

Toward HAZOP 4.0 Approach for Managing the Complexities of the Hazard and Operability of an Industrial Polymerization Reactor

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Abstract: Conventional HAZOP is a collaborative and multidisciplinary activity to identify the hazards associated to operability of the chemical processes. Then the consequences and required safeguards of each potential deviation or failure are assessed qualitatively one by one. It is performed with the assumption of “one failure at the time” for the process parameters. Furthermore, process complexities such as multiple failures, domino effects, time and amplitude dependent deviations etc. are avoided to keep the HAZOP brainstorming sessions systematic and effective. Therefore, the quality and outcomes of HAZOP study are relatively subjective and depend on the experience and competency of the HAZOP team. This simplified approach cannot fully cover the hazard identification and risk assessment of the complex processes such as polymerization. Furthermore, the incident investigations show that almost all major accidents have occurred due to multiple failures or domino effects. This paper aims at developing a practical methodology in the context of “Industry 4.0” and particularly illustrate how dynamic simulation liberates the HAZOP team from the simplification assumptions such as one failure at the time or neglecting the domino effects during the lifecycle of the complex processes. An industrial styrene bulk free radical polymerization process has been chosen as the case study to depict the applicability of the proposed method. In continuation of this research, the dynamic simulation integrated with Artificial Intelligence (AI) algorithms and Multivariable Process Monitoring (MPM) together with virtual collaboration tools will be invoked towards a more practical and effective HAZOP 4.0 platform. Such a platform can be the foundation of the further Process Safety Management (PSM) elements such as “Operating manuals”, “Training and Competency management”, “Condition monitoring and predictive maintenance”, “Management of Change”, “Pre-Start-up Safety Review”, etc.

Keywords: Dynamic HAZOP, Dynamic Simulation, Polymerization Plant, Process Complexity, HAZOP 4.0.

1. INTRODUCTION

Major accidents are the large emission, fire and explosion. They lead to major loss of life, environmental impacts, property damage and production shortfalls (Mihailidou et al., 2012). Process safeguards are in place to minimise the risk of major accidents to as low as reasonably practicable (ALARP). API 14C (ISO 10148) provides the prescriptive guidelines for eight categories of major process equipment like vessels, pumps, compressors, heat exchangers, etc. used in upstream oil & gas installations. It calls for implementation of at least two levels of protections, independent and diverse for those process hazards which may lead to major accidents. However, for the more complex processes like reactors and distillation columns designers should rely on the dedicated Process Hazard Analysis (PHA).

Process Hazard Analysis (PHA) can be performed using different techniques. Hazard and Operability (HAZOP) study is one of the most effective techniques for identification of possible process operability hazards (Salimi and Vande

Capelle, 2011, Dunjo et al., 2010, Herrera et al., 2018, Abbasi et al., 2018). HAZOP is a qualitative approach in which the process, control and instrumentation, safety and the other disciplines identify the process hazards and corresponding safeguards in a brainstorming session. The quality of HAZOP is highly dependent on the knowledge, experience and judgement of HAZOP team (Salimi, 2017).

In conventional HAZOP study, the facilitator who is an Independent Competent Person (ICP) controls the brainstorming by applying the process deviation checklist with the assumption of one failure/deviation at the time and excluding domino effects. Furthermore, the amplitude and duration of deviation/failure cannot be evaluated. This simplified approach is effective for the simple processes. However, for complex processes such as distillation or polymerization, the simplified approach may not be effective. This research aims at demonstrating how the dynamic simulation of a good model of process is applied as a supporting study to the HAZOP by providing an objective platform on which the HAZOP team (i.e. beside of their

knowledge and their experience) can examine some further credible hazardous scenarios and failures of the process equipment and/or safeguards. Many research activities (Janosovsky et al., 2019; Danko et al., 2018; Berdouzi et al., 2017) attempted to apply the computerized quantitative analysis to overcome the complexities commonly ignored in the conventional HAZOP study as described in the following:

1. Amplitude and duration of the deviation/failure: This issue can be examined utilizing dynamic simulation of the process which cannot be evaluated in the conventional HAZOP study. Relevant researches can be found in the work of Eizenberg et al. (2006) and Labovsky et al. (2007).

2. Simplification of method for covering “one failure/deviation” at the time: Very often “one failure/deviation” at the time scenarios are considered in the conventional HAZOP study which is applicable for simple unit operations, while dynamic simulation can provide a valuable tool for evaluating multiple failures/deviations. In fact, for complicated unit operations, process parameters interactions cannot be simply neglected. Moreover, investigation of major incidents shows that “Multiple failures” are root causes of major incidents (HSE, 2019). Nonetheless, it seems there is no publication addressing a thorough investigation of multiple failures/ deviation scenarios in the context of HAZOP study for complex unit operations. To the best of our knowledge, the only publication investigating simultaneous deviations in multiple process parameters is the work of Danko and et al. (2017) in which deviation scenarios are investigated in the scope of one node for a simplified alkylation process.

3. Ignoring the “Domino effect”: Investigation of domino effects in the context of HAZOP study is a demanding task, but for simplification, it is excluded from the brainstorming sessions. A domino effect scenario is defined as “a happening in which a primary event initiates another event, and therefore, the “secondary” event is occurred as a result of the primary event. Due to escalation effect, the secondary accidents could be more severe than the primary one. There are publications highlighting the important role of domino effects in process industries incidents (Darbra et al. 2010, Necci et al., 2015). Nevertheless, very few numbers of publications discussed this issue due to complexity of the analysis. For instance, propagation effects of single deviations for an alkylation process with the aid of dynamic simulation can be found in the work of Murillo et al. (2018). In another research, this issue is investigated considering steady state simulation of the process under study (Janosovsky et al., 2019).

In this research, to demonstrate the previous three limitations and suggest a practical method to overcome them, the HAZOP of a polymerization plant has been chosen as the case study. Polymerization chemical processes are prone to thermal runaway among all other chemical reaction types and are therefore featured as the most common complex chemical processes involved in thermal runaway incidents (Barton et al. 1989, Saada et al., 2015). A significant number of these incidents were relevant to styrene production and handling (Zhao et al., 2019). Despite this, safety analysis of this process type is rarely investigated, and the lessons have not

been learned. Therefore, this paper deals with a real practical styrene bulk free radical polymerization reactor available in the industry.

This paper continues with a brief description for HAZOP 4.0 in Section 2. In Section 3, the conventional HAZOP is discussed. Then the complex scenarios are identified and assessed utilizing the dynamic simulation of the process. For this purpose, the derivation of the mathematical model is first provided. Dynamic simulation results successfully show how dynamic HAZOP results in better consequence analysis rather than the conventional HAZOP study. The steps shown in Fig. 1 will be applied to take the dynamic HAZOP of this case study towards HAZOP 4.0. Finally, in Section 4, the conclusion is provided.

2. WHAT IS HAZOP 4.0?

Today’s world is facing a new revolution of manufacturing called “Industry 4.0”. ISA 95 (IEC 62242), Enterprise-Control System Integration, is an international standard to address the development of automation interface between enterprise and control systems. HAZOP is a crucial activity for design of control and safety system and plant management and plays the role of a bridge between process safety engineering and safety management system. Therefore, the conventional HAZOP method should be evolved to HAZOP 4.0. To achieve HAZOP 4.0 which will be used as the fundamental process hazard identification and risk management, the ecosystem of the physical process and associated automation parts should be considered in conjunction with the process safety management system as the core of manufacturing management system. To the best of our knowledge, there is no publication investigating a clear definition and scope of HAZOP 4.0. HAZOP 4.0 should become a live, lifecycle and collaborative activity and integrated in process safety management framework. Fig. 1 illustrates the logical diagram of this proposed approach.

Industrial Internet of Thing (IIoT) is the key to transform the process industry to achieve HAZOP 4.0. The HTML5 and OPC protocol enable to combine the Information Technology and Operational Technology of the chemical or unit operation processes. In other words:

1. On one hand AI and open source database tools like SharePoint lists, integrates and processes the checklists, code-based requirements, historical data and lesson learned for the best use of HAZOP team and users.
2. On the other hand, dynamic simulation and OPC enable the HAZOP team and users examine the complex processes and hazardous scenarios.
3. Ontologies and model repositories that capture the limitations of and the assumptions behind the stored models make it possible to detect the right level of abstraction and complexity, e.g. for fault propagation (Eggersmann et al. 2004, Oppelt et al. 2015).

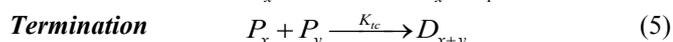
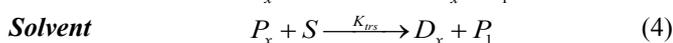
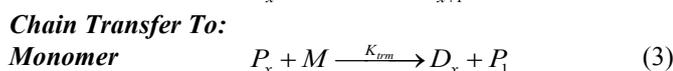
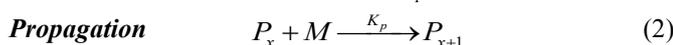
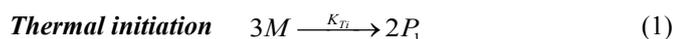
This paper focuses on how dynamic simulation can help to improve the conventional HAZOP study of complex processes (as highlighted in Fig. 1). Further steps of HAZOP 4.0 approach will be investigated in our future works.

3. APPLICATION OF HAZOP 4.0 TO AN INDUSTRIAL STYRENE POLYMERIZATION PLANT

3.1 Process Description

In this paper, the proposed safety methodology is applied to an industrial real complex two cascade polystyrene polymerization reactors (See Fig. 2). In this process, fresh styrene monomer from the storage tank is mixed with the feed from recycle drum (consists of unreacted monomers and ethylbenzene as solvent). The homogenous mixture is then passed through the heat exchanger E-1 to reach the design temperature before entrance to the first reactor. The inlet mass flowrate of the first and the second reactors are 6.13 ton/h. Polymerization reaction is carried out in two cascade continuous stirred tank reactors of volume 21 m³. The reactors are cooled by heat exchangers E-2 and E-3. Under these conditions the operating temperature and solid content in the first and second reactors are 415 K, 38% and 425 K, 63% respectively.

Styrene bulk free radical polymerization involves significant complexities due to intricate kinetic mechanism including thermal initiation, propagation, chain transfer and termination. Styrene polymerization kinetics for this case study are summarized as follows:



where temperature dependence of reaction rate constants is assumed by Arrhenius equation. The reaction is highly

exothermic, and the heat released in both reactors is removed by separate condensers using evaporative cooling mechanism. In case of temperature rise, the rate of polymerization (living radical release and chain propagation speed) and heat production increases exponentially, however, the rate of heat removal only increases almost linearly. As a result, the temperature may rise to the point where the polymerization reaction is very rapid and uncontrollable, called thermal runaway. In the contrary, when the temperature decreases significantly, the polymerization stops. These are challenging issues in this process case study and this paper aims at establishing a procedure to manage these complexities (For a detail systematic approach to manage complexities of process industries please see Salimi, 2017).

3.2 Conventional HAZOP Study

The Conventional HAZOP study of this polymerization plant is investigated in this subsection. The styrene polymerization process shown in Fig. 2 can be divided into the three following nodes:

- Node 1:** Feed Preparation including P-1, MX-1, E-1.
- Node 2:** 1st polymerization reactor including R-1, E-2, P-2.
- Node 3:** 2nd polymerization reactor including R-2, E-3, P-3.

The conventional HAZOP checklist is applied to identify all the credible hazards associated to the operability of the process. The severity (S), frequency (F) and Risk (R) are ranked with a simple qualitative (Low, Medium, High) categories. At this stage, causes and consequences are specified without any safeguard in place. Furthermore, the typical complexities:

- (C1) Amplitude and time dependency of failures
- (C2) Multiple deviations/failures
- (C3) Domino effect

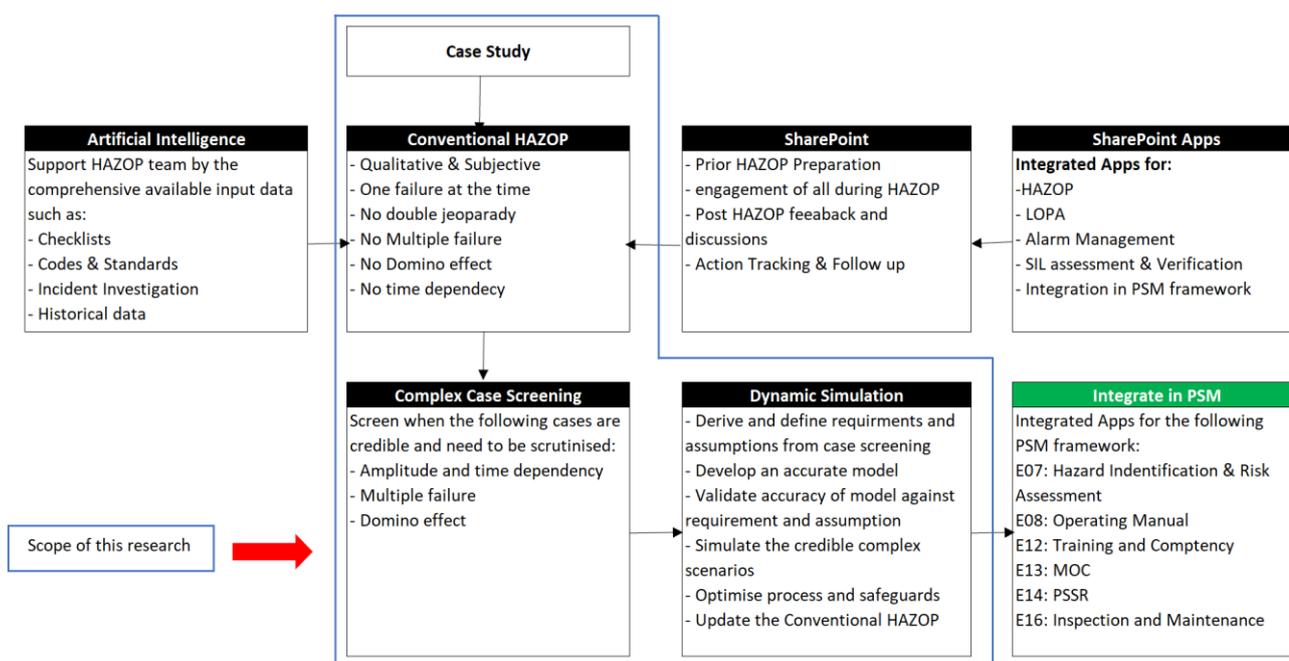


Figure 1. Our proposed HAZOP 4.0 Logical Diagram.

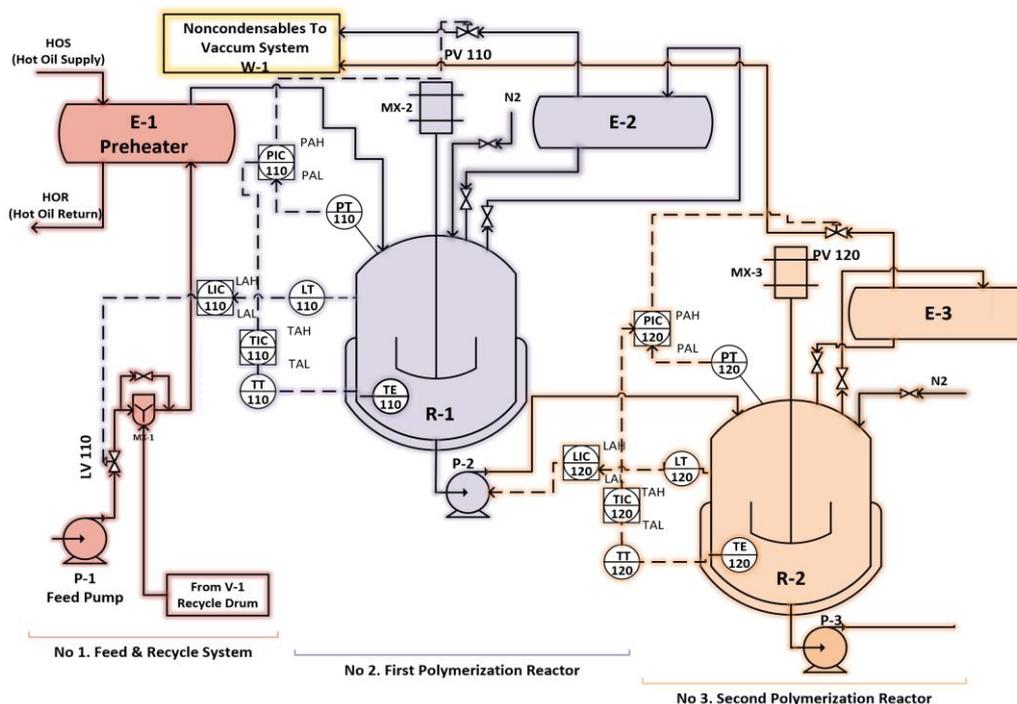


Figure 2. Schematic of a real industrial cascade free radical styrene polymerization process.

are screened to be scrutinised with the dynamic model of process. This approach is summarised in Table 1 for three credible deviation scenarios based on lessons learnt from past accidents and the experiences of the plant operators. Besides, this is the first time that the complexity of different scenarios is evaluated in the HAZOP worksheets.

As it is evident from Table 1, the conventional HAZOP study considers single deviations/failures at the time in each node and ignores its adverse effect on the upstream and downstream nodes. Moreover, the effects of duration and amplitude of deviations cannot be considered in this study and the results is highly dependent on the engineering judgement of the HAZOP team. It is worthy to mention that for simple unit operations, the conventional study may be considered as an effective approach. However, for complex unit operations where many equipment and streams interact, this simplified approach could be misleading, unless a modular design of the unit operations guaranties intramodular safety by *a)* coping with disturbances locally and *b)* providing measures to decouple the network of material, energy and information streams in a way that prevents fault propagation (Pfeffer and Urbas, 2017). However, this approach is neither economical nor organisationally feasible for the highly integrated world scale petrochemical plants.

3.3 Strategy of Basic Process Control Systems (BPCS)

To compensate for small changes in process parameters, control strategies are utilized. The control structure of this chemical plant is also illustrated in Fig. 2. Level Indicator and Controller 110 or shortly LIC110 is used to control the volume of reacting mixture in the first reactor by manipulating styrene monomer feed flowrate. The temperature is regulated via temperature indicator and

controller (TIC110) which operates in cascade on the pressure indicator and controller (PIC110). PIC110 regulates the pressure valve PV110 on the vapor line connected to the vacuum system in order to provide vaporization which is condensed in the first reactor heat exchanger and then refluxed to the reactor. LIC120, TIC120 and PIC120 with the same structure are used for the second reactor. The control parameters of these two polymerization reactors are listed in Table 2.

The deviation scenarios considered in the conventional HAZOP study, are furthered discussed in the presence of control loops as follows:

Scenario 1: Less/No cooling water flow rate to the heat exchanger E-2

As mentioned in the conventional study, the consequence of Less/No cooling water to the heat exchanger is the increased temperature and polymerization rate. First, a failure with small amplitude is resolved by regulating the vaporization rate through PV110. Then, for a failure with larger amplitudes, runaway reaction may occur. Therefore, different amplitudes of failures have different outcomes, which invoke different actions to reduce the risk level. However, this issue cannot be accomplished during the conventional study. Therefore, dynamic simulation is utilized as a supportive tool to add this value to the HAZOP study.

Scenario 2: Higher feed temperature and simultaneous malfunctioning of the pressure valve PV110

In case of higher feed temperature (failure in node 1), the pressure valve, PV110, plays a significant role to compensate for the consequence of this failure. Now, if this control valve does not perform appropriately (failure in node 2), a hazardous situation may occur. Consequence analysis of simultaneous failures/deviations is excluded from the conventional HAZOP study to keep the HAZOP

Table 1. Conventional HAZOP Study (without safeguard) for node 2, the first polymerization reactor.

Deviations	Possible Causes	Consequences	Complexity	Risk Ranking		
				S	F	R
Less/No cooling water to condenser	1- Operator mistake 2- Failure of cooling water supply	Increased temperature and rate of polymerization which may lead to runaway reaction.	C1	High	Low	High
High feed temperature	1- Heat exchanger control loop failure	Increased rate of polymerization in the first reactor which increases the solid content.	C1, C2	Medium	Low	Medium
Low pressure	1- PV110 Failure 2- PIC110 Failure	Decreased temperature and rate of vaporization in first reactor which leads to decreased solid content.	C3	Medium	Medium	Medium

Table 2. Control parameters for styrene polymerization process.

Control	Type	Controlled Variable	Manipulated Variable
LIC 110	PI	Reactor Volume	Monomer Styrene Input Feed
TIC 110 Cascaded with PIC 110	PI	Temperature	PV110/ Rate of Vaporization
LIC 120	PI	Reactor Volume	P-2 Speed Control/ Mass outlet flowrate of 1 st Reactor
TIC 120 Cascaded with PIC 120	PI	Temperature	PV120/ Rate of Vaporization

brainstorming sessions possible and time effective. Therefore, consequence analysis of simultaneous multiple failures/deviations scenario is another added value to the conventional study utilizing dynamic simulation.

Scenario 3: PV110 failure

Pressure valve PV110 is a mechanical control valve for regulating the reactor temperature. The consequence of this failure is investigated in the conventional study in the scope of the node at which the failure occurs (first polymerization reactor). However, the consequence of this failure can affect the second polymerization reactor which ignores in the conventional study. Dynamic simulation is also utilized in this case in order to investigate failure/deviation propagation in the upstream and downstream nodes.

3.4 Dynamic Model of the Case Study Process

The complex reaction kinetics for styrene polymerization plant results in extremely nonlinear dynamics. Considering these kinetic mechanism, rate expressions of styrene polymerization for different species, can be derived. However, the degree of polymerization is high, and the number of differential equations needed to be solved is very large. Therefore, a well-known method in kinetic mechanism of polymerization, called the method of moments (Mastan and Zhu, 2015), is used to reduce the number of equations to a manageable size. The i^{th} ($i=0, 1, \dots$) moment of living and dead polymers in this method are defined as follows:

$$\lambda_i = \sum_{x=1}^{\infty} x^i [P_x] \quad (7)$$

$$\mu_i = \sum_{x=1}^{\infty} x^i [D_x] \quad (8)$$

where subscript 0 denotes the molar concentration of total living radicals and dead polymers. Considering the above kinetic mechanism integrated with the method of moments, the material balances of different species and enthalpy

balances of the first reactor and condenser have the following forms:

$$\frac{d(\rho_{mix} V_R)}{dt} = \dot{m}_f - \dot{m}_t + \dot{m}_c - \dot{m}_v \quad (9)$$

$$\frac{d(\lambda_0 V_R)}{dt} = (2K_{Ti}[M]^3 - (K_{tc} + K_{td})\lambda_0^2)V_R \quad (10)$$

$$\frac{d(\mu_1 V_R)}{dt} = -\frac{\dot{m}_t}{\rho_{mix}}\mu_1 + (K_{trm}\lambda_1[M] + K_{trs}\lambda_1[S] + (K_{tc} + K_{td})\lambda_0\lambda_1)V_R \quad (11)$$

$$\frac{d([M] V_R)}{dt} = \frac{\dot{m}_f}{\rho_f}[M]_f - \frac{\dot{m}_t}{\rho_{mix}}[M] + R_M V_R \quad (12)$$

$$\frac{d([S] V_R)}{dt} = \frac{\dot{m}_f}{\rho_f}[S]_f - \frac{\dot{m}_t}{\rho_{mix}}[S] - K_{trs}[S]\lambda_0 V_R \quad (13)$$

$$\frac{d(\rho_{mix} C_{p_{mix}} T_R V_R)}{dt} = \dot{m}_f C_{p_f} T_f - \dot{m}_t C_{p_{mix}} T_R + (-\Delta H)R_M V_R - \dot{m}_v (C_{p_v} T_R + \Delta H_v) + \dot{m}_c C_{p_c} T_c \quad (14)$$

$$\frac{d(\rho_c C_{p_c} T_c)}{dt} = \frac{\dot{m}_v}{V_{shell}} (C_{p_v} T_R + \Delta H_v) - \frac{\dot{m}_c C_{p_c} T_c}{V_{shell}} - \frac{UA_c}{V_{shell}} (T_c - T_w) \quad (15)$$

$$\frac{d(\rho_w C_{p_w} T_w)}{dt} = \frac{\dot{m}_w \rho_w C_{p_w}}{V_{tube}} (T_{w_f} - T_w) + \frac{UA_c}{V_{tube}} (T_c - T_w) \quad (16)$$

with,

$$R_M = -2K_{Ti}[M]^3 - (K_p + K_{trm})[M]\lambda_0 \quad (17)$$

in which the reaction rate constants for each reaction step are chosen from the experimental work of Hui et al. (1972). Definition of model variables are also given in the nomenclature section.

To provide pressure gradient for driving the vapor from the reactor to the condenser, a vacuum system is connected to the condenser. The pressure valve, PV110, in line between the condenser and the vacuum system is used to regulate the vaporization rate. To formulate the vaporization rate, the reactor equilibrium pressure is calculated. In this study, the assumption of ideal vapor liquid equilibrium is made. Partial pressure of the i^{th} component (p_i) in the gaseous mixture is given by Dalton's law:

$$p_i = y_i P_R \quad (18)$$

where P_R is the reactor pressure and y_i the molar fraction of species in the vapor phase. The activity of the monomer and solvent in polystyrene, is determined by Flory Huggins equation:

$$\ln\left(\frac{p_i}{p_s^i}\right) = \ln(\phi_i) + \phi_p + \chi\phi_p^2 \quad (19)$$

in which, p_s^i is the pure vapor pressure of the i^{th} component (given by Antoine equation), ϕ_i the volume fraction of volatile component, ϕ_p the volume fraction of polymer and χ the Flory Huggins interaction parameter. Vaporization rate is now calculated as follows:

$$\dot{m}_v = K_{MTC}(P_R - P_c) \quad (20)$$

where P_c is the condenser pressure formulated based on the installed valve type (PV110). K_{MTC} is the mass transfer coefficient. In this paper, the temperature dependence of physical properties such as density, specific heat capacity and vapor pressure are taken into account. The same procedure is also taken to derive the mathematical model of the second reactor.

3.5 Dynamic Simulation Results

Conventional HAZOP study of the styrene polymerization plant was discussed for three undesired situations in Subsection 3.2. Dynamic HAZOP study for these scenarios is provided in this subsection. This analysis is performed utilizing the dynamic process simulation derived in Subsection 3.4. The process dynamic simulation is developed in MATLAB software. Utilizing a mathematical model, the effects of amplitude and duration of deviations, multiple deviations/failures and domino effect scenarios can be evaluated. The following simulation results successfully show how dynamic simulation is used as a supportive tool for better consequence analysis in the conventional HAZOP study. However, the issues such as the cost and efforts to develop appropriate dynamic models, and verifications of the models and the simulated faults are still important in practical implementations.

Simulation Results of Scenario 1: In case of a small step decrease in cooling water flowrate to the heat exchanger, reactor temperature starts to rise due to increased temperature of the refluxed condensate liquid to the reactor. Full condensation in the heat exchanger is often seen for small step decrease in the mentioned cooling flowrate. Temperature rise in the reactor is compensated by regulating the vaporization rate. For larger steps in reduction of the cooling

water flowrate, improper condensation may occur which leads to an increase in load of the vacuum system and loss of the material. In case of "No flow" of cooling water, there is no condensation in the heat exchanger and runaway reaction starts (See Fig. 3). Therefore, the dynamic simulation of "Less/No flow" of cooling water reveals different consequences which should be analysed more accurately with consideration of different amplitudes of failures. Obviously, the consequence analysis provided by dynamic simulation cannot be achieved during the conventional study.

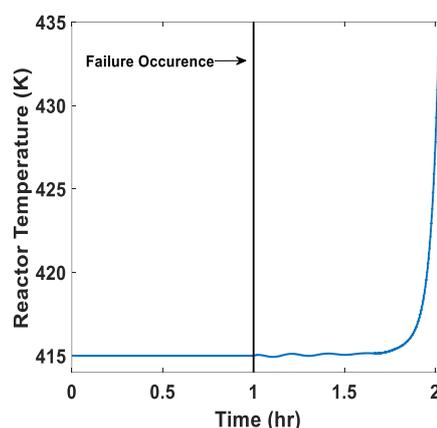


Figure 3. Evolution of "No" flow of cooling water.

Simulation Results of Scenario 2: In case of a step increase in monomer feed temperature, reactor temperature starts to rise. To compensate for it, cascade control loop commands the pressure valve, PV110, to be opened more, leading to an increase in the vaporization rate (See Fig. 4(a)). Obviously, this control valve plays an important role in compensating the consequences of this failure. In this case, if the pressure valve does not work (second failure), different consequences may arise for different amplitudes of feed temperature. Simulation results in the presence of both failures are illustrated in Fig. 4(b). For smaller step changes, reactor temperature reaches a higher steady state value leading to an increase in the solid content. For feed temperatures higher than 387K, the vaporization rate will be larger than condensation rate which leads to a sudden pressure and temperature increase in the reactor and finally thermal runaway. In this simulation scenario, a single "high feed temperature" failure is controlled by the correct operation of cascade loop. However, in the case of simultaneous failures occurrences, there is a risk of thermal runaway. This issue highlights the importance of assessing multiple failures scenario in the dynamic HAZOP study which cannot be identified in the conventional analysis. Besides, we have not seen such a study in the dynamic HAZOP publications.

Simulation Results of Scenario 3: In this subsection, failure of control valve in node 2, PV110, is analysed. Besides, it is shown how its adverse effect propagates in the downstream node. In case of failure, this control valve opens completely. In this situation, the pressure above the reactor is instantaneously decreased leading to an increased rate of vaporization in the first reactor. This results in sudden decrease of temperature, which extensively affect the first

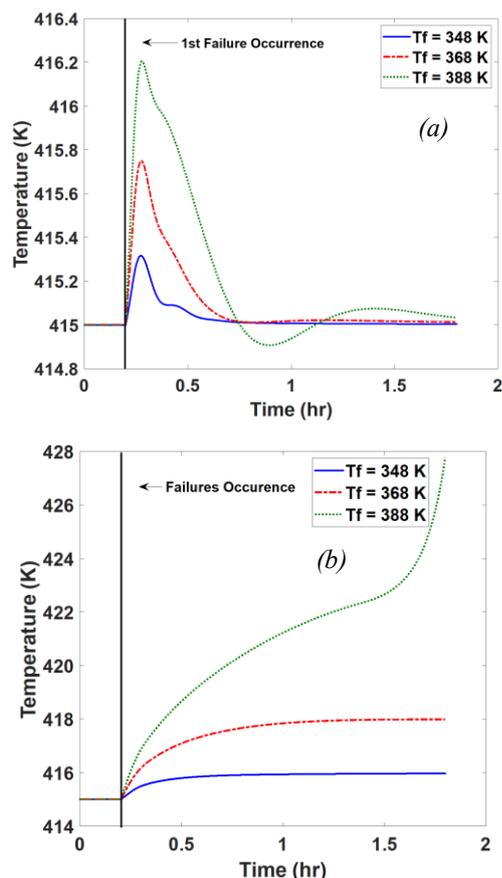


Figure 4. Evolution diagram of failures, (a) Feed temperature step increase, (b) Feed temperature step increase and simultaneously PV110 does not work.

reactor solid content. Dynamic simulation results are illustrated in Fig 5. The adverse effect of this failure is started in node 2 and propagated to the second reactor (node 3). As it is seen from Fig. 5(a), temperature decreases suddenly in the first reactor leading to a stop in the reaction, since there is no release of free radical due to low temperature. The initial effect of temperature decrease in the first reactor is temperature reduction in the second reactor. This enforces the temperature controller to compensate for it by decreasing the vaporization rate. The adverse consequence of this failure is the lower conversion in both reactors compared with nominal conditions (Fig. 5(b)). This scenario is not considered dangerous, but undesirable since it leads to plant shutdown and start-up procedures are needed to restart the plant.

4. CONCLUSION

In this research, a new approach of safety analysis, named as HAZOP 4.0, was presented for complex processes in the context of industry 4.0. Different steps of the proposed methodology are illustrated in Fig. 1. The basis of the method is the fusion of mathematical modelling with conventional HAZOP study in order to assess failure amplitude and duration, multiple deviations/failures, and domino effects scenario into this study. Simulation results depicted how ignoring these scenarios in conventional HAZOP study can lead to undesirable and hazardous situations. Although, investigation of multiple failures and domino effect scenarios

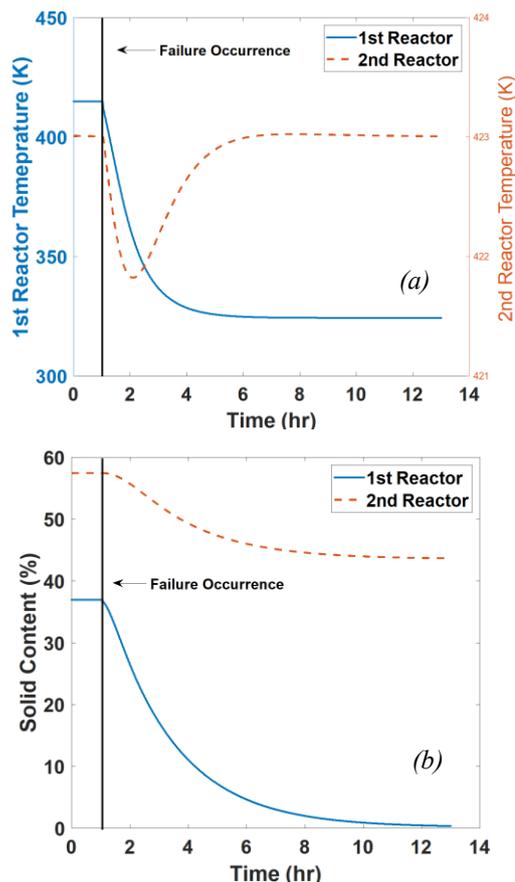


Figure 5. Evolution diagram of PV110 failure, (a) Temperature (b) Solid content.

with the aid of dynamic simulation is a breakthrough, it is tedious task when the process is too complex, and the number of interactive parameters is high. In our future work some new approaches incorporating AI algorithms and multivariable process monitoring (Mastali et al., 2008; Kazemi et al., 2019) will be suggested. Furthermore, other steps of the proposed HAZOP 4.0 methodology will be thoroughly investigated.

Nomenclature

A_c	Heat transfer area of condenser (m^2)
$[•]$	Species concentration (mol/m^3)
C_p	Specific heat capacity ($J/(kg K)$)
D_x, P_x	Dead and living polymer chain with length x
K	Reaction rate constant
\dot{m}	Mass flowrate (kg/s)
\dot{m}_r	Reactor outlet mass flow rate (kg/s)
T_c, T_w	Condenser and coolant water temperature (K)
T_R	Reactor temperature (K)
U	Overall heat transfer coefficient ($W/m^2 K$)
V_R	Reactor holdup (m^3)
V_{shell}	Volume of vapor space in the condenser (m^3)
V_{tube}	Volume of coolant fluid in the condenser (m^3)
ΔH	Heat of reaction ($kJ/mol K$)
ΔH_v	Heat of vaporization (J/mol)
ρ	Liquid density (kg/m^3)

Subscriptst

<i>c</i>	Condensation
<i>f</i>	Feed condition
<i>mix</i>	Reacting mixture
<i>v</i>	Vaporization
<i>w</i>	Coolant water
<i>x,y</i>	Chain length

REFERENCES

- Abbasi, T., Abbasi, T. and Abbasi, S. A. (2018). Role of HAZOP in assessing risk of accidents in chemical process industries: capability and lacunae. *International Journal of Engineering, Science and Mathematics*, 7(1), 482-499.
- Barton, J. A., & Nolan, P. F. (1989). Incidents in the chemical industry due to thermal runaway chemical reactions. *Hazards X: Process Safety in Fine and Speciality Chemical Plants*, 115, 3-18.
- Berdouzi, F., Olivier-Maget N. and Gabas, N. (2018). Dynamic Simulation for Risk Analysis: Application to an Exothermic Reaction. *Process Safety and Environmental Protection*, 113, 149-163.
- Carlos, M., Fatine, B., Nelly, O. M. and Nadine, G. (2018). Deviation propagation analysis along a cumene process by using dynamic simulations. *Computers & Chemical Engineering*, 117, 331-350.
- Danko, M., Frutiger, J., Jelemenský, L. and Sin, G. (2017). Monte Carlo based framework to support HAZOP study. *In Computer Aided Chemical Engineering*, 40, 2233-2238.
- Danko, M., Janosovsky, J. Labovsky, J. and Jelemensky, L. (2018). Fault propagation behavior study of CSTR in HAZOP. *Chemical Papers*, 72(3), 515-526.
- Darbra, R. M., Palacios, A., & Casal, J. (2010). Domino effect in chemical accidents: Main features and accident sequences. *Journal of hazardous materials*, 183(1-3), 565-573.
- Dunjó, J., Fthenakis, V., Vílchez, J. A. and Arnaldos, J. (2010). Hazard and operability (HAZOP) analysis: a literature review. *Journal of Hazardous Material*, 173(1-3), 19-32.
- Eggersmann, M., von Wedel, L., & Marquardt, W. (2004). Management and reuse of mathematical models in the industrial design process. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 27(1), 13-22.
- Eizenberga, S., Shacham, M. and Brauner, N., (2006). Combining HAZOP with dynamic simulation-Applications for safety education. *Journal of Loss Prevention in the Process Industries*, 19, 754-761.
- Health and Safety Executive (HSE), Table of Case Studies and Technical Measures, [Cited 10/01/2019]: <http://www.hse.gov.uk/comah/sragtech/casestudyind.htm>
- Herrera, M., Luna, Costa, A. and Lemes, E. (2018). Risk Analysis: A generalized Hazop methodology state-of-the-art, applications, and perspective in the process industry. *Journal of Vigilância Sanitária em Debate*, 6(2), 106-121.
- Hui, A. W., & Hamielec, A. E. (1972). Thermal polymerization of styrene at high conversions and temperatures. An experimental study. *Journal of Applied Polymer Science*, 16(3), 749-769.
- Janosovsky, J., Danko, M., Labovsky J. and Jelemensky, L. (2019). Software approach to simulation-based hazard identification of complex industrial processes. *Computers and Chemical Engineering*, 122, 66-79.
- Kazemi, Z., Safavi A. A., Pouresmaeili S. and Naseri F. (2019). A practical framework for implementing multivariate monitoring techniques into distributed control system. *Control Engineering Practice*, 82, 118-129.
- Labovsky, J., Svandova, Z., Markos, J., and Jelemensky, L. (2007). Model-based HAZOP study of a real MTBE plant, *Journal of Loss Prevention in the Process Industries*, 20, 230-237.
- Mastali, M., Safavi, A. A., & Palizban, H. A. (2008). An Easy to Interpret Fault Detection Approach to Multivariable Statistical Process Monitoring. In *16th Iranian Conference on Electric Engineering*.
- Mastan, E., Zhu, S. (2015). Method of moments: A versatile tool for deterministic modeling of polymerization kinetics. *European Polymer Journal*, 68, 139-160.
- Mihailidou, E. K., Antoniadis, K. D. and Assael, M. J. (2012). The 319 major industrial accidents since 1917. *International review of chemical engineering*, 4(6), 529-540.
- Murillo, C., Berdouzi, F., Nelly, O.M., and Gabas, N. (2018), Deviation propagation analysis along a cumene process by using dynamic simulations, *Computers and Chemical Engineering*, 117, 331-350.
- Necci, A., Cozzani, V., Spadoni, G., & Khan, F. (2015). Assessment of domino effect: State of the art and research Needs. *Reliability Engineering & System Safety*, 143, 3-18.
- Oppelt, M., Barth, M., & Urbas, L. (2015). The role of simulation within the life-cycle of a process plant. *Results of a global online survey*.
- Pfeffer, A. and Urbas, L. (2017). HAZOP studies for engineering safe modular process plants. *2017 22nd IEEE International Conference on Emerging Technologies and Factory Automation (ETFA)*, 1-4.
- Saada, R., Patel, D., & Saha, B. (2015). Causes and consequences of thermal runaway incidents—Will they ever be avoided?. *Process Safety and Environmental Protection*, 97, 109-115.
- Salimi, F., and Salimi, F. (2017). *A Systems Approach to Managing the Complexities of Process Industries*. Elsevier.
- Salimi, F., Vande Capelle, T. (2011). Application of SIL assessment, Bow-tie and API 14C to ensure a thorough Safety Concept, In *66th Annual Instrumentation Symposium for the Process Industries*.
- Zhao, L., Zhu, W., Papadaki, M. I., Mannan, M. S., & Akbulut, M. (2019). Probing into Styrene Polymerization Runaway Hazards: Effects of the Monomer Mass Fraction. *ACS Omega*, 4(5), 8136-8145.