



Fault Detection in the Green Chemical Process: Application to an Exothermic Reaction

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The chemical industry's activities are often controversial due to the high risks that they represent. Over the past decades, serious industrial events affecting lives, facilities and environment have heightened society's awareness of the negative effects of technology. Among the most hateful events in the chemical industries are the phenomena of thermal runaway that often result in operator errors. Predicting and controlling them is essential to the processes design and safe operation. The objective of this work is to develop a method for early detection of malfunctions in a chemical reactor based on a reference model, before resulting in a critical event. For this, the reaction of perhydrolysis of formic acid to peroxyformic acid by hydrogen peroxide is used as a test case to simulate the reaction in abnormal operating mode. This exothermic reaction is composed of several secondary decomposition steps. The kinetic model of the reaction was determined in order to simulate the reaction in an abnormal mode with defects related to operator error. The detection method has been validated by simulation data. A performance analysis of the proposed detection method was carried out showing the robustness and the efficiency of this method, in presence of various errors due to the operator. The proposed method can contribute to the safety of chemical reactors in the chemical industry.

1. Introduction

Since the industrial revolution especially in chemical engineering, a large number of the accidental events around the whole world have occurred leaving behind them so many deaths, injuries, disabled people and environmental damages. Several scientific studies have been done on the problem of accidents in the chemical industries, wanting to understand the reasons that lead to these events and trying to find relevant solutions to reduce this great risk. Balasubramanian and Louvar (2002) have revealed that 26% of the major petrochemical plant accidents are due to thermal runaway. Dakkoun et al. (2018) found that 25% of events in the chemical industry in France are due to thermal runaway. This dangerous phenomenon is often encountered in the chemical industry whose consequences remain harmful and still responsible for many accidents in the world. This critical scenario is becoming a serious problem in the chemical industry (Jiang et al., 2016a). In particular, thermal runaway can result in an explosion, a high gas and / or vapor emission that can be flammable and / or toxic. The outbreak of the reactor and the explosive combustion of the emitted gases may lead to the destruction of buildings and the formation of secondary fires, which can aggravate the overall consequences by domino effect (Hemmatian et al., 2014). From a chemical engineering viewpoint, thermal runaway occurs when the heat-flow rate released by the reactions becomes higher than the one exchanged with the surroundings. Hence, the thermal accumulation increases and the reaction temperature keeps rising, which speeds up the heat-flow rate released (Jiang et al., 2016b). The catastrophic accidents in Seveso (1976) and Bhopal (1984) are also due to thermal runaways. This phenomena often results from operator errors that could occur if the system is poorly controlled. This result is corroborated by Dakkoun et al.(2018) for a study done on the causes of runaway accidents in France and for the same study done by Saada et al. (2015) in United Kingdom. These errors can be due to a lack situation awareness (Nazir et al.,2012). A minor error between humans or between humans and machines increases the risk, which can lead to an event (Nazir et al.,2013). Preventing the accidents is an important challenge. System monitoring is

one possible effective solution. The purpose of monitoring is to alert and inform the user of the appearance of faults so that they can react as quickly as possible. For this reason, this work focuses on the first phase of monitoring which is the detection of defects in chemical reactors. In the literature, several studies have focused on the development of methods for early detection of runaway reactions in batch and semibatch reactors. These methods are based either on a model of the reaction kinetics (Pierrri et al., 2008) and on estimation techniques (Benkouider et al., 2009) or on artificial intelligence like Principal Component Analysis (Choi et al., 2005) and Neural Networks (Zhang, 2008). In this context, a detection method based on the kinetic reaction model using a dynamic detection threshold is proposed in this paper. The practical case of perhydrolysis of formic acid by hydrogen peroxide is considered to validate the method using different performance criteria. This paper is organized as following. Section 2 is about the presentation of the problem statement, the explanation of the reaction and the considered defects. Section 3 describes the method of detection used in this work. Section 4 is devoted to the evaluation of the performance of this method based on the simulations carried out. Finally, the conclusions are given in Section 5.

2. Problem statement

2.1 Reaction model

In this paper, an exothermic reaction in a batch reactor under isoperibolic mode has been study. It is the reaction of perhydrolysis of formic acid by hydrogen peroxide (Eq 1). The normal operating conditions of this reaction are given in Table 1 and a numerical model of the temperature variations is reported in Figure 1. The product of the reaction which is peroxyformic acid is widely used in green chemical industry as intermediates for the production of epoxidized vegetable oils (Leveneur et al., 2012).



The kinetic expression of this reaction is determined by Zheng et al. (2016).

$$R_{\text{perh}} = K_{\text{perh}} \sqrt{K_{\text{FAD}}^C \frac{\text{HCOOH}}{\text{H}_2\text{O}}} \left([\text{HCOOH}] [\text{H}_2\text{O}_2] - \frac{1}{K^C} [\text{HCOOOH}] [\text{H}_2\text{O}] \right) \quad (2)$$

where K_{FAD}^C is the parameter of association of the formic acid and K^C the equilibrium parameter of the perhydrolysis reaction and [...] represents the concentration of the chemical compound in mol/l. k_{perh} is the reaction rate constant for the reaction of perhydrolysis determined by modified Arrhenius equation for

$$T_{\text{ref}}=67 \text{ }^\circ\text{C} \text{ as follows: } k_{\text{perh}} = k_0 e^{\left(\frac{-E_a}{R} \left(\frac{1}{T_R} - \frac{1}{T_{\text{ref}}} \right) \right)} \quad (3)$$

The kinetic parameters and thermodynamic constant given by: $k_0=0.15 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $E_a=150000 \text{ J/mol}$ and $\Delta H_R=-5580 \text{ J/mol}$.

The corresponding reaction presents a several secondary decomposition reactions (Eq 4 and Eq 6) allowed to increase the heat of the reaction that is clearly visible when the normal operating conditions of the reaction are exceeded. The presence of hydrogen peroxide as a reagent in the reaction increases its level of risk, because The decomposition of hydrogen peroxide (Eq 4) can occur in the presence of some metals (at the ppm level) or when the reaction is beyond normal operation, which can lead to thermal runaway accidents (Fauske Hans K., 2006).



The kinetic expression of this reaction is $R_{\text{dec},1} = k_{\text{dec},1} [\text{HCOOOH}]$ (5)

where $k_{\text{dec},1}$ is the reaction rate constant for the first reaction of decomposition of peroxyformic acid determined by modified Arrhenius equation with $k_0=0.00121 \text{ s}^{-1}$, $E_a=80500 \text{ J/mol}$ and $\Delta H_R=-230000 \text{ J/mol}$.



The kinetic expression of this reaction is $R_{\text{dec},2} = k_{\text{dec},2} [\text{HCOOOH}]$ (7)

where $k_{\text{dec},2}$ is the reaction rate constant for the second reaction of decomposition of peroxyformic acid determined by modified Arrhenius equation with $k_0=0.0001 \text{ s}^{-1}$, $E_a=80200 \text{ J/mol}$ and $\Delta H_R=-153000 \text{ J/mol}$.



The kinetic equation of the hydrogen peroxide is determined by Vernières-Hassimi et al. (2017). The kinetic expression of this reaction and Arrhenius parameters are detailed for the following cases.

$$1) \text{ In the case of spontaneous decomposition: } R_{\text{spontaneous}} = k_{\text{spont}} [\text{H}_2\text{O}_2] \quad (9)$$

where k_{spont} is the reaction rate constant for the spontaneous decomposition of hydrogen peroxide determined by modified Arrhenius equation with $k_0=0.0000924 \text{ s}^{-1}$, $E_a=150000 \text{ J/mol}$ and $\Delta H_R=-95000 \text{ J/mol}$.

$$2) \text{ In the case of decomposition by copper sulfate: } R_{\text{dec},3} = R_{\text{spontaneous}} + R_{\text{catalyzed by Cu}} \text{ with}$$

$$R_{\text{Catalyzed by Cu(II)}} = 2 * k_A * \frac{[\text{Cu}^{2+}][\text{H}_2\text{O}_2]^2}{[\text{H}_3\text{O}^+]} + 2 * k_B * \frac{[\text{Cu}^{2+}]^2 \cdot [\text{H}_2\text{O}_2]}{[\text{H}_3\text{O}^+]^{1/2}} \quad (10)$$

where k_A and k_B are the reaction rate parameters for the reaction of decomposition of hydrogen peroxide catalyzed by copper sulfate. These parameters are determined by modified Arrhenius equation with $k_{0A}=0.0163 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$, $k_{0B}=0.0035 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$, $E_{aA}=162000 \text{ J/mol}$, $E_{aB}=69700 \text{ J/mol}$, and $\Delta H_R=-93200 \text{ J/mol}$.

After

establishing the material balance for a batch reactor, the differential equations for these reactions are:

$$\frac{dC_{\text{HCOOH}}}{dt} = -R_{\text{perh}} + R_{\text{dec},2}; \quad \frac{dC_{\text{HCOOOH}}}{dt} = R_{\text{perh}} - R_{\text{dec},2} - R_{\text{dec},1}; \quad \frac{dC_{\text{H}_2\text{O}_2}}{dt} = -R_{\text{perh}} - R_{\text{dec},3}; \quad \frac{dC_{\text{H}_2\text{O}}}{dt} = R_{\text{perh}} + R_{\text{dec},1} + R_{\text{dec},3} \quad (11)$$

The energy balance in the batch reactor is expressed by the thermal accumulation in the reactor, which is equal to the Reactions Heat-Flow Rate and the Heat Exchange to the Heat Carrier. The differential equation is given by:

$$\sum m_R C_{PR} \frac{dT_R}{dt} = UA (T_j - T_{\text{Reaction}}) + q_{rx} \quad \text{with} \quad q_{rx} = -\sum R_{\text{Reaction}} \cdot V_R \cdot \Delta H_{\text{Reaction}} \quad (12)$$

where m_R and C_{PR} are respectively the initial mass and reaction heat capacity of the reaction mixture, U is the overall heat-transfer coefficient, A is the heat transfer area and T_j is heat carrier temperature circulating in the reactor jacket.

2.2 Defects

When the reaction occurs in an abnormal mode, it is characterized by the occurrence of one fault affecting the parameters of normal operating conditions. The dysfunctional scenarios selected in this study are based on the operator's errors according to the studies carried out in this field (Dakkoune et al., 2018). This is the most common cause in the chemical industry and may lead to thermal runaway scenarios. The operator errors considered in this study are:

Fault 1: errors in the initial charge, i.e. the initial concentrations of reagents (hydrogen peroxide and formic acid) rather 0.3 mol / l.

Fault 2: presence of small amounts of impurities (metals such as copper sulfate) due to insufficient cleaning of the reactor for example.

Table 1: Normal operating conditions

Parameters of system	Values
Sample volume	1.2 L
Initial concentration of formic acid FA	2.5 mol/l
Initial concentration of hydrogen peroxide HP	3 mol/l
Jacket temperature	70°C
Initial temperature of reaction T_r	70°C
Initial concentration of copper sulfate (impurity) Cu	0 mol/l

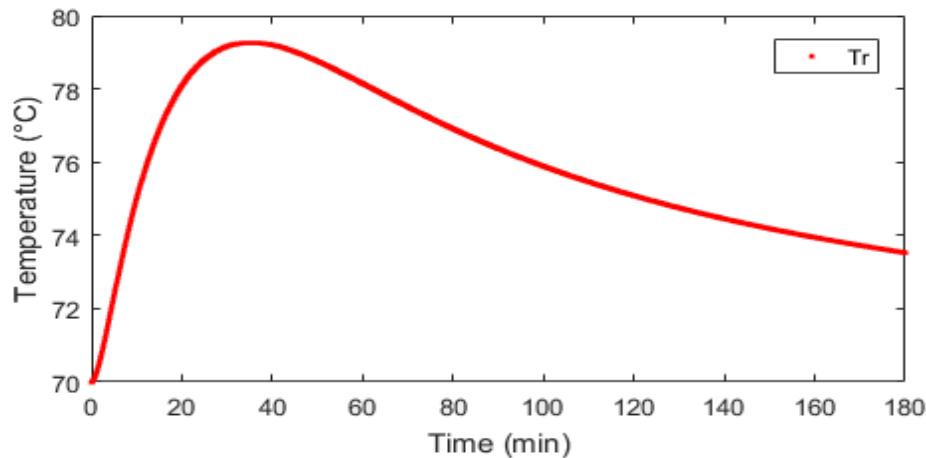


Figure 1: Simulated mixture temperature (T_r) during the perodrolysis of acid formic.

3. Detection method

The detection method is based on the computation and use of a dynamic threshold. This threshold is computed according to the two following principles.

- 1) The change in the initial concentration of the reagents (FA and HP) as well as the presence of an impurity (Cu) in small quantity can cause a rise in the maximum temperature of the reaction above 80 °C. The behavior is considered as a faulty one if this maximal temperature reaches 80 °C.
- 2) A marge of tolerance M_T is considered in order to avoid false alarms (in particular during the first minute of the reaction during which the faulty and normal behaviors are very similar).

Consequently the detection threshold $DT(t)$ given in (Eq 13) defines a dynamic tolerance range:

$$D_{LIMIT}(t) = \max [\min [T_{FA}(t), T_{HP}(t), T_{Cu}(t)], T_{Nominal}(t) + M_T] \quad \text{with :} \quad (13)$$

- $T_{Nominal}(t)$: temperature variation of the reaction for the nominal conditions.
- $T_{FA}(t)$: temperature variation of the reaction that does not exceed 80 °C for the maximal acceptable concentration of FA that equals 2.66 mol.l⁻¹.
- $T_{HP}(t)$: temperature variation of the reaction that does not exceed 80 °C for the maximal acceptable HP concentration that equals 3.22 mol.l⁻¹.
- $T_{Cu}(t)$: temperature variation of the reaction that does not exceed 80 °C for the maximal acceptable Cu concentration that equals 0.013 mol.l⁻¹.

The definition of $D_{LIMIT}(t)$ aims to avoid non detections and false alarms. The use of the “min” operator in (Eq 5) reduces the rate of non-detections: the dynamic tolerance range is constrained at each point t by the minimal value $T_{FA}(t)$, $T_{HP}(t)$, or $T_{Cu}(t)$. On the other hand, the use of the “max” operator with the nominal temperature $T_{Nominal}(t)$ plus the maximum noise (0.1 °C) reduces the rate of false alarms. Note that this condition delays the detection. Figures 2 illustrates $D_{LIMIT}(t)$ and $T_{Nominal}(t)$.

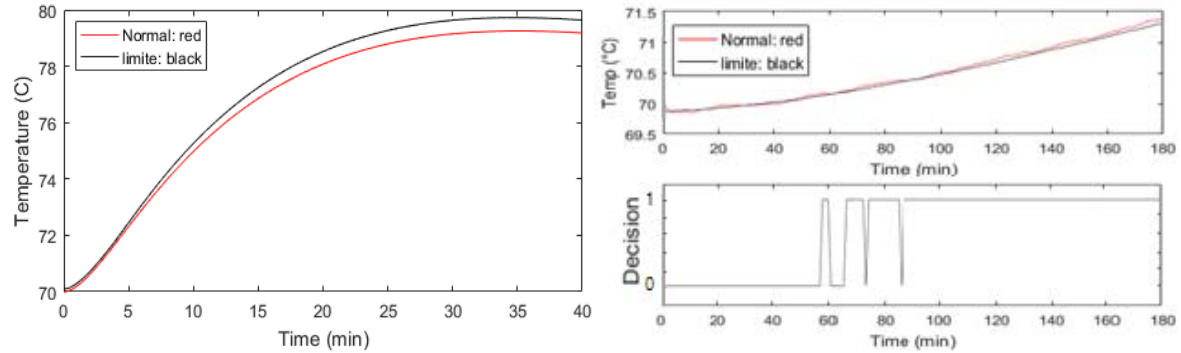


Figure 2: $D_{LIMIT}(t)$ compared to $T_{Nominal}(t)$ (in left) and fault detection and decision (in right).

The detection is performed by comparing the measured temperature with the dynamic threshold. Note that because of the noise, the measured temperature T is filtered using a N -points average filter $f(T)$.

The decision function $D(t)$ is defined such that (Figure 2): $D(t) = 1$ if $f(T(t)) > D_{LIMIT}(t)$ or $D(t) = 0$, otherwise.

A fault is finally detected at date t if $D(k) = 1$ for n successive points $k \in \{t-n+1, \dots, t-1, t\}$.

4. Results and discussion

In order to evaluate the performance of the proposed detection method and to ensure that the system is well monitored, a set of 100 simulations with random conditions including faults were carried out. An uniform bounded noise of ± 0.1 °C is also considered. This level of precision is achieved with temperature sensors such as the Pt100 sensors used with calorimetric reactor. Such sensors have better accuracy than the ones used with industrial plants. An average filter with $N = 10$ points of measurement is used. By varying the margin of tolerance M_T (M_T varies within $[0 : 0.2]$) as well as the number of consecutive measurement points n such that $D(t) = 1$ (n varies within $[0 : 20]$). The performance of this detection method will be evaluated by calculating three main features:

The non-detection rate (R_{ND} expressed as a percentage) is the ratio between the number of undetected defects and the number of defects experienced by the system (Figure 4).

The false alarm rate (R_{FA} expressed as a percentage) is the ratio between the number of nuisance detections and the number of alarms (Figure 4).

The average delay to detection (ADD expressed in time units) is the time between the occurrence of a fault and the date of the alarm. This parameter gives an indication of the speed of detection (Figures 3 and 4).

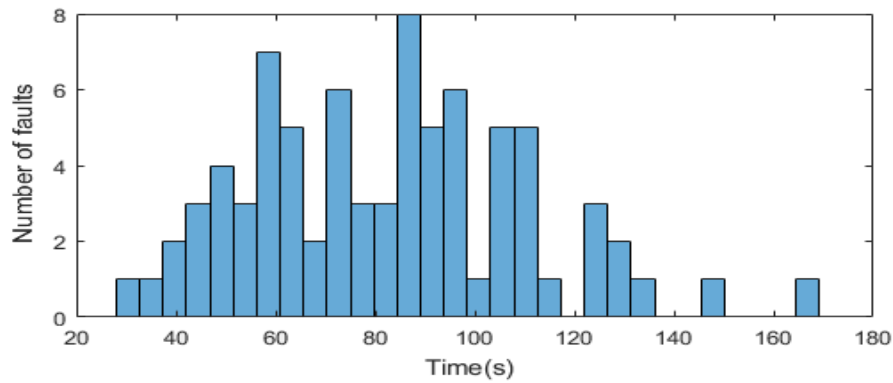


Figure 3: Histogram of the detection delay for $M_T=0.1$ and $n=5$.

The performance of the detection method depends on two important parameters: The margin of tolerance M_T and the number of consecutive measurement points n when the detection is validated have both a big influence on the characteristics of the detection as shown in the following figures.

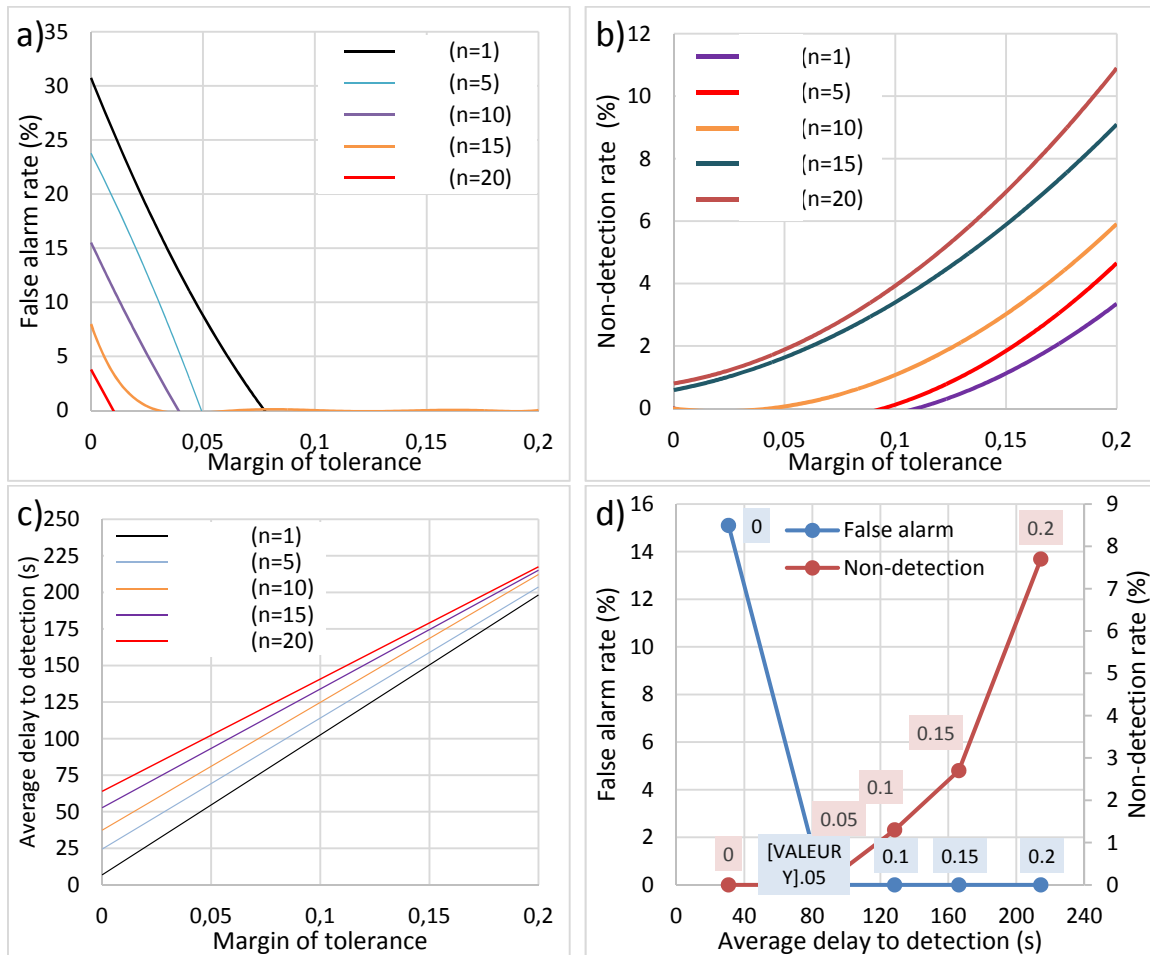


Figure 4: Influence of the M_T and n indicators on R_{FA} (a), Influence of the M_T and n indicators on R_{ND} (b), Influence of the M_T and n indicators on ADD (c), Influence of M_T in R_{FA} , R_{ND} and ADD when $n=10$ (d).

Figure 4 shows the influence of the margin of tolerance index and the number of consecutive measurement points on false alarm rates (Figure 4-a), non-detection rates (Figure 4-b) and on average delay to detection (Figure 4-c). From these 3 figures, we notice that when the tolerance margin increases, R_{FA} decreases progressively. On the contrary, R_{ND} increases as well as the average delay of the detection. The same is observed when n increases, R_{FA} decreases and R_{ND} increases. Figure 4-d, gathers together the 3 performance parameters (R_{ND} , R_{FA} and ADD) for different values of M_T when $n = 10$ which seems to be a

suitable value (Figure 4-a, b, c). According to this figure, it seems that to have small values of R_{ND} and R_{FA} , with a reasonable value of ADD, it is necessary to choose $M_T = 0.05$. This value of M_T give the best compromise in order to reduce strongly the false alarm rate without significantly degrading the non-detection rate and remaining within an acceptable average detection delay of 86 seconds.

From the results found, it is clear that the parameters M_T and n have a major influence on the performance of the detection, hence the need to make an early detection according to the desired priority goals and to focus on another tool that can improve the fault detection performances.

5. Conclusions

In this paper, a fault detection method based on reference a model was designed and applied to a batch reactor. The proposed method requires the kinetic model of the reaction. The detection method provides good results for numerous simulations and it allows early detection of the defect with an average delay of 86 seconds, if we take into account that the reaction reaches its maximum temperature after 30 min. Then, the time to react and control the system is sufficient for the operator to react quickly in a correct way, by injecting the solvent into the reactor or by increasing the temperature of the reactor cooling for example. The future work is to confirm the proposed method by experimental tests and to continue the study by developing a fault isolation method.

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