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INVESTIGATION OF NONLINEAR BEHAVIOUR OF CHEMICAL REACTORS USING ASPEN HYSYS AS A USEFUL TOOL FOR MODEL-BASED HAZARD IDENTIFICATION

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Introduction

An essential task in chemical industry is maintaining high quality of products and acceptable level of risk and environmental pollution. In the majority of chemical productions, a chemical reactor, a vessel where reactions are carried out, is a central unit. Reliability of a chemical reactor and its safe operation depends on the identification of its operation malfunctions and possible hazardous consequences. Modern chemical processes have been modified towards extreme operation conditions due to legislative and economic pressures. These modifications have however raised safety concerns. For reactor operation in a safe regime it is important to have qualitative and quantitative knowledge about the limits of the key process parameters controlling the operating regime of the reactor. The necessity of appropriate process safety analysis (PHA) techniques in loss prevention has been well recognized after the occurrence of several tragic accidents that could have been avoided. Safety analysis methods based on mathematical modelling and computer simulation of chemical processes have significantly lower time and cost requirements compared to 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 automated hazard identification. Currently, FMEA and HAZOP study are the most preferred methods in the automation of process safety analysis. A literature review of the HAZOP-related research proved that nearly 40 % of published literature is focused on automating HAZOP². The objective of a HAZOP study is to monitor and list the causes, propagation and consequences of process variable deviations leading to potential hazard and operability problems in the examined system. A process variable deviation is generated by the combination of guide words (more, less, none …) and process variables (temperature, pressure, flow …). These principles were successfully applied to various case studies consisting of mathematical modelling and hazard identification of multiphase chemical reactors, e.g. reactive distillation column⁴, tubular reactor⁵ and fixed bed catalytic reactor⁶. This methodology contributed to the decrease of the possibility of overlooking hazards and to the increase of the efficiency of the hazard identification process⁷. Therefore, fundamentals of the HAZOP study were adopted in this work for model-based hazard identification.

Products of Aspen Technology Inc. were chosen for mathematical modelling of chemical units because of the access to one of the most extensive property databases and frequent application in chemical engineering. Aspen HYSYS was selected as a simulation tool because of its manageable data transfer between external software and simulation environment. Various studies proved good agreement between the simulation results employing Aspen HYSYS and Aspen Plus⁸,⁹.

Two case studies were selected for the presentation of potential benefits of using Aspen HYSYS as a simulation tool in model-based hazard identification. The first case study is focused on the multiple steady states phenomenon in ammonia production. The process variable deviations leading to operability problems of plug flow reactor (PFR) were investigated. The system of nitroglycerin manufacture in a continuously stirred tank reactor (CSTR) with cooling coils was analysed in the second case study. The feed parameter deviations and cooling system failures potentially leading to dangerous exceeding of the maximum allowable reactor temperature were investigated.

The first case study – ammonia synthesis

Ammonia is a widely used compound in chemical industry, e.g. in the manufacture of fertilizers, cleaning agents or explosives. It is produced in a fixed-bed catalytic reactor according to the following heterogeneously catalysed reaction:

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

(1)

A mathematical model of the presented production includes a fixed-bed reactor with three beds, feed preheater and a refrigeration unit with a vapour–liquid flash separator (Figure 1). The fixed-bed reactor system consists of three segments – beds in series with feed quenching between each bed to adjust the optimal temperature profile in the reactor system. The feed preheater is modelled as a simplified heat exchanger, where feed is preheated by the outlet stream from the fixed-bed reactor. The product stream leaving the feed
The process variables were set to the design values that were adjusted to correlate with the current trends in ammonia production industrial units, where the reaction rate is given by Froment and Bischoff\textsuperscript{11} and optimised for higher activity of modern catalysts\textsuperscript{12}. Operating pressure was 20 MPa. Part of the “fresh feed” stream was preheated from temperature of 250 °C to temperature of 424 °C, while the other part of the stream was quenched between every bed. The hot medium in the feed preheater (product stream “R103out”) was cooled from 525 °C to 436 °C. The composition and mass flow of the “fresh feed”, “R103out” and the final product stream “liquid ammonia” are presented in Table I. Design characteristics of the individual beds are summarized in Table II.
Table I  
Design operation parameters – ammonia synthesis

<table>
<thead>
<tr>
<th>Stream</th>
<th>Mass flow [10^3 kg/h]</th>
<th>Mole fraction NH₃</th>
<th>Mole fraction N₂</th>
<th>Mole fraction H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh feed</td>
<td>252</td>
<td>0.04</td>
<td>0.24</td>
<td>0.72</td>
</tr>
<tr>
<td>R103out</td>
<td>252</td>
<td>0.17</td>
<td>0.21</td>
<td>0.63</td>
</tr>
<tr>
<td>liquid ammonia</td>
<td>50</td>
<td>0.98</td>
<td>0.00</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table II  
Design parameters of the individual beds

<table>
<thead>
<tr>
<th>Bed No.</th>
<th>Length [m]</th>
<th>Diameter [m]</th>
<th>Total volume [m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.5</td>
<td>0.9</td>
<td>6.7</td>
</tr>
<tr>
<td>2</td>
<td>15.1</td>
<td>0.9</td>
<td>9.6</td>
</tr>
<tr>
<td>3</td>
<td>23.9</td>
<td>0.9</td>
<td>15.2</td>
</tr>
</tbody>
</table>

The first case study - results and discussion

Using the HAZOP principles mentioned earlier, a list of temperature, pressure, flow and composition deviations for every stream was created and investigated. The fundamental requirement for the simulation of the effect of a process variable deviation is the value of the deviation. The range of the process variable deviation D (as defined in Equation (2)) varied according to the 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 it was set from – 30 % to + 30% (from 175 °C to 325 °C). The value of the step change of parameter was set to 1 %.

\[
D = \frac{\text{deviated value of the parameter} - \text{original value of the parameter}}{\text{original value of the parameter}} \times 100
\]  

(2)

Figure 3. Effect of the “fresh feed” temperature on reaction conditions - (a) “R103out”, “R102out” and “R101out” temperature, (b) overall hydrogen conversion
Process simulations in the Aspen HYSYS environment were performed for all possible process variable deviations and the simulation results were scanned in the prepared software for any abnormal situations. Such a situation occurred with “fresh feed” temperature deviation. The effect of temperature deviation in the “fresh feed” stream on the temperature of stream “R103out” and on the overall hydrogen conversion in the reactor is shown in Figure 3. A dramatic change of the reaction conditions occurred when “fresh feed” temperature was decreased by 18 %, to 205 °C. The “R103out” temperature and the overall hydrogen conversion dropped from ca. 510 °C to 210 °C and from ca. 33 % to 5 %, respectively. This step decrease of reaction parameters indicated a shift from the design steady state with the desired production rate of ammonia to a steady state with lower reaction rates. When the “fresh feed” temperature was set back to 250 °C, the reaction conditions remained in the steady state located on the lower solution branch. Operation of the unit had to be interrupted and a new reactor start-up procedure had to be carried out. The process behaviour between the higher and lower solution branches is described by unstable steady states. The ammonia synthesis modelling in the Aspen HYSYS environment was not able to identify positions of these unstable steady states. A more complex overview of the “fresh feed” temperature deviation is presented in Figure 4, where the impact on the temperature of all process streams is shown. Temperature of streams “7”, “purge” and “liquid ammonia” was constant, because the refrigeration output temperature was set to 8 °C. Input and output stream temperatures in the individual reactor beds dramatically dropped when the “fresh feed” temperature was decreased by 18 %.

Figure 4. Effect of the “fresh feed” temperature deviation throughout the process

The second case study – nitroglycerin production

Nitroglycerin has wide applications in pharmaceutical industry and as an ingredient for industrial explosives. Nitroglycerin is usually produced by glycerol nitration. During its manufacturing process, many hazardous events occur because of the significant thermal instability of nitroglycerin in the processes of nitration and purification. The nitration process can be expressed as an esterification reaction of glycerol and nitric acid in the presence of sulphuric acid as a dehydrating agent according to the reaction scheme:

\[
\begin{align*}
C_3H_5(OH)\_3 + 3HNO_4 & = C_3H_5(ONO_2)_3 + 3H_2O
\end{align*}
\]  

The reaction rate can be expressed as a kinetic reaction model where the reaction order with respect to the glycerol and nitric acid is 0.935 and 1.117, respectively. The production of nitroglycerin can be operated as a batch or a continuous process. The Biazzi continuous process is one of the most common nitroglycerin production variants. Two inlet streams, mixed acid containing nitric and sulphuric acid and pure glycerol were fed in a CSTR in this case study. Brine was used as a coolant in the internal cooling coils. The reaction mixture was a heterogeneous liquid phase containing produced nitroglycerin and water, inert sulphuric acid and unreacted glycerol and nitric acid. In the Aspen HYSYS environment, to create a mathematical model of CSTR, additional vapour outlet stream is required although its mass flow was zero in this case study. According to the basic concept, mathematical model of a CSTR was built up from Aspen HYSYS models of “Continuously Stirred Tank Reactor” and “Cooler” (Figure 5). The two models were connected by heat flow. Although the heat transfer rate was not taken into account, this simplified reactor cooling system was sufficient for the proposed model-based hazard identification because only the value of the heat removal was monitored. Design values of
the key operation parameters are presented in Table III. The liquid volume in “CSTR100” was 35 l and the desired heat removal in “CSTR100” was 23.9 kW; therefore, the desired heat flow of the energy stream “Q” was – 23.9 kW. The achieved glycerol conversion in the Aspen HYSYS simulation of the design operating point was 99.4 %, which is in good agreement with the experimental data.

Table III
Design operation parameters – nitroglycerin production

<table>
<thead>
<tr>
<th>Stream</th>
<th>Mass flow [kg/h]</th>
<th>Temperature [°C]</th>
<th>( \text{C}_3\text{H}_5(\text{OH})_3 )</th>
<th>( \text{HNO}_3 )</th>
<th>( \text{H}_2\text{SO}_4 )</th>
<th>( \text{C}_3\text{H}_5(\text{ONO}_2) )</th>
<th>( \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycerol</td>
<td>63.6</td>
<td>19</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>mixed_acid</td>
<td>311.6</td>
<td>19</td>
<td>0.00</td>
<td>0.51</td>
<td>0.49</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>products</td>
<td>375.2</td>
<td>15</td>
<td>0.00</td>
<td>0.08</td>
<td>0.41</td>
<td>0.41</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The second case study - results and discussion

Safety restriction of the reaction temperature in glycerol nitration is the decomposition temperature of nitroglycerin. Various studies observed that nitroglycerin can be decomposed in the temperature range of 20 to 30 °C. Therefore, the critical reaction temperature was set to 30 °C and the hazard identification process was performed. A list of possible temperature, flow and composition deviations for every stream was created and investigated. Simulation results were scanned in the prepared software for any stable states where temperature in the reactor exceeded the critical reaction temperature. The range of process variable deviations \( D \) (as defined in Equation (2)) was set from – 30 % to + 30%. Effect of the heat removal deviation on the “products” temperature is depicted in Figure 6. Effect of “glycerol” parameters deviation on the “products” temperature was negligible. The X mark represents the operating point in which the “CSTR100” temperature exceeded the critical reaction temperature. The empty circle represents the last operating point for which the Aspen HYSYS solver found numerical solution. Above and under this point, numerical solution of the mathematic model in the Aspen HYSYS environment was not found and the reaction was switched off.

Figure 6. Effect of heat removal in “CSTR100” on the temperature of stream “products” (X mark – exceeding the critical temperature, empty circle – last numerical solution)
When the failure in the 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 at a dangerous point where runaway can occur (Figure 6). When the cooling control system was corrected and the heat removal was set back to 23.9 kW, the design operating point was restored. A similar behaviour was observed in case of “glycerol” mass flow deviation. When the mass flow of stream “glycerol” was increased by 12 %, to ca. 71.2 kg/h, critical temperature in the reactor was exceeded and the runaway effect was possible (Figure 7a). Simulation results above the critical temperature of 30 °C were not in agreement with real behaviour of the reactive system observed in past accidents in manufacture of nitroglycerin because the reaction kinetics of nitroglycerin decomposition was not taken into account in the Aspen HYSYS model.

Conclusion

Automated model-based hazard identification applied to two case studies was presented. Aspen HYSYS simulation environment was found to be capable of successful mathematical modelling of two different reactor models, plug flow reactor and continuously stirred tank reactor, where the reaction took place in the gaseous and liquid phase, respectively. In the case study of nitroglycerin manufacture, numerical problems occurred in the region of reaction temperatures near 0 °C and hindered the possibility of model-based hazard identification in a wider range of process variables. Different evaluation methods of the simulation results were applied. In the first case study, a sudden step change in the reaction conditions was observed, recorded and further monitored. In the second case study, the user set value of the critical temperature in the reactor was monitored and when exceed, actual operating parameters were recorded. The presented safety analysis results are in good agreement with those obtained by conventional HAZOP studies. Integration of automated model-based hazard identification in the PHA techniques can potentially lead to the reduction of time and cost required for appropriate process safety analysis. It can be successfully applied at the design stage of the chemical production, for the operation of an already existing chemical unit as well as for educational purposes and training of operators.

Acknowledgments

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Literature