spont}$ and $-E_{a,spont}$ are respectively the pre-exponential factor and the activation energy for the spontaneous decomposition of hydrogen peroxide.

Table 1: Kinetic and thermodynamic parameters for Eq(2), Eq(5) and Eq(6) (Zheng et al., 2016) for $T_{ref} = 67\ °C$, and for Eq(8) for $T_{ref} = 140\ °C$ (Vernières-Hassimi et al., 2017).

Symbol parameter	Value	Unit	Symbol parameter	Value	Unit
$k_{0,perh}$	0.15	$L.mol^{-1}.s^{-1}$	$k_{0,decomp2}$	0.0009	s^{-1}
$E_{a,perh}$	150,000	$J.mol^{-1}$	$E_{a,decomp2}$	20,200	$J.mol^{-1}$
$\Delta H_{r,perh}$	-5,580	$J.mol^{-1}$	$\Delta H_{r,decomp2}$	-163,000	$J.mol^{-1}$
$k_{0,decomp1}$	0.001	s^{-1}	$k_{0,spont}$	0.0000924	s^{-1}
$E_{a,decomp1}$	20,000	$J.mol^{-1}$	$E_{a,spont}$	150,000	$J.mol^{-1}$
$\Delta H_{r,decomp1}$	-359,000	$J.mol^{-1}$	$\Delta H_{r,spont}$	95,000	$J.mol^{-1}$

The ordinary differential equations describing the mass and heat balances in a batch reactor can be written according to Eq(9), Eq(10), Eq(11), Eq(12) and Eq(13). These equations were numerically solved using a Runge-Kutta integration method.

$$\frac{dC_{HCOOH}}{dt} = -R_{r,perh} + R_{r,decom2} \tag{9}$$

$$\frac{dC_{HCOOOH}}{dt} = R_{r,perh} - R_{r,decom1} - R_{r,decom2} \tag{10}$$

$$\frac{dC_{H_2O_2}}{dt} = -R_{r,perh} - R_{r,spont} \tag{11}$$

$$\frac{dC_{H_2O}}{dt} = R_{r,perh} + R_{r,decom1} + R_{r,spont} \tag{12}$$

$$\rho V_R C_{P,R} \frac{dT_r}{dt} = \sum R_{r,y}(-\Delta H_y)\, V_R - UA\,(T_r - T_j) \tag{13}$$

Where ρ, V_R and $C_{P,R}$ are respectively the mass density, the volume and heat capacity of the reaction mixture. $R_{r,y}$ and ΔH_y are respectively the rate and the enthalpy of the reaction y. U is the overall heat transfer coefficient. T_j is the temperature of the cooling fluid. The model was validated experimentally by our team *(Dakkoune et al., 2020)*. Figure 1 represents the simulated and experimental measurement of the reactor temperature for the reaction of $2.8\ mol.L^{-1}$ of H_2O_2 and $2.5\ mol.L^{-1}$ of $HCOOH$ with a total volume of 1.2 L carried out in an isoperibolic mode where the initial temperature of the reactor and the jacket temperature were fixed at 70 °C.

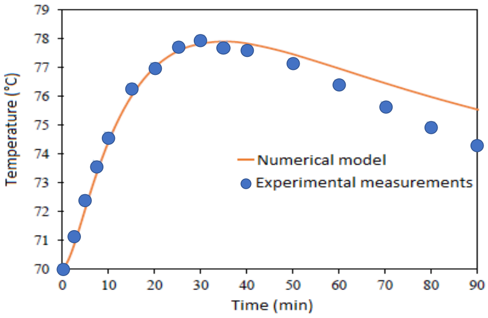

Figure 1: Simulation and experimental measurement of the reactor temperature in normal isoperibolic bacth mode with $[H_2O_2]_0 = 2.8\ mol.L^{-1}$, $[HCOOH]_0 = 2.5\ mol.L^{-1}$, $T_{r0} = T_j = 70\ °C$, $V_R = 1.2\ L$

3. Thermal runaway criteria

Strozzi and Zaldivar (J.M. Zaldívar et al., 2003) developed a general criterion to define the thermal runaway and the boundaries between the runaway and non-runaway situations for different types of reactors. This criterion states that the process operates in runaway condition when the divergence derived from the differential equations that describe the thermal behaviour of the process, is positive on a segment of the reaction path.

The divergence criterion can be applied without a knowledge of the differential equations of the system, using only the temperature or pressure measurement (Bosch et al., 2004). The divergence can be calculated by applying state space reconstruction techniques using the theory of embedding (Zaldívar et al., 2005). Then to determine the divergence, is equivalent to check ΔV_{ps} which can be expressed as follows (Zaldívar et al., 2005):

$$\Delta V_{ps} = \frac{V_{ps}(t) - V_{ps}(t - \Delta t_1)}{\Delta t_2} \tag{14}$$

Where Δt_1 is the time between two volumes calculation. Δt_2 is the time between two state variable points, in this case it is the time between two temperature measurements.

Thomas and Bowes criterion indicated that the reactor is under runaway situation when an inflexion point in the temperature vs time plan, appears before the maximum temperature. The situation of safe operating can be expressed if the following statements are true (Thomas and Bowes, 1961) (Varma et al., 1999):

$$\frac{d^2T}{dt^2} < 0 \; while \; \frac{dT}{dt} > 0 \tag{15}$$

4. Results and discussion

In order to apply the thermal runaway criteria for the early detection, the reaction model previously presented was used to simulate the system when faulty situations occur. Those faults refer to failures of the cooling system which have a direct effect on the thermal behaviour of the reactor. A few case studies were chosen and the results are presented in Table 2. This table represents the results obtained using both criteria for the detection of thermal runaway. A third order Golay-Savitzky filter has been used to reduce the noise of the temperature derivatives for the application of the Thomas and Bowes criterion.

Table 2 includes the time of failure that corresponds to the cooling system error, which in this study was fixed to 2000 seconds after the reacting system first operates. The detection time (expressed in time unit), represents the date in which the alarm is triggered. It gives an idea of the detection delay, i.e. the time between the occurrence of a faulty situation in the cooling system and the date of the alarm.

As can be seen, runaway situation was detected for the studied cases after the cooling system failure occurred. Figure 2 shows the results of the simulated temperatures and the criteria application for the first case study of Table 2. At the beginning of the reaction, the temperature profile follows the Arrhenius law similarly to the normal temperature profile illustrated in Figure 1. Whereas a failure in the cooling system appears at 2000 seconds from the launch of the reaction. That event will change the shape of the temperature profile as shown in Figure 2a, and the cooling temperature increases in a linear way from 70 °C to 76°C with a rate of 1°C/ 20 s. Using the divergence criterion, the thermal runaway is detected 51 seconds after the fault has occurred. This situation is detected when the first value of ΔV_{ps} has become positive with time as shown in Figure 2b. Using the Thomas and Bowes criterion, the first and the second derivatives of the reactor temperatures become positive as shown in Figure 2c and Figure 2d, this situation corresponds to thermal runaway. As it can be seen in Figure 2d an inflexion point appears in the temperature profile before the temperature maximum. It was detected 24 seconds after, which is relatively earlier than the divergence criterion.

It should be mentioned that the first and second derivatives of temperature in the beginning of the reaction are positive, this situation can be explained due to the fact that the reaction is activated slowly which leads to a convex form of its temperature profile. In this case, the Thomas and Bowes criterion generates a false alarm about thermal runaway, since at the beginning of the reaction, no fault was simulated and the temperature profile (Figure 2a) follows the normal profile illustrated in Figure 1.

The same conditions were maintained for case study 2 with a difference in the rate of temperature rise of 1°C/ 30 s, which means that the temperature will take longer time from the onset of the failure to stabilize at a final value. In this case, the fault was detected using both of the criteria with an advance time for Thomas and Bowes.

For case studies 3, 4, 5 and 6 an analysis of the effect of the cooling temperature rate on fault detection was conducted. The final cooling temperature was fixed to a value of 78° C with a linear increase rate that varies from 1°C/ 20 s to 1°C/ 50 s, respectively. As the temperature increases slowly, the detection time becomes more important for the divergence criteria.

Table 2: Summary of detection times(s) using thermal runaway criteria for different cooling failures

Case study	Final Cooling temperature	Rate of temperature rise	Time of failure (s)	Detection time (s) (Divergence criterion)	Detection time (s) (Thomas and Bowes)
1	76	1°C/ 20 s	2000	2051	2024
2	76	1°C/ 30 s	2000	2054	2021
3	78	1°C/ 20 s	2000	2065	2049
4	78	1°C/ 30 s	2000	2055	2023
5	78	1°C/ 40 s	2000	2078	2054
6	78	1°C/ 50 s	2000	2084	2056

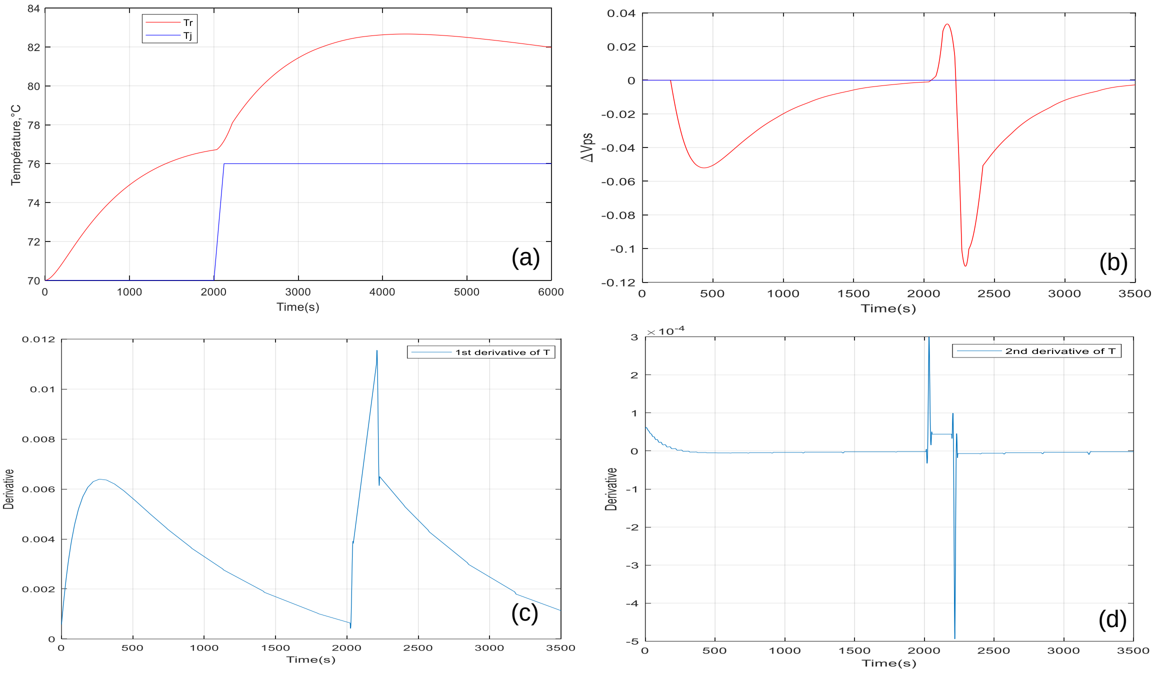

Figure 2: Simulated results for case study 1. (a) Simulated temperatures of the reactor and the cooling system. (b) ΔV_{ps} for divergence application using temperature measurements inside the reactor. (c-d) first and second derivatives of the reactor temperature, respectively for Thomas and Bowes criterion.

5. Conclusions

In this paper, simulation studies were carried out for the detection of thermal runaway. These studies were based on the application of runaway criteria and were conducted on an exothermic reaction in a batch isoperibolic operating mode. The applied criteria allow an early and on-line detection of faults with an average delay of 38 seconds after fault occurrence for the Thomas and Bowes criterion given by Eq(15), and an average delay of 65 seconds in the case of divergence. These results show a good detection of faults that may lead the system to be corrected before reaching the maximum temperatures. Furthermore, the advantage of using these criteria is that they can be used directly without knowledge of the reaction model.

The detection time presented earlier in the results section refers to a low noise level, but in many cases this level can be higher. The main disadvantage of using the Thomas & Bowes criterion given by Eq(15) is that the temperature derivatives increase the noise level of the measurements, and this level increases further when calculating the second derivatives. Thus, the results provided by this criterion are strongly affected by the derivatives errors. To overcome this problem, the signal can be filtered, but the more the signal is filtered, the longer the detection time. However, the divergence criterion does not have this disadvantage. For this reason, it can be used as a better criterion for online detection of system faults.

Nomenclature

A – heat transfer area, m^2
$C_{P,R}$ – specific heat capacity of the reaction, J.kg^{-1}.K^{-1}
$E_{a,y}$ – activation energy of the reaction y, J.mol^{-1}
$k_{0,y}$ – rate constant of reaction y, s^{-1}
K^C – equilibrium parameter, -
K^C_{FAD} – association parameter of formic acid
R – gas constant, J.mol^{-1}.K^{-1}
$R_{r,y}$ – rate of reaction y, mol.L^{-1}.s^{-1}
T – temperature, K
t – time, s
T_j – jacket temperature, K
T_r – reaction temperature, K
T_{r0} – initial reaction temperature, K
T_{ref} – reference temperature, K
U – overall heat transfer coefficient, W.m^{-2}.K^{-1}
V_{ps} – phase space volume, -
V_R – volume of reaction, L
y – reaction: perhydrolysis of formic acid (perh), first decomposition of peroxyformic acid (decom1), second decomposition of peroxyformic acid (decom2) and spontaneous decomposition of hydrogen peroxide (spont)
ρ – mass density, kg.L^{-1}
ΔH_y – enthalpy of reaction y, J.mol^{-1}
Δt_1 – time delay, s
Δt_2 – time step, s
ΔV_{ps} – state space volume variation, -
$[\,]_0$ – initial concentration, mol.L^{-1}

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