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# Using Dynamic Simulation for Risk Assessment: Application to an Exothermic Reaction

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## Abstract

Evaluation of industrial risks is essential to safely drive and perform chemical processes. The well-known HAZOP (HAZard and OPerability) analysis is largely applied to identify major accidental scenarios. However, the quantification of process deviation effects, useful for appropriate decision making, is a real challenge. In this paper, HAZOP method is combined with a dynamic simulation tool (Aspen Dynamics) to determine consequences of the deviations from normal operating conditions that may lead to severe accidents. Moreover, it will permit to test process design modifications to improve the safety level. A process involving an exothermic reaction (oxidation of sodium thiosulphate by hydrogen peroxide) conducted in a semi-batch reactor, likely to lead to a runaway scenario, is used to demonstrate the advantages of the proposed procedure.

**Keywords**: Process safety, Dynamic simulation, Risk assessment, HAZOP method, Runaway scenario.

## 1. Introduction

The risk assessment is a major requirement in the industrial context. Risk identification is essential for ensuring safe design and operation of a process. Several techniques are available to analyse hazardous situations (Marhavilas et al., 2011). Among them, the HAZard and OPerability study (HAZOP) is a well-known technique largely applied (IEC 61882, 2001). Initially, HAZOP method was a qualitative one. However, risk quantification is of high importance for appropriate decision making. The determination of the effects of failure scenarios is a real challenge (Baybutt, 2015).

Dynamic simulation tools (such as Aspen Dynamics, UniSim Design, ProSim Batch) are useful for predicting the process behaviour (Luyben, 2012). Many simulations of industrial process plants can be found in the literature (Lou et al., 2006; Luyben, 2002, 2012). Combining HAZOP with dynamic simulation can provide the means to investigate and evaluate the scenario consequences (Eizenberg et al., 2006a, 2006b). Nowadays, the challenge is to simulate the process degraded modes and especially the propagation of the deviations along the process line. As a matter of fact, the dynamic simulation of the whole plant is difficult and time-consuming. However, we suggest applying this methodology to process sections, where safety problems can occur. It will provide dynamic and quantitative data, essential to insure the process safety.

The aim of this study is to develop a quantitative methodology by combining HAZOP with dynamic simulation in order to perform a detailed safety analysis. In the first part, the methodology is summarized. Then, the case study is presented. The simulated scenarios, previously put in evidence by the HAZOP method, concern complete loss of cooling in batch and semi-batch modes.

## 2. Methodology

Part of HAZOP procedure is to study the consequences of process deviations. For complex and nonlinear systems, it is not straightforward to assess the effects of deviations (Eizenberg et al., 2006a, 2006b). The interest of dynamic simulation is to provide the dynamic evolution of process variables and to quantify the effects of faults. The purpose is to evaluate the consequences of operational disturbances on the plant safety. Thanks to this information, ways to reduce the risks can be proposed.

Our methodology includes the following steps. First, the steady state mode of the process is simulated under normal operating conditions. Next, the dynamic model in normal mode is built by adding process controllers. Aspen Plus (dedicated to steady state simulation) and Aspen Dynamics are chosen. Then, the study of process deviations, put in evidence by HAZOP method, is investigated. The time evolution of critical parameters allows the knowledge of the system response (dynamics and magnitude). These results are essential for the choice of safety measures. It permits the definition of preventive or protective required devices. This methodology is illustrated in the following case study.

## 3. Case Study

The chosen reaction is the oxidation of sodium thiosulphate, $Na_2S_2O_3$, by hydrogen peroxide, $H_2O_2$, (Chetouani, 2004). It has been particularly studied in safety analysis (Chetouani et al., 2003; Benaissa et al., 2008; Benkouider et al., 2012). The stoichiometric scheme is:

$$2\ Na_2S_2O_3 + 4\ H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4\ H_2O \quad (1)$$

This liquid homogeneous reaction is irreversible, fast, and highly exothermic (Lo and Cholette, 1972). The kinetics can be described by:

$$r = k \cdot [Na_2S_2O_3] \cdot [H_2O_2] \quad with\ k = k_0 \cdot \exp\left[\frac{-E_a}{R \cdot T}\right] \quad (2)$$

$k_0 = 2 \cdot 10^7$ $m^3.mol^{-1}.s^{-1}$ and $E_a = 6.82 \cdot 10^4$ $J.mol^{-1}$.

The reaction enthalpy is $\Delta Hr = -586.2$ $kJ.mol^{-1}[Na_2S_2O_3]$.

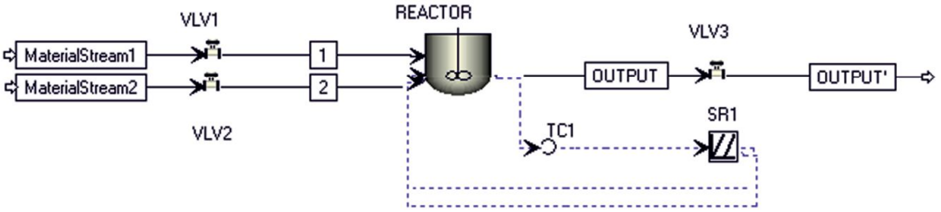

Figure 1: Fed-batch reactor flowsheet

The process (Figure 1) consists of a standard semi-batch reactor of 100 L. The tank is filled by two material feeds: the aqueous sodium thiosulphate through the inlet (“MaterialStream1”) and the dosing of aqueous $H_2O_2$ (“MaterialStream2”). The reactor temperature (333.15K) is controlled by the set of the temperature controller “TC1” and the Split-Range device “SR1”. This system allows the cooling and the heating of the reactor. There is a valve on each stream (“VLV1” for the Material feed 1, “VLV2” for the Material feed 2 and “VLV3” for the output). The process is simulated with Aspen Dynamics. The thermodynamic model is NRTL. In normal functioning, the operating conditions are summarized in Table 1. The $Na_2S_2O_3$ conversion rate is equal to 87 %.

Table 1: Normal operating conditions

| | | MaterialStream1 | MaterialStream2 |
|---|---|---|---|
| Weight percent | $Na_2S_2O_3$ | 11% | - |
| | $H_2O_2$ | - | 20% |
| | $H_2O$ | 89% | 80% |
| Temperature (K) | | 293.15 | 333.15 |
| Flowrate ($L.h^{-1}$) | | 120.9 | 31.2 |

The process protocol is illustrated in Figure 2. It is composed of several steps:

- feeding of $Na_2S_2O_3$ (MaterialStream1) during 1200 seconds,
- heating to increase the mixture temperature from 293.15 K to 333.15 K,
- dosing of $H_2O_2$ (MaterialStream2) during 1200 seconds, at a constant temperature of 333.15 K,
- reaction at constant temperature (333.15 K) during 4800 seconds.

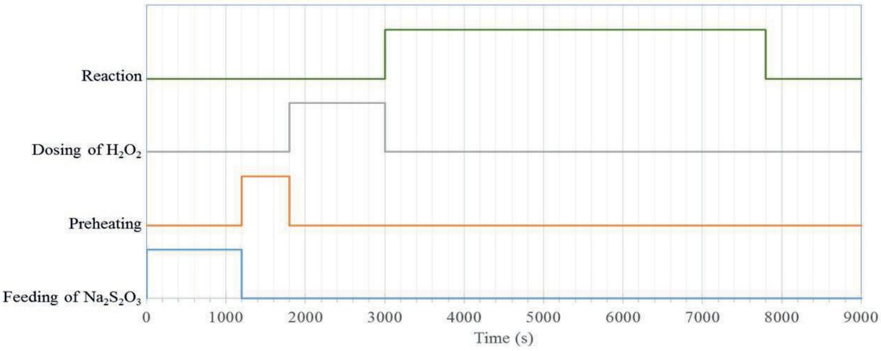

Figure 2: Process protocol in normal conditions

## 4. Risk assessment

HAZOP analysis was carried out on the reactor part. The most hazardous scenarios were identified. As expected, the worst case scenario corresponds to the complete loss of cooling. This scenario has been underlined by Stoessel (Stoessel, 2008). The four studied scenarios are the following (the first three ones are provided by HAZOP analysis and the last one illustrates the interest of setting up a safety barrier):

- Scenario 1 (batch mode): “MORE temperature in the reactor due to adiabatic conditions”;
- Scenario 2 (semi-batch mode): “MORE temperature in the reactor due to complete loss of cooling at time corresponding to reactant maximum accumulation” (t = 2880 s)
- Scenario 3 (semi-batch mode): “MORE temperature in the reactor due to complete loss of cooling at half dosing time (t = 2160 s)
- Scenario 4 (semi-batch mode): scenario 3 with a safety instrumented system (SIS) that interrupts the dosing when the temperature is greater than the threshold value of 336.15 K.

## 5. Results

In this part, the simulations of the 4 scenarios previously described are analysed.

### a- Adiabatic batch reactor (scenario 1)

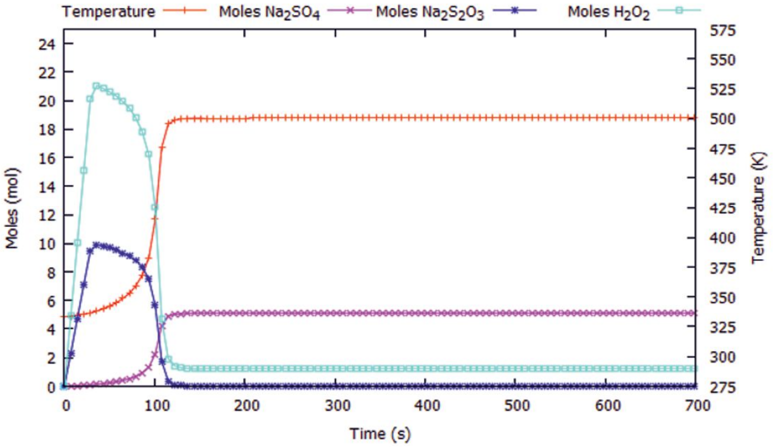

Figure 3: Adiabatic batch reactor temperature and molar quantity evolutions (scenario 1)

The feeding of both reactants is operated during 30 seconds. Figure 3 shows the evolution of reactor temperature and molar quantities in adiabatic conditions. It shows that the temperature rises rapidly, taking only 150 s to rise from 333.15 K to 500.15 K ($\Delta T_{ad}$= 167 K). 500.15 K corresponds to the Maximum Temperature of the Synthesis Reaction (MTSR). The conversion rate of $Na_2S_2O_3$ is equal to 100 %. According to Stoessel criteria (Stoessel, 2008), the runaway severity is low. Nevertheless, the probability of a potential runaway is high due to the system dynamics. So, the consequences of this adiabatic temperature rise must be elucidated by carrying out experimental calorimetric tests. These experiments are in progress.

### b- Complete loss of cooling in a semi-batch reactor (scenario 2)

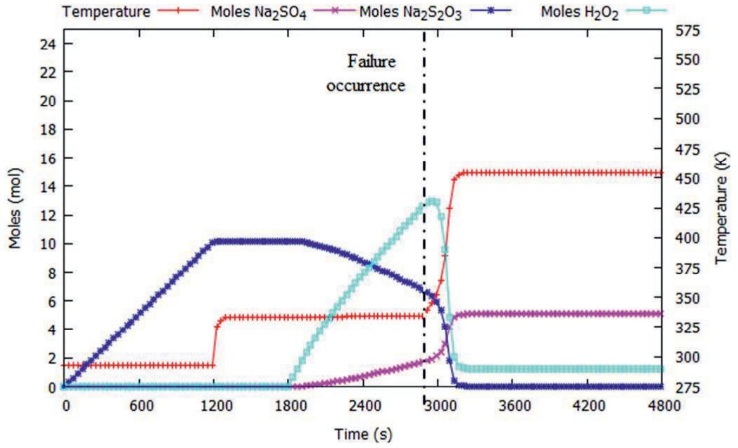

Figure 4: Temperature and molar quantity evolutions in a semi-batch reactor (scenario 2)

The considered failure is a complete loss of cooling after the dosing of the second reactant (aqueous $H_2O_2$). The failure occurs at t = 2880 s, which corresponds to the maximum accumulation of $H_2O_2$. According to Figure 4, the MTSR is equal to 455 K and the temperature increase takes 360 s (conversion rate of $Na_2S_2O_3$ equal to 100%). The adiabatic temperature rise is equal to 122 K, less than the one estimated in batch adiabatic mode (scenario1).

c- Complete loss of cooling in a semi-batch reactor (scenario 3)

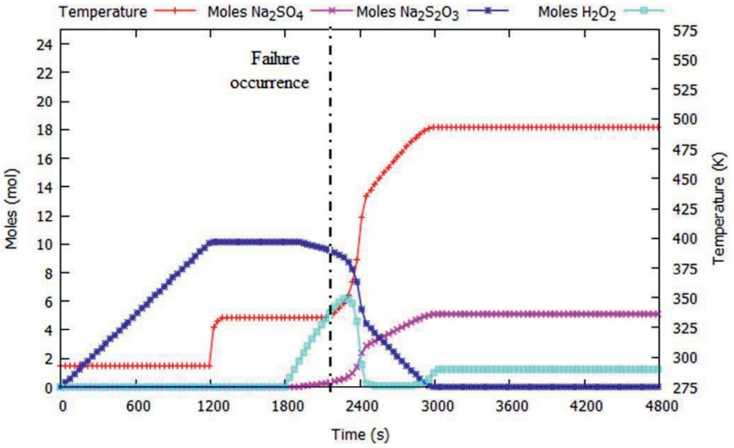

Figure 5: Temperature and molar quantity evolutions in a semi-batch reactor (scenario 3)

In this scenario, the loss of cooling occurs at t = 2160 s, during the dosing. The MTSR equal to 493 K is reached after 790 s (Figure 5). The adiabatic temperature rise is equal to 160 K, more than the adiabatic temperature rise estimated in scenario 2. The severity of this scenario is greater than the previous one, because the dosing is not interrupted when the failure occurs.

d- Introduction of a safety instrumented system (scenario 4)

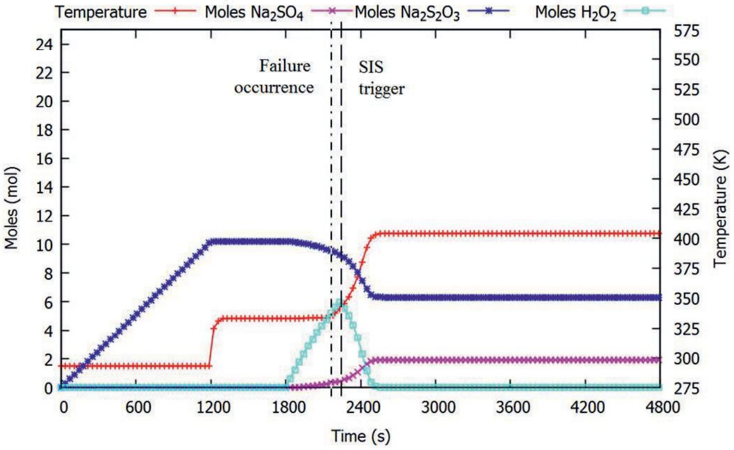

Figure 6: Temperature and molar quantity evolutions (scenario 4)

In order to prevent a potential thermal runaway, a safety instrumented system (SIS), that interrupts the dosing when the temperature is greater than the threshold value of 336.15 K, is introduced (normal temperature plus 3K). The reactor temperature reaches this threshold value at t = 2232 s, i.e. 72 seconds after the cooling loss. The conversion of $Na_2S_2O_3$ is only 38 % since all dosed $H_2O_2$ is consumed. The temperature reaches 404 K ($\Delta T_{ad}$= 71 K) in less than 360 s. In this case, the MTSR is 89 K less than the one of the scenario 3.

## 6. Conclusion and perspectives

A quantitative methodology for safety analysis has been developed using dynamic simulation to determine the reactor behaviour during major failure scenarios. In this work, we chose to simulate an exothermic synthesis in a semi-batch reactor since it represents the most dangerous operational unit in the chemical industry. The simulation results give an estimation of the probability and the severity of potential runaway risk.

The perspective of this research work is to apply this methodology to complex processes with consecutive unit operations. The challenge is to investigate the propagation of the deviations along the process line. Moreover, dynamic simulation allows to manage appropriate control strategy and to define the required safety barriers, such as safety instrumented systems, essential to prevent risks.

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