

# Quantitative Risk Analysis using Dynamic Simulation: Deviation Propagation along Propylene Glycol Process

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Currently, there is a strong demand for quantitative risk analysis. There is a challenge in describing the process dynamic behaviour in case of failures. We suggest a methodology that combines dynamic simulation (with ASPEN PLUS DYNAMICS™ 9.0 tool), lessons learnt from accidents to identify the most likely deviations and risk matrices. In fact, there is a real interest in knowing the system behaviour during malfunctions for safety analyses. For this purpose, dynamic simulation is an efficient tool to predict the time evolution of process parameters during deviations from normal operating conditions. Moreover, the knowledge of the process dynamic behaviour and the profiles of the operating parameters during a degraded mode permits adequate safety barrier recommendations. The case study concerns a continuous process of propylene glycol (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>) production. The synthesis reaction involves three consecutive competitive reactions leading to the formation of by-products: di and tri glycols (C<sub>6</sub>H<sub>14</sub>O<sub>3</sub> and C<sub>9</sub>H<sub>20</sub>O<sub>4</sub> respectively). The process is composed of a CSTR reactor and two distillation columns in series. The objective is to study the propagation of deviations along the process. This work provides a new perspective on risk quantification through the analysis of deviation propagation along a process involving cascade distillation columns.

## 1. Introduction

One of the limitations of risk analysis methods such as HAZOP is the inability to take into account multiple simultaneous failures and deviation propagation (Baybutt, 2014). So, there is a need to study the propagation of deviations along a process, but also the interactions with safety devices. Janosovsky et al. (2017) highlight the importance and interest of process simulation to analyze deviation propagation. Simulation provides additional information needed for risk assessment. Thus there are few works on the simulation of transient phases in order to ensure safe operation (Bodizs et al., 2015; Manenti, 2012). In fact, mismanagement of transient stages can lead to numerous accidents (Srinivasan et al., 2005). The determination of operating parameters can be problematic during the start-up and shutdown steps (Markos et al., 2005). Simulation makes possible to choose the most judicious regulation configuration and eliminate those generating risks of deviation (Manenti, 2012).

Simulation is also used to obtain quantitative information on degraded mode (Luyben, 2012a, 2012b; Manca and Brambilla, 2012; Eizenberg et al., 2006; Svandova et al., 2005). The simulation results make possible to quantify the consequences of deviations and thus enrich the risk assessments (Svandova et al., 2005). They can help prioritize and classify the causes of deviations by analyzing the effects (Kang and Guo, 2016). Simulation is also used to determine the causes of an accident (Manca and Brambilla, 2012). It is an interesting tool for analyzing deviation propagation (Gabbar et al., 2014; Komulainen et al., 2012).

This work proposes a methodology of quantitative risk analysis, which combines a risk assessment method, the lessons learnt from previous accidents and the dynamic simulation of process deviations. A study of deviation propagation has been carried out for a process involving a hydrolysis reaction. The process is composed of a reactive unit and of a separation unit. This case study demonstrates the feasibility of studying the propagation of deviation along a process.

## 2. Methodology

The goal of our work is to use dynamic simulation to enrich safety studies. A risk analysis methodology is developed to quantify the effects and describe the kinetics of the hazard phenomena. This quantification is essential to justify and validate by simulation the appropriate risk barriers. The steps of this methodology are illustrated in Figure 1.

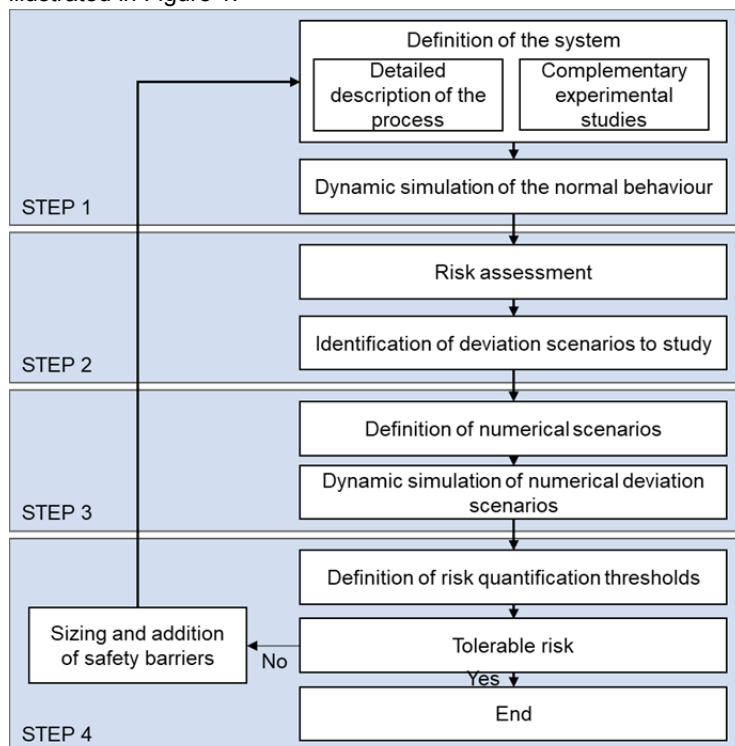


Figure 1: Steps of the methodology

It relies on dynamic simulation under ASPEN PLUS DYNAMICSTM 9.0 and includes 4 steps. The first step concerns the definition of the system and its simulation in normal operation. For this, the process is described in detail. The reactions, the sizing of the apparatus and the operating conditions are defined. The second step concerns the definition of deviation scenarios to study more finely. Lessons learnt from accident are first performed. Then, a risk analysis is carried out. In our case, this is a HAZOP study. In view of the results of these both studies, a set of deviation scenarios is highlighted. These scenarios need to be analyzed more finely in order to quantify the amplitude and kinetics of their effects. The third step concerns the simulation of deviation scenarios. To begin, the deviation scenarios defined in step 2 are translated into numerical scenarios. There are sequences of events that represent the progress of the simulation stages of deviation scenarios in the form of algorithms. The simulations of the numerical scenarios make it possible to obtain the time profiles of the parameters and the effects of the deviations. The fourth step allows reaching a tolerable risk level. For this, criteria for quantifying risk are defined. Safety barriers are added until a tolerable risk level is reached. When a barrier is added to the process, the definition of the system is reconsidered in order to take into account the cases where this safety barrier induces additional risks. Subsequently, the simulation validates its performance.

## 3. Case study

The case study relates to the process of the hydrolysis reaction of 1,2 propylene oxide and the separation of its products. Figure 2 is a simplified schematic of the process. The reactor feeds consist on the one hand of an equivolumic mixture of propylene oxide and methanol and on the other hand, water. The temperature is equal to 297.15 K and the pressure is equal to 1.5 bar. This synthesis involves three consecutive competitive reactions leading to the formation of by-products: di and tri glycols ( $C_6H_{14}O_3$  and  $C_9H_{20}O_4$  respectively). The temperature increase favors the formation of these by-products. The separation is carried out consecutively to the reaction phase. The first separation (distillation column C1) eliminates the majority of the methanol ( $CH_3OH$ ) and a part of the water of the reaction medium. The second separation (distillation column C2)

allows the recovery of water and few traces of unreacted reagent  $C_3H_6O$ . The bottom products of column C2 consist mainly of propylene glycol and the both bi-products.

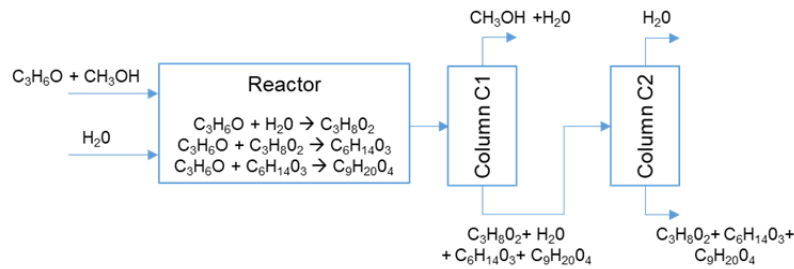


Figure 2: Process of hydrolysis reaction of 1,2 propylene oxide and separation of its products

The process flow diagram is represented in Figure 3. The process consists of a continuous reactor CSTR with a volume of  $1.14 \text{ m}^3$  (Fogler, 1999) and two distillation columns in cascade. The reactor is equipped with a temperature and level controllers. The control strategy used for the columns has been proposed by Luyben (2010).

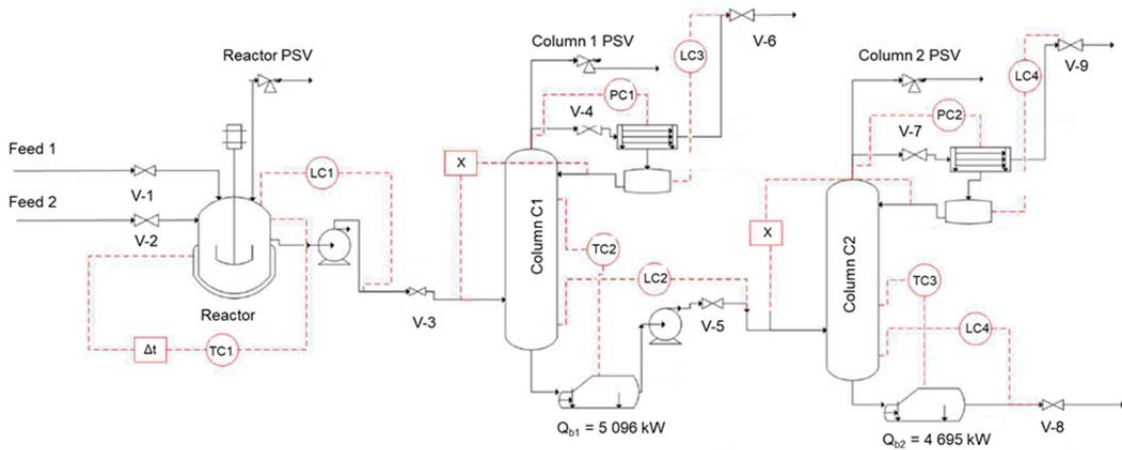


Figure 3: Process flow diagram of the hydrolysis of 1,2 propylene oxide

#### 4. Lessons learnt from accidents and selection of the scenario

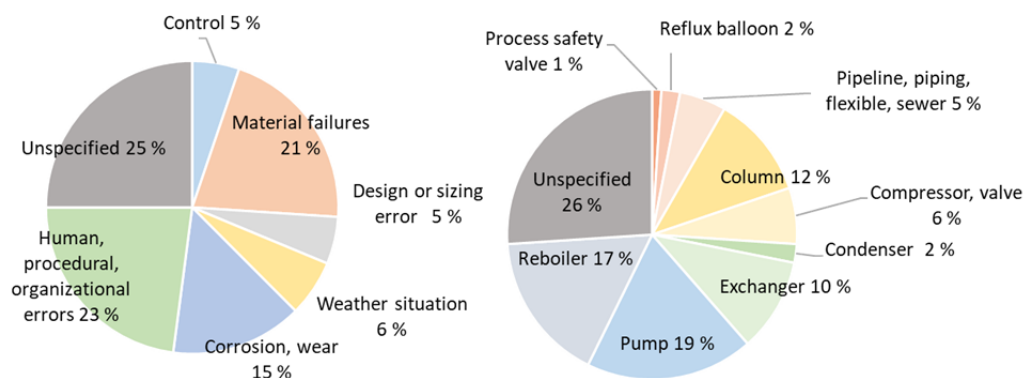


Figure 4: Causes and equipment involved in atmospheric distillation column accidents

According to Kister (2003), the number of failures in distillation columns is increasing despite technological advances. Lessons learnt from accidents analysis on atmospheric distillation is made by using the ARIA database. In France, 96 incidents and / or accidents between 1990 and 2017 are recorded. Figure 4 summarizes the results of this study. The most common causes are material failures, corrosion, wear and human (procedural and organizational) errors. Concerning the equipment involved in the accidents, there are

mainly reboiler and pumps. These results are confirmed by the statistical study carried out by Kister in 2003 on 900 accidents (Kister, 2003): these both devices are highlighted. It can be noted that the main risks of distillation columns are weeping, flooding and overpressure.

According to this accidentology, the deviation scenario consists of a variation of reboiler heating. A temperature increase of C-1 reboiler takes place at  $t = 5.5$  h. The heating power  $Q_{b1}$  increases until the value of 6 007 kW (increase of 15 % from normal condition). The amplitude value of the deviation is chosen to allow the mathematical integration (convergence of the model). For greater variation amplitudes, convergence problems are present. Note that the steady state is established at  $t = 3$  h.

## 5. Simulation results

The bottom product of column C1 (W1) is the feed of column C2 (Figure 2). The increase in the heating of column C1 causes the variation of several operating parameters of the bottom products of column C1: temperature, pressure, flow, molar composition.... Table 1 presents the effects of the scenario on column C2 feed (W1).

Table 1: Characteristics of column C2 feed (W1) before and after the deviation

| Parameter          | Steady state before deviation | Steady state after deviation |
|--------------------|-------------------------------|------------------------------|
| Temperature        | 376.45 K                      | 381.65 K                     |
| Pressure           | 1.07 bar                      | 1.11 bar                     |
| Flowrate           | 111.47 kmol.hr <sup>-1</sup>  | 43.77 kmol.hr <sup>-1</sup>  |
| $X_{C_3H_8O_2}$    | 0.122                         | 0.310                        |
| $X_{C_6H_{14}O_3}$ | 0.005                         | 0.013                        |
| $X_{C_9H_{20}O_4}$ | 0                             | 0.001                        |
| $X_{CH_3OH}$       | 0.005                         | 0.006                        |
| $X_{H_2O}$         | 0.868                         | 0.671                        |

The temperature increase of the reboiler of column C1 induces an increase of the flooding factors of the theoretical stages of column C1 (Figure 5). The flooding factor of the below feed stage is greater than 80%. A risk of flooding is then present. At the bottom of the column, the flow rate decreases by 38% (Table 1). Column C2 is then affected. The flooding factors of all theoretical stages of column C2 (Figure 5) decrease. A risk of weeping is then present.

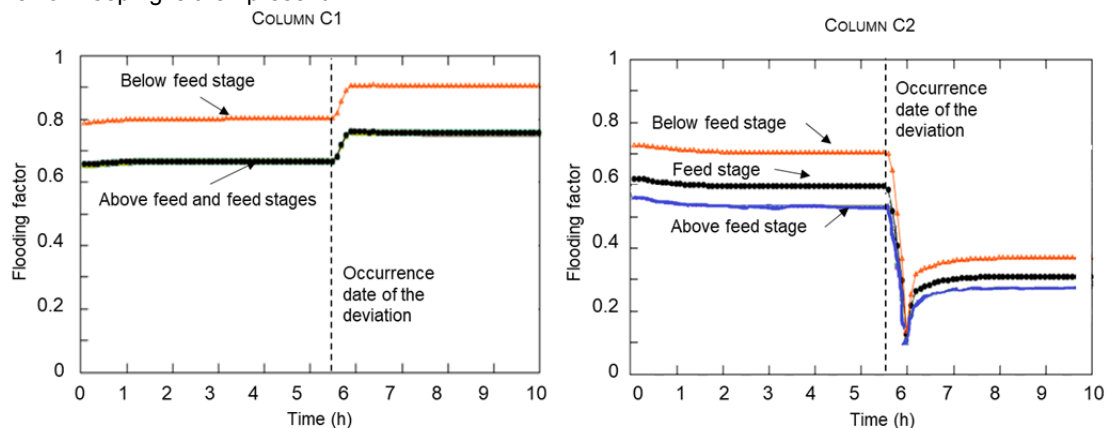


Figure 5: Time evolution of the flooding factors for the columns C1 and C2 during the deviation

Figure 6 shows the effects of the deviation on the temperature and flowrate of the distillate (D2) and the bottom product (W2) of column C2. Note that the distillate flow rate (D2) oscillates because of the controllers that cannot correct this deviation.

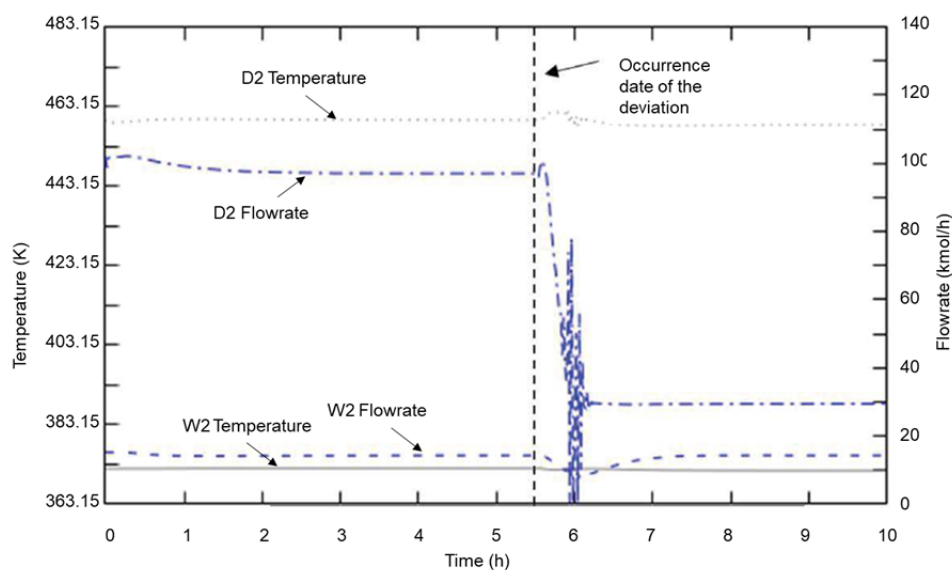


Figure 6: Time evolution of temperature and flowrate of the residue (W2) and the distillate (D2) of column C2

## 6. Risk quantification

The effects of the deviation on both columns are then quantified. For this, thresholds and ranges of acceptability of the three risks (overpressure, flooding and weeping) are defined in table 2.

Table 2: Thresholds of overpressure, flooding and weeping risks

| Scale | Overpressure                                |                             | Flooding               |                             | Weeping                                     |                             |
|-------|---|-----------------------------|------------------------|-----------------------------|---|-----------------------------|
|       | $\Delta P$ (mbar.m <sup>-1</sup> )          | $\Delta t_p$ (h)            | $n_F/NET$ (%)          | $\Delta t_F$ (h)            | $\Delta P$ (mbar <sup>-1</sup> )            | $\Delta t_p$ (h)            |
| 1     | $\Delta P \leq \Delta P_n$                  | $\Delta t_p \leq 0.2$       | $n_F/NET \leq 33$      | $\Delta t_F \leq 0.2$       | $\Delta P \leq \Delta P_n$                  | $\Delta t_p \leq 0.2$       |
| 2     | $\Delta P_n < \Delta P \leq \Delta P_{max}$ | $0.2 < \Delta t_p \leq 0.5$ | $33 < n_F/NET \leq 66$ | $0.2 < \Delta t_F \leq 0.5$ | $\Delta P_n < \Delta P \leq \Delta P_{max}$ | $0.2 < \Delta t_p \leq 0.5$ |
| 3     | $\Delta P > \Delta P_{max}$                 | $\Delta t_p > 0.5$          | $n_F/NET > 66$         | $\Delta t_F > 0.5$          | $\Delta P > \Delta P_{max}$                 | $\Delta t_p > 0.5$          |

The maximum pressure drop accepted by a column,  $\Delta P_{max}$ , is commonly 11 mbar/m.  $\Delta P_n$  is the pressure drop obtained during normal operation for each column. The duration  $\Delta t_p$  represents the time laps between the occurrence date of the deviation and the moment when the maximum value of the pressure drop is reached. The number  $n_F$  is the number of theoretical stages where the flooding factor is superior to 70 %. On the contrary, the number  $n_w$  is the number of theoretical stages where the flooding factor is inferior to 33 %. The duration  $\Delta t_F$  represents the time laps between the occurrence date of the deviation and the moment when the flooding factor is maximal, whereas the duration  $\Delta t_w$  represents the time laps between the occurrence date of the deviation and the moment when the flooding factor is minimal. Scales are defined in order to prioritize risks. The terms  $\Delta t_p$ ,  $\Delta t_F$  and  $\Delta t_w$  illustrate the dynamic of the hazard phenomena.

Table 3 presents the results obtained. The risk of flooding of column C1 and weeping of column C2 are quantified. No risk of overpressure is present.

Table 3: Quantification of the deviation effects

| Columns | Overpressure                       |                  | Flooding      |                  | Weeping                          |                  |
|---------|------------------------------------|------------------|---------------|------------------|----------------------------------|------------------|
|         | $\Delta P$ (mbar.m <sup>-1</sup> ) | $\Delta t_p$ (h) | $n_F/NET$ (%) | $\Delta t_F$ (h) | $\Delta P$ (mbar <sup>-1</sup> ) | $\Delta t_p$ (h) |
| C1      | 4.5                                | 1                | 100           | 0.25             | 0                                | >5               |
| C2      | 9                                  | 2                | 0             | >5               | 100                              | 0.12             |

## 7. Conclusions and perspectives

This study shows how dynamic simulation permits to model deviation propagation along the propylene glycol production process consisting of a CSTR reactor connected to a cascade of 2 distillation columns (C1 and C2). The proposed methodology includes 4 steps among which a step of process dynamic simulation, with ASPEN PLUS DYNAMICSTM 9.0 tool, under normal mode than under degraded mode. The accidentology is

a preliminary phase, made with French ARIA database, that puts in evidence the most likely accidental scenarios arising during atmospheric distillation column operation.

In this paper, the deviation chosen consists of increasing by 15 % from normal operating conditions the heat supplied by the C1 reboiler. Dynamic simulation has permitted to quantify the consequences of this deviation on the functioning of C1 and C2 columns in order to evaluate level risks of flooding, weeping or overpressure. It can be noted an increase of the flooding factors of all C1 column stages with a value greater than 80 % at C1 bottom stage (important risk of flooding). Moreover, it can be observed a decrease of the flooding factors of all C2 column stages reaching a critical value of 10 % due to deviation propagation (important risk of weeping).

The proposed quantitative risk analysis methodology offers real perspectives in the field of industrial risks management. It allows in particular, through the presented case study, to simulate the time evolution of operating parameters (concentration, pressure, temperature,...) and the behavior of safety devices, when a deviation appears and propagates along a cascade distillation columns. It constitutes an important decision-making tool. However, it is necessary to note that the deviation amplitude is limited because of divergence problems of the simulation program.

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