The role of a commercial process simulator in computer aided HAZOP approach

Ján Janošovský, Matej Danko, Juraj Labovský, Ľudovít Jelemenský*
Institute of Chemical and Environmental Engineering, Slovak University of Technology, Bratislava, Slovakia

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A B S T R A C T
Process safety is one of the key pillars of sustainable industrial development. In combination with the increasing use of computer aided process engineering, the demand for an appropriate model-based safety analysis tool capable to identify all hazardous situations leading to a major accident has increased. Commercial process simulators are equipped with extensive property databases and they employ high accuracy mathematical models providing the capability to simulate real behavior of a process operated within the area of the mathematical model validity. The main focus of this work is to improve standard hazard identification methods by the combination of hazard and operability (HAZOP) study and process simulation in commercial process simulator Aspen HYSYS. Software tool consisting of modules for computer simulation and complex analysis of simulation data will be proposed. The developed tool was applied to modern chemical productions exhibiting strong nonlinear behavior, where proper prediction of consequences can be very difficult. In the first case study, hazard identification in continuous glycerol nitration employing user-dependent analysis is presented. Mathematical methods of simulation data analysis independent of the user is demonstrated in the second case study of ammonia synthesis. Possibilities and limitations of the proposed tool are revealed and discussed in this work.

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1. Introduction

Several serious industrial accidents (e.g. Flixborough, Seveso, Bhopal and Tianjin disasters) in the past have underlined the importance of loss prevention approach in chemical industry. Dynamic development of industry has not only resulted in more efficient and profitable chemical productions, but also in the increase of plants complexity as well as the variety of chemicals and processes used in the plant. In addition, the majority of modern processes exhibit strong nonlinear behavior. Therefore, the task of identifying potential sources of hazards has become more complex (De Radaemarker et al., 2014). In combination with the ever growing use of computer aided process engineering, the demand for an appropriately detailed safety analysis tool capable to identify all hazardous situations leading to a major accident has increased. The safety point of view should be implemented not only in the design stage of any chemical plant, but also during the entire plant life cycle. Identification of all possible fault propagation paths is thus, for example, the key feature of proper design of control systems (Leveson and Stephanopoulos, 2014; Parmar and Lees, 1987; Seider et al., 2014).

Actual trend in computer aided loss prevention is to improve standard hazard identification methods by employing mathematical modeling and process simulation in commercially available simulators. Commercial process simulators are equipped with extensive property databases and utilize high accuracy mathematical models thus providing the capability to simulate real behavior of a process operated within the area of the mathematical model validity. Model-based hazard identification also benefits from the fact that mathematical modeling of the analyzed process is usually employed as a part of process design and optimization activities, e.g. optimization of biorefinery downstream processes employing SimSci PRO/II (Corbetta et al., 2016), design of hydrocarbons separation unit using Aspen Plus (de Riva et al., 2016) and Aspen HYSYS supported design of syngas production proposed by Sunny et al. (2016). If the use of process simulators is well implemented in the company policy, successful adoption of safety extensions for these simulators is more likely.

Model-based approach was applied not only in hazard identification, but also in reliability engineering (Favoro and Saleh, 2016) and quantitative risk assessment (Labovský and Jelemenský, 2011; Qi et al., 2014). While mathematical modeling in these areas is accepted by...
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Reaction order of glycerol</td>
</tr>
<tr>
<td>A</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>b</td>
<td>Reaction order of nitric acid</td>
</tr>
<tr>
<td>c</td>
<td>Molar concentration, $\text{mol}^{-1}$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy, $\text{J mol}^{-1}$</td>
</tr>
<tr>
<td>$p$</td>
<td>Partial pressure, bar</td>
</tr>
<tr>
<td>r</td>
<td>Reaction rate</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant, $\text{J K}^{-1} \cdot \text{mol}^{-1}$</td>
</tr>
</tbody>
</table>

### Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\beta$</td>
<td>Enhancement factor</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Catalyst bulk density, $\text{kg m}^{-3}$</td>
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</table>

the safety engineering community, model-based hazard identification is still subject of discussion because of model validity and its input parameters uncertainty (Labovská et al., 2014; Švandová et al., 2009). Published model-based tools vary in the complexity of mathematical models and simulation data evaluation methods. The complexity of mathematical models depends on whether they were constructed specifically for the analyzed system or the developed tool employed a group of mathematical models, e.g. a commercial process simulator. Although the computing time increases with the increase of model complexity, several efforts were made towards shortening the time required for the solution of large nonlinear systems, e.g. utilization of parallel computing (Danko et al., 2015; Labovský et al., 2015). The simulation data can be evaluated manually, automatically or by a combination of both ways. The majority of published works benefited from the robustness and complexity of the hazard and operability (HAZOP) study that belongs to the most used process hazard analysis procedures worldwide and is recognized as an effective and accurate hazard identification method in chemical industry (Dunjó et al., 2010; Kletz, 2001).

Eizenberg et al. (2006) combined a standard HAZOP study and process simulation in MATLAB in order to develop a software tool for better understanding of hazards for the safety education process. Similar approach was adopted in the work of Li et al. (2010). The examined system was a three-phase hydrogenation in an intensified stirred continuous reactor and the simulation results of hazardous cases generated based on the HAZOP principles were presented. HAZOP principles were also applied in the safety assessment based on parametric sensitivity analysis of the key operating parameters in a hydrogen production unit (Ghaseemzadeh et al., 2013).

Previously mentioned works focused on safety analysis based on a specific mathematical model of the unit under review. A disadvantage of such an approach is its limited application. If the safety analysis of another unit was required, it was necessary to decompose the current mathematical model and to form and validate a new set of equations describing the behavior of the new unit. Therefore, this approach is not suitable for the development of a universal model-based hazard identification tool. This limitation can be eliminated by involving the use of a commercial process simulation software with predefined and validated sets of unit operations commonly used in industry. In this case, the safety analysis of different units in a plant requires only switching between the generally prepared mathematical models.

A successful combination of the HAZOP study and simulation in Aspen Plus in the case study of biodiesel production was presented by Jeerawongsuntorn et al. (2011). Alternatives including standard and reactive distillation were analyzed for the purpose of the decision-making process improvement and safety instrumented system implementation. The K-Spice software was used for process simulation followed by the HAZOP analysis in the work of Enemark-Rasmussen et al. (2012). Results of the simulated deviations were recorded, evaluated and ranked according to the severity of deviations determined by the sensitivity measure. Tian et al. (2015) introduced the dynamic simulation-based HAZOP (DynSim-HAZOP) methodology employing dynamic simulation in process simulators such as Aspen Dynamics, Aspen Plus and Aspen HYSYS to perform model-based safety analysis of an extractive distillation column and an ammonia synthesis plant. Both Jeerawongsuntorn et al. (2011) and Tian et al. (2015) used monitoring of user defined threshold values (e.g. auto-ignition temperature or maximum allowed liquid level in the separator) in the simulation data evaluation. Enemark-Rasmussen et al. (2012) partially automated the process of data evaluation by quantifying the deviation effects and their ranking according to the sensitivity measure, i.e. comparing the change of the selected parameter (temperature, pressure...) to the change of the deviated parameter. The proposed ranking system allowed the elimination of deviations with negligible impact on the process. Systematic approach combining advantages of previously mentioned works applied in process simulation in Aspen HYSYS was proposed by Janošovský et al. (2016a) and it was further analyzed (Janošovský et al., 2016b).

Principal objective of this paper is to summarize issues with the developing computer aided hazard identification tool based on process simulation in the Aspen HYSYS environment. Two case studies focused on modern continuous productions exhibiting strong nonlinear behavior with various levels of complexity are presented. In the first case study, hazards of glycerol nitration in a continuously stirred tank reactor are identified and evaluated. The presence of the multiple steady states phenomenon in an ammonia synthesis reactor with a preheating system and the related numerical complications are discussed in the second case study.

2. Model-based HAZOP tool

Aspen HYSYS v8.4 simulation environment was selected as the commercial simulation tool. Aspen HYSYS is a powerful engineering software tool for steady state and dynamic

![Fig. 1 – Methodology of the proposed software tool.](image-url)
modeling designed for continuous processes consisting of multiple process units especially in gas and oil industry (AspenTech, 2015). All information necessary for the description of physico-chemical properties of individual components and their mixtures are contained in fluid packages stored in the Aspen HYSYS library. Its extensive size allows more effective search for the solution of complex mathematical models by providing an accurate estimation of all necessary model parameters and an appropriate numerical solver. Components not available in the Aspen HYSYS library can be specified as “Hypo Components” by entering the required properties (density, boiling point etc.) in the program. Although various studies found negligible differences between the process simulations in Aspen Plus and Aspen HYSYS (Øi, 2012; Smejkal and Šoš, 2002), the use of Aspen HYSYS in model-based hazard identification is scarce.

Deviations observed by a conventional HAZOP study are generated by a simple logic combination of guide words (more, less, none etc.) with process parameters (temperature, pressure, flow etc.). Such information is insufficient for mathematical modeling. The model-based HAZOP study requires not only the existence of the deviation but also its value and, in case of dynamic simulation, also its duration. Therefore, determination of the deviation range is added to the process of standard HAZOP deviation generation. In the final deviation list, deviations characterized as “higher temperature” or “lower flow” are not satisfactory; but instead, deviations like “temperature higher by 10%” or “flow lower by 10%” (in case of dynamic simulation, “flow lower by 10% lasting for one hour”) are to be given. This fundamental demand for deviation quantification in the model-based HAZOP study provides a promising way of at least partial elimination of the disadvantages of the conventional HAZOP study such as the possibility of overlooking hazardous events especially when they have never been observed before.

The amount of data necessary to be handled during a hazard identification process geometrically increases when the dimension of size is assigned to conventional HAZOP deviation. This task requires a robust software solution with well-arranged data structure to enable the expert HAZOP team to smoothly process and visualize complex relations between various process parameters. The increase in the amount of data being processed and the complexity of relations is even more significant when time dimension of a deviation is
considered. As summarized in Section 1, although dynamic process simulation provides more detailed insight into potential nonlinearity and operability problems resulting from process nonlinearity, the majority of possible industrial accidents can be, at least partially, revealed employing just the steady state simulation approach. For the simplicity and explanatory purpose, only possibilities of steady state simulation in the Aspen HYSYS environment are further discussed in this paper.

Methodology of the proposed software tool consists of a module utilizing Aspen HYSYS and a module for the application of HAZOP principles (Fig. 1). A unique software dictionary and infrastructure have been developed to ensure a reliable connection between the simulator and the HAZOP module. First, the access to Aspen HYSYS and the availability of an active simulation case and its flowsheet are tested. After the connection is established, information about individual units and streams is transferred and stored in the internal database. In the next step, parameters of individual streams available for the HAZOP study are highlighted for the user. The user is then able to select the desired parameters and to create their deviations using the default value range or creating a user specified value range. Only the application of quantitative guide words is currently considered. From the software engineering point of view, the use of qualitative guide words in computer aided approach is limited because of practically infinite possibilities of their interpretation. When the deviation list is complete, it is saved. When the process simulation is launched, deviations from the list are sent to the Aspen HYSYS environment and simulated one by one. This process is schematically illustrated for steady state simulation in Fig. 2. Generated deviations are stored in form of data containing four levels: <type><ID><parameter><deviation value>. Process footprints contain information also in four-level structure <type><ID><parameter><value after deviation>. In case of dynamic simulation, additional levels quantifying the dimension of time have to be introduced. After each simulation, steady state found by the Aspen HYSYS solver is stored in the internal database in form of a process footprint containing all necessary information about the individual units and streams. List of process footprints presents de facto the list of HAZOP consequences in form of pairs <deviation><process footprint>.

After the last deviation from the list is simulated, evaluation of the simulation data takes place. Consequences of each simulated deviation are investigated and hazardous events or operability problems are recognized. The investigation procedure presents predefined methods of analysis, e.g. parametric sensitivity analysis or user-defined critical values monitoring. Detected significant consequences are formulated in an HAZOP-like report which serves as a supporting process hazard analysis for the human expert HAZOP team. The scope and flexibility of the proposed methodology were demonstrated on two case studies focused on modern nonlinear processes frequently used in chemical industry.

### Table 1 – Kinetic parameters of glycerol nitration.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$9.78 \times 10^{22}$</td>
<td>$l^{-1.052} mol^{-1.052} min^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>14674.04</td>
<td>$K$</td>
</tr>
<tr>
<td>$a$</td>
<td>0.935</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$b$</td>
<td>1.117</td>
<td>Dimensionless</td>
</tr>
</tbody>
</table>

![Glycerol nitration model in Aspen HYSYS environment.](image)

#### 3. Results and discussion

#### 3.1. Case study 1—continuous glycerol nitration in stirred tank reactor

Nitroglycerin belongs to chemical compounds widely used in pharmaceutical industry (Boden et al., 2012) and as propellant ingredients (Pichtel, 2012). One of the most common indus-
tion and the composition of the reaction mixture correlated by Lu et al. (2008).

Several hazardous events occurred during the nitration reaction and product storage due to the thermal instability of nitroglycerin (Lu and Lin, 2009; Lu et al., 2008; Pichtel, 2012). Recommended temperature of the mixture in the reactor is 20 °C and thus the probability of thermal decomposition of nitroglycerin resulting in the runaway effect at above 30 °C is very high (Astuti et al., 2014). Therefore, appropriate safety assessment is needed to recognize potentially dangerous deviations leading to runaway situations. A HAZOP study utilizing the proposed software tool was performed. Deviated parameters for this case study were: flow of the stream “brine.in”, i.e. heat removal in unit “CSTR100”, and temperature, flow and composition of input streams “glycerol” and “mixed_acid”. The absolute and relative deviations were defined as:

\[
\text{absolute deviation} = \text{parameter value at failure state} - \text{design value of the parameter} \tag{3}
\]

\[
\text{relative deviation} = \frac{\text{absolute deviation}}{\text{design value of the parameter}} \times 100 \tag{4}
\]

The relative deviation range for this case study was set from −30% to +30% with the step of 1%. The evaluation of simulation data was focused on monitoring of the reactor temperature, i.e. user specified critical value of a selected parameter. The reactor temperature was assumed to be equal to the temperature of stream “product”. If the simulated deviation caused exceeding of the safety limit (temperature of 30 °C in the reactor), the deviation was highlighted for user and classified as dangerous.

Visualized effect of the analyzed deviations is depicted in Figs. 4–6. As it can be seen, safety constraints were exceeded in case of cooling system and glycerol flow control failure. Fig. 4 shows the effect of the heat removal deviation on the reactor temperature. When the cooling system failure caused heat removal decrease of more than 11%, the “product” temperature and temperature in the CSTR100 exceeded the critical value of 30 °C and runaway would have occurred. A similar effect was observed and is plotted in Fig. 5, where the effect of “glycerol” parameters deviation is shown. When mass flow of stream “glycerol” was increased, temperature in CSTR100 increased. Above the mass flow of approximately 71 kg/h (absolute deviation of 7.6 kg/h and relative deviation of 12%), the safety constraint was exceeded. On the other hand, the “glycerol” temperature deviation had negligible effect on process safety as well as the effect of “mixed_acid” parameters deviation (Fig. 6).

It is necessary to point out numerical problems regarding the solution in case of process variables deviation—heat removal in CSTR100, “glycerol” temperature and “mixed_acid” composition and mass flow (empty circles in Figs. 4–6). These problems cause significant decrease of the temperature in CSTR100 (below—100 °C) because the reaction was switched off by the Aspen HYSYS solver. Inability to find a satisfactory steady state was attributed to the presence of the heterogeneous liquid phase and values of reaction temperature near the freezing point. Aspen HYSYS was not capable of modeling the effect of solidification. Another important observation is the existence of steady states found above the critical temperature. Aspen HYSYS was unable to detect runaway effect in the CSTR100 because of the selected mathematical reactor model that takes into account only user defined chemical reactions. Thus, the reaction kinetics of nitroglycerin decomposition was not taken into account. Steady states found above 30 °C by the Aspen HYSYS solver were only hypothetical steady states contrary to the real behavior of the reaction mixture above 30 °C.

Although previously stated problems limit the extent of safety analysis, the developed software tool successfully identified hazardous events and generated a HAZOP-like report (Table 3) based on simulation data analysis using a user-specified critical value of the selected parameter. Results of the conducted HAZOP study were in good agreement with safety analysis done by Lu et al. (2008).

### Table 2 – Design parameters of glycerol nitration.

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>63.6</td>
<td>19</td>
<td>C3H5(OH)3, HNO3, H2SO4, C3H5(NO2)3, H2O</td>
</tr>
<tr>
<td>Mixed_acid</td>
<td>311.6</td>
<td>19</td>
<td>1.00, 0.00, 0.00, 0.00, 0.00</td>
</tr>
<tr>
<td>Product</td>
<td>375.2</td>
<td>15</td>
<td>0.00, 0.08, 0.41, 0.41, 0.10</td>
</tr>
<tr>
<td>Vapor_output</td>
<td>0.0</td>
<td>15</td>
<td>0.00, 0.08, 0.41, 0.41, 0.10</td>
</tr>
</tbody>
</table>

### Table 3 – HAZOP-like report on glycerol nitration.

<table>
<thead>
<tr>
<th>Deviation</th>
<th>Consequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat removal in CSTR100 lower by 11% “Glycerol” mass flow higher by 12%</td>
<td>Possible runaway</td>
</tr>
<tr>
<td></td>
<td>Possible runaway</td>
</tr>
</tbody>
</table>

Fig. 4 – Effect of heat removal deviation in CSTR100 on the temperature in CSTR100 (bold red line—runaway conditions, X mark—design point, empty circle—last numerical solution in Aspen HYSYS environment, where reaction rate was calculated). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3.2. Case study 2—ammonia synthesis

Ammonia has wide application in chemical industry, e.g. in the production of fertilizers, cleaning agents or explosives. It is produced by heterogeneously catalyzed hydrogenation of nitrogen in the gaseous phase (Eq. (5)). The reaction rate was given by Froment et al. (2010) and modified to include the effect of higher activity of modern industrial catalysts as presented in Eq. (6). Kinetic parameters (Morud and Skogestad, 1998) are summarized in Table 4.

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]  

(5)

\[
\eta_{\text{hydrogenation}} = \frac{\beta}{P} \left( A_{2} e^{\frac{E_{2}}{RT}} \frac{P_{\text{H}_2}^{1.5}}{P_{\text{N}_2}} - A_{-2} e^{\frac{E_{-2}}{RT}} \frac{P_{\text{H}_2}}{P_{\text{N}_2}} \right)
\]  

(6)

![Fig. 5 - Effect of mass flow (a) and temperature (b) of stream “glycerol” on the temperature in CSTR100 (bold red line—runaway conditions, X mark—design point, empty circle—last numerical solution in Aspen HYSYS environment, where reaction rate was calculated). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 6 - Effect of mass flow (a), temperature (b) and composition (c) of stream “mixed_acid” on the temperature in CSTR100 (X mark—design point).](image2)

<table>
<thead>
<tr>
<th>Table 4 – Kinetic parameters of ammonia synthesis.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>$A_2$</td>
</tr>
<tr>
<td>$E_{2}$</td>
</tr>
<tr>
<td>$A_{-2}$</td>
</tr>
<tr>
<td>$E_{-2}$</td>
</tr>
<tr>
<td>$\beta$</td>
</tr>
</tbody>
</table>

One of the most used industrial ways of ammonia synthesis is its continuous production in an adiabatic fixed-bed catalytic reactor. Fixed-bed reactors usually consist of several beds connected in series with feed quenching between the beds. The purpose of feed quenching is to achieve optimal temperature profile throughout the whole reactor system. The goal of this
case study was to reproduce the strongly nonlinear process behavior that occurred in German ammonia plant in 1989 and was well documented by Mancusi et al. (2000). The cause of the unusual behavior of the reaction mixture was the presence of the steady state multiplicity phenomenon in ammonia synthesis (Laššák et al., 2010; Mancusi et al., 2000; Morud and Skogestad, 1998; Pedemera et al., 1997). Although identification of paths between stable and unstable steady states generally requires complex mathematical methods such as bifurcation and continuation analyses (Labovský et al., 2006; Labovský et al., 2007), AspenTech software was successfully used to obtain approximate locations of stable steady states of an industrial acetic acid dehydration system (Li and Huang, 2011). The ammonia plant under review consisted of one reactor separated to three segments and a feed preheater. The reactor system was extended by a separation unit consisting of a refrigeration system and a flash separator (Fig. 7). Design values of the key operating process variables (Table 5) were specified by Janosovský et al. (2015). Operating pressure was 20 MPa and the total reactor volume was 31.52 m³ with the diameter of 0.9 m.

The Peng–Robinson equation of state with parameters from the internal Aspen HYSYS library was used to calculate the properties of gaseous mixtures. Reaction types pre-defined in Aspen HYSYS did not satisfactorily correlate reaction kinetics in Eq. (6). Therefore, HYSYS extension containing the proposed kinetics was registered through the customization procedure. According to previous studies (Honkala et al., 2005; Lisal et al., 2005), the Aspen HYSYS model of “Plug Flow Reactor” was selected as the appropriate mathematical model for ammonia synthesis reactor performance simulation. Model of the feed preheating system was built from the Aspen HYSYS model of “Heat Exchanger”. The overall heat transfer coefficient was calculated to approach the observed behavior of the preheater (Morud and Skogestad, 1998). Although no material recycle was present, the “Recycle” unit had to be applied because of the energy recycle (heat generated by the reaction was partially transferred from stream “R103out” to stream “4” in the preheater). In this form, mathematical model of ammonia synthesis in the Aspen HYSYS environment was verified and ready for HAZOP analysis.

For this case study, results of the HAZOP study applied for the operating pressure and the temperature of “fresh feed” are discussed. Operating pressure relative deviation was set from −50% to +100% with the step of 5% (equal to the operating pressure absolute deviation of 1 MPa). Parameters of “fresh feed” were deviated in the range of relative deviations from −30% to +30% with the step of 2% (equal to the temperature absolute deviation of 5 °C). The effect of the “fresh feed” temperature and the operating pressure on the temperature profile of the reaction mixture is plotted in Fig. 8. Step change of the temperature of streams “R103out”, “R102out” and “R101out” was clearly caused by steady state multiplicity. If the temperature of “fresh feed” was decreased by 18% or the operating pressure was lowered by more than 25%, the reactive system was shifted towards lower solution branch, where the reaction rate was practically equal to zero. Even after the deviated parameter was set back to the design value, the reactive system remained in the steady state with low reaction conversion. To restore the original design point, new reactor start-up was required. Solution branches composed of stable steady states were plotted. However, the Aspen HYSYS solver was incapable of finding the position of unstable steady states during the simulation.

Unlike the first case study, definition of critical values by the user was not employed. On the contrary, mathematical methods of analysis independent from the user have been developed. Fig. 9 shows possible graphical output of such an analysis when applied on the data set plotted in Fig. 8b. The curves in Fig. 9 were constructed as follows: the starting position of the analysis was the design point (on the higher solution branch). Operating pressure was first increased and then decreased; i.e. only the shift from the higher to the lower solution branch is described by these curves. Parameters used in the analysis are defined by Eqs. (3), (4) and (7).

As depicted, a small change of one parameter caused a significant change of another one, e.g. operating pressure absolute deviation of −6 MPa (−30%) resulted in a sudden decrease of the “R103out” temperature by more than 250 °C (50%) (Fig. 9a, b). This phenomenon was more significantly exposed in the parametric sensitivity analysis (Fig. 9c), where the peak of the “R103out” temperature sensitivity to the operating pressure was clearly identified in the region of the operating pressure absolute deviation of −6 MPa. It was possible to automatically detect nonstandard behavior of the analyzed reactive system by monitoring these step changes. This approach is particularly applicable to strongly nonlinear

![Ammonia plant in Aspen HYSYS environment.](image)

**Table 5 - Design parameters of ammonia synthesis.**

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Fresh feed</td>
<td>252</td>
<td>250</td>
<td>0.239, 0.719, 0.042</td>
</tr>
<tr>
<td>4</td>
<td>127</td>
<td></td>
<td>0.239, 0.719, 0.042</td>
</tr>
<tr>
<td>Quench1</td>
<td>58</td>
<td>250</td>
<td>0.239, 0.719, 0.042</td>
</tr>
<tr>
<td>Quench2</td>
<td>35</td>
<td>250</td>
<td>0.239, 0.719, 0.042</td>
</tr>
<tr>
<td>R101out</td>
<td>185</td>
<td>520</td>
<td>0.215, 0.645, 0.140</td>
</tr>
<tr>
<td>R102out</td>
<td>220</td>
<td>530</td>
<td>0.210, 0.630, 0.160</td>
</tr>
<tr>
<td>R103out</td>
<td>252</td>
<td>525</td>
<td>0.209, 0.625, 0.166</td>
</tr>
<tr>
<td>6</td>
<td>252</td>
<td>436</td>
<td>0.209, 0.625, 0.166</td>
</tr>
<tr>
<td>Liquid ammonia</td>
<td>50</td>
<td>8</td>
<td>0.003, 0.015, 0.982</td>
</tr>
</tbody>
</table>
processes characterized by a rapid or a step change of certain process parameters, e.g. systems exhibiting steady state multiplicity.

Despite the inability to simulate real behavior of the reactive system in the region of unstable steady states, the proposed software tool satisfactorily simulated sudden changes of operating conditions between the higher and lower solution branch. Location of the found stable steady states was in strong agreement with the solution diagrams obtained by Laššák et al. (2010) and Mancusi et al. (2000). Operability problems corresponding to those observed in industrial ammonia plants were detected and summarized in a HAZOP-like report (Table 6). In addition, the HAZOP study was accelerated by implementation of mathematical methods for partially automated identification of hazards and operability problems.

### 4. Conclusions

Process hazard analysis supported by a commercial process simulator can be a very powerful tool for the analysis of unexpected operating conditions resulting from nonlinear process behavior. In this paper, construction of a mathematical model in the Aspen HYSYS environment and steady state simulations applied to two case studies were discussed. Hazards and operability problems identified were in good agreement with industrial practice. Process simulations in Aspen HYSYS benefited from the pre-defined property fluid packages and mathematical models of frequently used unit operations. However, several modifications of the pre-defined models were necessary in order to simulate real process behavior. In the first case study, alterations in the built-in model parameters and interaction with the user were crucial to recognize valid results of computer simulations. The Aspen HYSYS built-in solver was unable to find steady state solutions in the whole range of deviations. In the second case study, a set of robust mathematical methods for proper HAZOP analysis of the reactive system exhibiting steady state multiplicity were developed, but the region of unstable steady states remained unidentified.

Resulting from the general simulation environment of Aspen HYSYS, the developed tool can be adapted to other chemical processes while maintaining its reliability and accuracy. Universal application of the proposed tool presents a promising way of more effective and less time consuming procedure of hazard identification based on HAZOP principles. The presented output reports can serve as a guide for human HAZOP expert team or in the design and operation phase of modern chemical plants.

### Table 6 – HAZOP-like report on ammonia synthesis.

<table>
<thead>
<tr>
<th>Deviation</th>
<th>Consequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating pressure lower by 70%</td>
<td>Operability problem—reaction</td>
</tr>
<tr>
<td>“Fresh feed” temperature lower by 18%</td>
<td>Operability problem—reaction</td>
</tr>
<tr>
<td></td>
<td>conversion too low</td>
</tr>
<tr>
<td></td>
<td>conversion too low</td>
</tr>
</tbody>
</table>

**Fig. 8** – Effect of “fresh feed” temperature (a) and operating pressure (b) on the temperature of streams ‘R103out’ (black square), “R102out” (red circle) and “R101out” (blue triangle) (design point—thick square). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 9** – Effect of operating pressure deviation on the “R103out” temperature.
Robustness and applicability of numerical methods currently employed in the proposed software tool are strictly limited by the Aspen HYSYS built-in solver capability. Future research will be focused on the elimination of revealed disadvantages of Aspen HYSYS modeling and on the expansion of the range of software application towards dynamic simulations. The use of Aspen HYSYS will be extended by developed modules for the simulation of modern industrial production and separation units and by utilization of numerical procedures optimized for process safety engineering purposes. With such modules, more effective analysis of complex fault propagation paths and in-depth investigation of deviation–consequence interactions will be achievable.

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References


