Slovak Society of Chemical Engineering
Institute of Chemical and Environmental Engineering
Slovak University of Technology in Bratislava

PROCEEDINGS

43rd International Conference of the Slovak Society of Chemical Engineering

Hotel Hutník
Tatranské Matliare, Slovakia
May 23–27, 2016

Editor: prof. Jozef Markoš

ISBN: 978-80-89597-35-2, EAN: 9788089597352

Janošovský, J., Danko, M., Labovský, J., Jelemenský, Ľ.: Perspectives in model-based hazop study, Editor: Markoš, J., In *Proceedings of the 42nd International Conference of the Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 766–772, 2016.

Perspectives in Model-Based HAZOP Study

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Abstract
Hazard and operability (HAZOP) study is one of the most widely used process hazard analysis techniques for examining the hazards of a system and its operability problems. The possibility of hazard identification by applying the HAZOP procedure using a mathematical model is discussed. The model-based HAZOP study is meant to be very powerful tool in process safety engineering. The selected case studies were focused on multiple steady states phenomena. It would be presented that process simulation using Aspen HYSYS environment can be a feasible way to perform process safety analysis based on mathematical modelling.

Introduction

Safety engineering and loss prevention have become a more important issue in chemical industry in the last 40 years. Modern chemical processes have been modified towards extreme operation conditions due to legislative and economic pressures. These modifications have been consistently raising safety concerns. Chemical reactor is the central unit in majority of chemical productions. The reliability of a chemical reactor and its safe operation depends on the identification of its operability problems and possible hazardous consequences. For safe operation of reactive system it is important to have qualitative and quantitative knowledge about the limits of the key process parameters used for controlling the operating regime of the system. To identify these limits and to understand the danger of chemical processes, the necessity of appropriate process safety analysis (PHA) techniques in loss prevention was well recognized. However, conventional PHA techniques are expensive and time-consuming activities requiring assembly of experienced human expert teams. On the contrary, safety analysis methods based on mathematical modelling and computer simulation of chemical processes have significantly lower time and cost requirements compared to these conventional methods. Several PHA techniques such as What-If analysis, Failure Modes and Effects Analysis (FMEA) and Hazard and Operability (HAZOP) study represent potential candidates for the basis of automated hazard identification (Khan et al., 2015). Currently, FMEA and HAZOP study were the most preferred methods in the automation of process safety analysis. A literature review of the HAZOP-related research proved that ca. 40 % of published literature was in the recent past focused on automating HAZOP (Dunjó et al., 2010). The objective of the HAZOP study is to monitor the causes, propagation and consequences of process variable deviations leading to potential hazard and operability problems in examined system and to state recommended actions in order to avoid loss of lives and property. A process variable deviation is generated by meaningful application of guide word to a process variable (Kletz, 2001). These principles were successfully applied to various case studies consisting of mathematical modelling and hazard identification of multiphase chemical reactors e.g. reactive distillation column (Labovský et al., 2007), tubular reactor (Labovský et al., 2006) and fixed bed catalytic reactor (Laššák et al., 2010). This methodology contributed to decreasing the possibility of overlooking hazards and to increasing the efficiency of the hazard identification process (Labovská et al., 2014). Therefore, the fundamentals of HAZOP study were implemented for the proposed methodics of model-based hazard identification. Aspen HYSYS was selected as a simulation tool because of its frequent use in chemical industry and manageable data transfer between external software and simulation environment. Two case studies were selected for presentation of potential benefits of using Aspen HYSYS in model-based hazard identification. The presented case studies were focused on mathematical modelling of different reactor models and methods of simulation data evaluation.

The first case study – ammonia synthesis

Ammonia synthesis is process whereby nitrogen is changed from an inactive N_2 molecule to active NH_3. A small value of the equilibrium constant of ammonia synthesis in the range of low pressures forced the reaction conditions in the area of higher temperature and pressure. Ammonia is industrially produced in a fixed-bed catalytic reactor according to the following reaction scheme in the presence of solid catalyst:

$$N_2 + 3H_2 = 2NH_3 \quad (1)$$

A mathematical model of presented production consisted of fixed-bed reactor, feed preheater and refrigeration unit with vapour–liquid flash separator. The fixed-bed reactor system consists of three beds with feed quenching between each bed to adjust the optimal temperature profile and thus sufficient values of equilibrium constants in the reactive system. The feed preheater was modelled as a simplified heat exchanger, where feed was preheated by the outlet stream from the fixed-bed reactor. The cooled stream of products leaving feed preheater was additionally cooled to the desired temperature in the refrigeration unit. The outlet stream from refrigeration

system is separated to the liquid ammonia and gaseous purge in the flash separator. The structure of reactor system units corresponded to an industrial ammonia synthesis reactor, where existence of multiple steady states and temperature oscillations was observed (Morud and Skogestad, 1998). The mathematical model of the proposed system prepared in Aspen HYSYS environment is depicted in Figure 1. To calculate the physicochemical properties of pure components and their mixtures, Peng-Robinson equation of state with parameters from internal Aspen HYSYS database was used. The plug flow reactor model was selected for mathematical modelling of individual segments of the fixed-bed reactor. A simple end point method was selected in the Aspen HYSYS Heat Exchanger Model with the overall heat transfer coefficient calculated in order to simulate conditions described by Morud and Skogestad (1998) in an industrial accident in Germany, 1989.

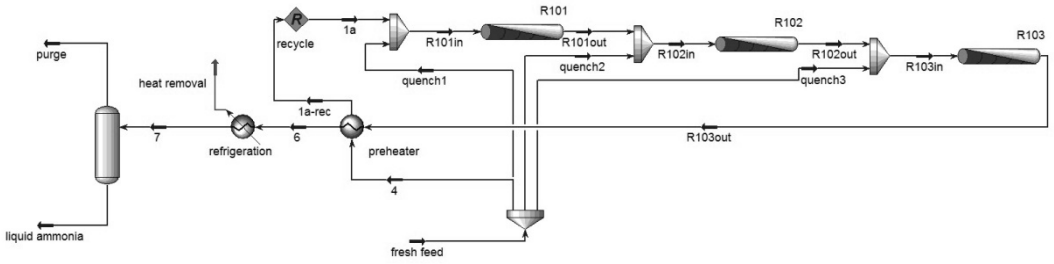

Figure 1. Ammonia synthesis model in Aspen HYSYS

The process parameters were adjusted to correlate with the current trends in ammonia production industrial units, where the reaction rate was given by Froment and Bischoff (1990) and optimised for higher activity of modern catalysts (Janošovský et al., 2015). The operating pressure was 20 MPa. Approximately one half of the "fresh feed" stream was preheated in "preheater", while the other half of the stream was quenched to every bed. The hot medium in "preheater" (product stream "R103out") was cooled and then separated. The compositions, temperatures and mass flows of key process streams are presented in Table I.

Table I
Design operation parameters – ammonia synthesis

Stream	Mass flow [10^3 kg/h]	Temperature [°C]	Mole fraction		
			NH_3	N_2	H_2
fresh feed	252	250.0	0.042	0.240	0.718
R101in	185	369.5	0.042	0.240	0.718
R101out	185	519.6	0.140	0.215	0.645
R102in	220	476.3	0.123	0.219	0.658
R102out	220	529.8	0.160	0.210	0.630
R103in	252	493.8	0.144	0.214	0.642
R103out	252	525.0	0.166	0.209	0.625
liquid ammonia	50	8.0	0.982	0.003	0.015

The first case study - results and discussion

Using the HAZOP principles mentioned earlier, list of temperature, pressure, flow and composition deviations for every stream was created and investigated. The fundamental requirement for model-based HAZOP study is the value of the deviation. The range of process variable deviation *D* (as defined in Eq. 2) varied according to parameter in this case study, e.g. the deviation range for the operating pressure was set from – 50 % to + 50 % (from 10 to 30 MPa) and for the feed temperature was set from – 30 % to + 30% (from 175 °C to 325 °C). The value of the step change of parameter was set to 1 %.

$$D = \frac{deviated\ value\ of\ the\ paramter - original\ value\ of\ the\ parameter}{original\ value\ of\ the\ parameter} * 100 \quad (2)$$

Process simulations in Aspen HYSYS environment were performed for all meaningful process variable deviations and simulation results were scanned in prepared software for any abnormal situations e.g. sudden change of parameter value. Such a situation occurred in "fresh feed" temperature deviation. The effect of temperature deviation in "fresh feed" stream on the temperature of stream "R103out" and on the overall

hydrogen conversion in reactor is shown in Figure 2. As depicted, dramatic change of reaction conditions occurred when "fresh feed" was decreased by 18 %, to 205 °C. Similar response of reactive system was observed in the case of operating pressure deviation. Drop of operating pressure by 30 % to 14 MPa caused analogous dramatic change of reaction conditions. This step decrease of reaction parameters indicated the shift from design steady state with desired production rate of ammonia to a steady state with lower reaction rates. When the failure causing deviation was corrected and the value of deviated parameter was set back to design intent, the reaction conditions remained in a steady state located on the lower solution branch. The operation of the unit had to be interrupted and new reactor start-up procedure had to be carried out. The ammonia synthesis modelling in Aspen HYSYS environment was able to identify only stable steady states. The process behaviour between the higher and lower solution branches is determined by the unstable steady states. The solver and numeric algorithms implemented in Aspen HYSYS were unable to identify positions of these unstable steady states.

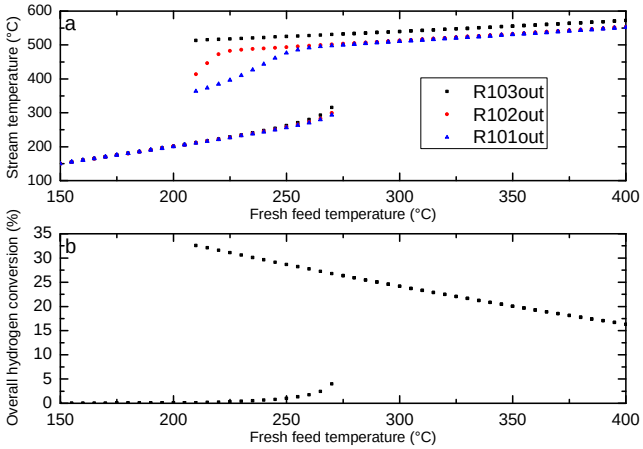

Figure 2. Effect of the "fresh feed" temperature on reaction conditions - (a) the "R103out", "R102out" and "R101out" temperature, (b) the overall hydrogen conversion

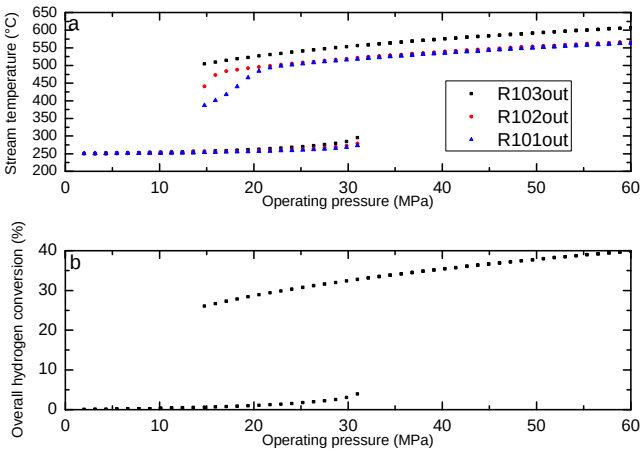

Figure 3. Effect of the operating pressure on reaction conditions - (a) the "R103out", "R102out" and "R101out" temperature, (b) the overall hydrogen conversion

The second case study – nitroglycerin production

Nitroglycerin is widely used in the pharmaceutical and explosives industry. Nitroglycerin is usually produced by the glycerol nitration. Significant thermal instability of nitroglycerin caused many industrial accidents in the process of nitration and purification. The main reaction in nitration process is the esterification reaction of glycerol and nitric acid in the presence of sulfuric acid as a dehydrating agent (Eq. 3).

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(ONO_2)_3 + 3H_2O \quad (3)$$

The reaction rate can be expressed as kinetic reaction model where the reaction order with respect to the glycerol and nitric acid is 0,935 and 1,117, respectively (Lu et al., 2008). The manufacture of nitroglycerin can be operated in batch or continuous regime. The Biazzi continuous process is one of the most common used

nitroglycerin manufacturing options. A mathematical model of proposed nitroglycerin production included continuously stirred tank reactor (CSTR) and simplified cooling system. Two inlet streams, mixed acid containing nitric and sulfuric acid and pure glycerol, were fed in CSTR in this case study. Nitric acid was supplied in excess. Brine was used as a coolant in internal cooling coils. Reaction mixture was a heterogeneous liquid phase containing reaction products, inert sulfuric acid and unreacted glycerol and nitric acid. In Aspen HYSYS environment, to create mathematical model of CSTR, additional vapour outlet stream with zero flow was required. According to basic concept, mathematical model of reactive system was built up from Aspen HYSYS models of "Continuously Stirred Tank Reactor" and "Cooler" (Figure 4). The two models were connected through heat flow. Although the heat transfer rate was not taken into account, this simplified reactor cooling system was sufficient for proposed model-based hazard identification because only the value of heat removal was monitored. Design values of key operation parameters are presented in Table II. The volume of reaction mixture in "CSTR100" was 0.035 m^3. The desired heat removal in "CSTR100" was set to 23.9 kW. To calculate the physicochemical properties of pure components and their mixtures, Wilson equation of state with parameters from internal Aspen HYSYS database was used. The achieved output molar concentration of glycerol in the Aspen HYSYS simulation of design operating point was in good agreement with experimental data provided by Lu et al. (2008) and by Astuti et al. (2014).

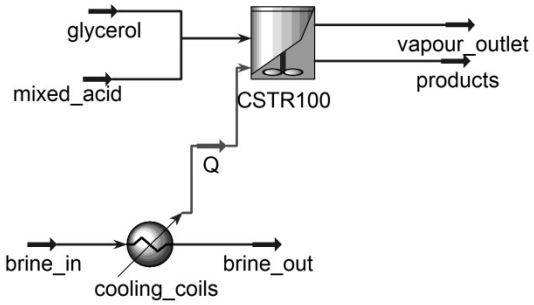

Figure 4. Nitroglycerin manufacture model in Aspen HYSYS

Table II
Design operation parameters – nitroglycerin manufacture

Stream	Mass flow [kg/h]	Temperature [°C]	Mass fraction				
			$C_3H_5(OH)_3$	HNO_3	H_2SO_4	$\boldsymbol{C_3H_5(ONO_2)_3}$	H_2O
glycerol	63.6	19	1.00	0.00	0.00	0.00	0.00
mixed_acid	311.6	19	0.00	0.51	0.49	0.00	0.00
products	375.2	15	0.00	0.08	0.41	0.41	0.10

The second case study - results and discussion

In many industrial accidents involving nitroglycerin, runaway effect was observed. Nitroglycerin thermal decomposition took place at 30 °C (Astuti et al., 2014). Therefore, nitration process should be carried out below this temperature. List of possible temperature, flow and composition deviations for every stream was created and investigated. The critical reaction temperature was set to 30 °C. Simulation results were scanned in prepared software for any stable states where temperature in reactor exceeded critical reaction temperature. The range of process variable deviation *D* (as defined in Eq. 2) was set from – 30 % to + 30%. The value of the step change of parameter was set to 1 %. According to fundamentals of CSTR modelling, the temperature in reactor was assumed to be equal to temperature of stream "products". The effect of heat removal deviation on "products" temperature is depicted in Figure 5. The effect of "mixed_acid" and "glycerol" parameters deviation on "products" temperature is presented in Figure 6 and 7, respectively. Generated deviations of "mixed_acid" parameters on "products" temperature were negligible from the point of view of process safety. But the deviation of heat removal and "glycerol" temperature caused shift from safe operation regime to a dangerous one where runaway effect was unavoidable. When the failure in cooling control system occurred and the heat removal in "CSTR100" was decreased by 11 % to the approximate value of 21.3 kW, the critical temperature in "CSTR100" was exceeded and the reactive system was operated in dangerous point (Figure 5). When the cooling control system was corrected and the heat removal was set back to 23.9 kW, the design operating point was restored. The similar behaviour was observed in the case of "glycerol" mass flow deviation. When the mass flow of stream "glycerol" was increased by 12 % to ca. 71.2 kg/h, the critical temperature in reactor was exceeded and runaway effect was possible (Figure 7a). The X mark represents operating point in which "CSTR100" temperature first time exceeded critical reaction temperature. The empty circle represents last operating point for which Aspen HYSYS solver found numerical solution. Above and under this point, numerical solution of

mathematic model in Aspen HYSYS environment was not found, the reaction rate calculation was switched off and reactor model was switched to a model of separator. Simulation results above the critical temperature in reactor were not in agreement with real behaviour of reaction mixture observed in past accidents in manufacture of nitroglycerin. The reason in is that the reaction kinetics of nitroglycerin decomposition was not taken into account in Aspen HYSYS model.

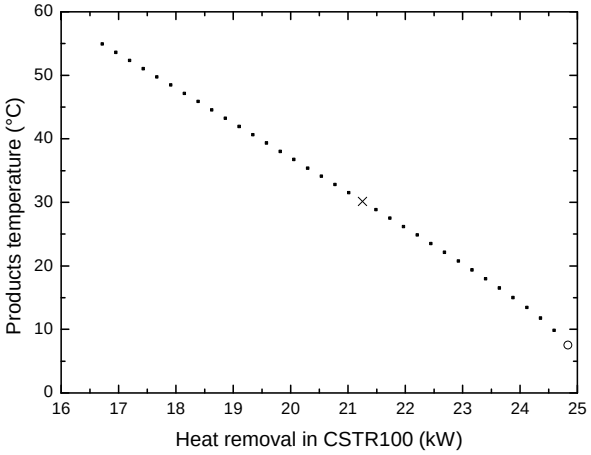

Figure 5. Effect of heat removal in "CSTR100" on temperature of the stream "products" (X mark – exceeding of the critical temperature, empty circle – last numerical solution)

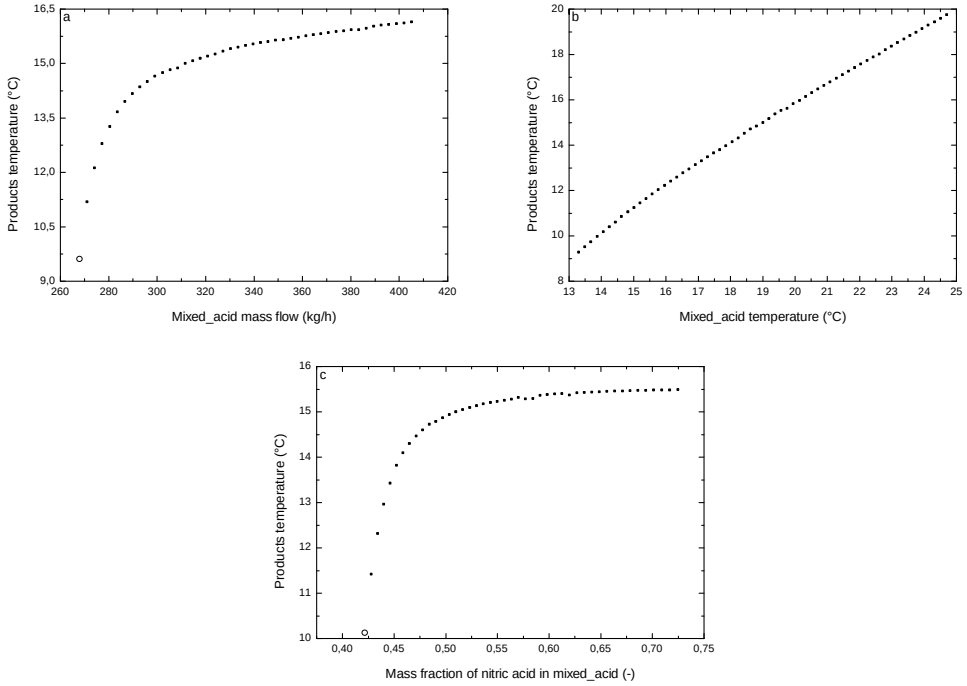

Figure 6. Effect of "mixed_acid" parameters on temperature of the stream "products" (X mark – exceeding of the critical temperature, empty circle – last numerical solution) – (a) mass flow, (b) temperature, (c) mass fraction of nitric acid in "mixed_acid"

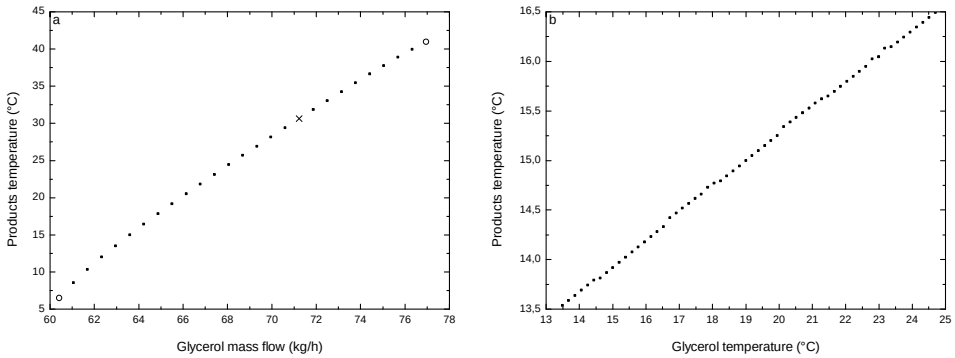

Figure 7. Effect of "glycerol" parameters on temperature of the stream "products" (X mark – exceeding of the critical temperature, empty circle – last numerical solution) – (a) mass flow, (b) temperature

Conclusion

This paper focused on creating a methodology of simulation data evaluation from the point of view of safety engineering. Automated model-based HAZOP study principles were applied to two case studies in presented work. Process simulation in Aspen HYSYS environment was found to be capable of appropriate mathematical modelling of two different reactor models, plug flow reactor and continuously stirred tank reactor, where reaction took place in the gaseous and liquid phase, respectively. In the case study of ammonia synthesis, process operation only in stable steady states was observed. In the case study of nitroglycerin manufacture, numerical problems occurred in region of reaction temperature near 0 °C and hindered the possibility of model-based hazard identification in wider range of process variables. Different evaluation methods of simulation results were performed. In the first case study, sudden step change in reaction conditions was observed, recorded and further monitored. In the second case study, user-set value of critical temperature in reactor was monitored. Presented safety analysis results were in good agreement with conventional HAZOP studies. Presented results proved that not only presence of deviation, but also its value (and duration) should be considered in order to perform sufficient process safety analysis. The integration of automated model-based hazard identification in PHA techniques can potentially lead to more efficient prevention of the loss of lives and property. It can be successfully applied at the design stage of the technology, for the operation of an already existing chemical unit, for educational purposes, for improving the decision making process and training of operators in chemical plant.

Acknowledgments
This work was supported by the Slovak Scientific Agency, Grant No. VEGA 1/0749/15 and the Slovak Research and Development Agency APP-14-0317.

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