Journal of Loss Prevention in the Process Industries 29 (2014) 155–162

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp

Model-based hazard identification in multiphase chemical reactors

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ARTICLE INFO

Article history:
Received 8 July 2013
Received in revised form
28 November 2013
Accepted 11 February 2014

Keywords:
Model-based safety analysis
Multiple steady states
Continuation
Dynamic simulation
MTBE

ABSTRACT

Chemical productions operated in extreme conditions (high pressure, high temperature) require a detailed analysis of all potentially dangerous situations that can lead to a major industrial accident and thus cause a loss of life and property. Many accidents in the near or distant history underline the need of a detailed safety analysis in process industries, not only in the phase of plant design but also during the operation of the plant. It would be shown that simulation of a chemical unit using an appropriate mathematical model and the nonlinear analysis theory can be a suitable tool for safety analysis. This approach is based on mathematical modeling of a process unit where both the steady-state analysis, including the analysis of the steady states multiplicity and stability, and the dynamic simulation are used. Principal objective of this paper is to summarize problems regarding the model-based hazard identification in processes. A case study, focused on phenomena of multiple steady states in ammonia synthesis reactor will be presented. The influence of the model complexity and model parameters uncertainly on the quality of safety analysis would be underline.

1. Introduction

Chemical units include a wide range of hazards arising from the process itself, properties of the chemicals and their handling, such as fire, explosion and exposure to toxic substances. Statistics show that modern chemical industry is one of the safest industries in the world (Kletz, 2001); however, there still is real potential of major industrial accidents with catastrophic impact. This fact suggests that the role and responsibility of chemical engineers are mainly in providing reliable operation, optimization of material and energy consumption in the production and to minimize losses due to accidents.

Chemical productions operated in extreme conditions (high pressure, high temperature) require a detailed analysis of all potentially dangerous situations that can lead to a major industrial accident and thus cause a loss of life and property. Many accidents in the near or distant history underline the need for a detailed safety analysis in process industries, not only during plant design but also in the operation phase of the plant (AICHE, 1992; Mannan & Lees, 2005). It is also very important to note that safety analysis is often subject of official approval of constructions by the national government authorities.

Most of the major process units were developed based on the scale up of smaller (laboratory or pilot) units operated with minimal attention to safety. The design of a real industrial unit is always a compromise between technological, economic and safety requirements. To find a compromise between the number of installed safety elements and the planned investment costs is particularly problematic.

Currently, there are two basic approaches that can be applied to safety analysis and hazard identification in process industries. The first group of hazard identification method is based on theoretical approaches considering expert examination of the technological process in order to identify potential sources of hazard (HAZOP, What-if FMEA, FMECA, FTA, HRA and their modifications, or combination) (Crawley & Tyler, 2003). The strength of the standard methods is in considering also trivial errors that could trigger undesired events. Furthermore, many efforts have been recently made to improve the effectiveness of HAZOP, exploiting, for instance, the strength of plant digital representation and the utilization of the knowledge-based approach.

The established methods are mostly carried out manually and thus still involve many disadvantages which can be summarized in several points:

- these methods are time consuming and expensive;
- there is a possibility of overlooking a potentially dangerous situation and its consequences especially when a particular situation (deviation) has never occurred before;

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http://dx.doi.org/10.1016/j.jlp.2014.02.004
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- requirements on the cooperation of engineers who have experience with the particular type of the process.

The introduced limitations of "standard" hazard identification methods can be eliminated (at least partially) by the second approach based on mathematical modeling and simulation of chemical processes and technologies used to identify known but mainly unknown hazards which have never occurred in practice (Labovský, Švandová, Markoš, & Jelemenský, 2007a, 2007b; Molnár, Krajčiová, Markoš, & Jelemenský, 2004; Molnár, Markoš, & Jelemenský, 2005; Švandová, Markoš, & Jelemenský, 2006). This second approach is a progressive and economically advantageous hazard evaluation method transferring real chemical processes to virtual reality to identify and then simulate the development of a possible accident from its beginning to the final state in the process of risk assessment. Principal advantage of this approach is based on deep knowledge of the physical and chemical phenomena, and the behavior of the processes of chemical technology and equipment, which allows predicting the system's behavior in situations that are exceptional and unlikely to occur (Seveso, Bhopal), thereby avoiding dangerous situations, or developing effective measures (means) to minimize the impact on humans, environment and property. Mathematical modeling is used as a tool for the description of the processes and equipments behavior under designed conditions and the simulation of system behavior (processes and equipments) on the change of the system parameters due to a failure. The effect of parameter changes depends on the parameter deviations from the designed values and on the duration of the deviations. Deviations from the expected values of the parameters lead to two types of response: a reversible change (returning the system to its original state after returning to the original parameter value), and irreversible changes (system settles in another steady state after the restoration of parameter values).

On the other hand, the application of mathematical modeling in the identification of hazards is not trivial, which is probably the reason of the absence of a universal and complex system or methodology enabling to perform such an analysis. Many existing applications, as well as the research in this field, can be characterized as a process simulator operated by experts to carry out an extensive series of simulations using the results of the simulations to evaluate the safety of the intended unit (Eizenberg, Shacham, & Brauner, 2006; Labovský, Jelemenský, & Markoš, 2006; Labovský, Laššák, Markoš, & Jelemenský, 2007; Labovský, Švandová, Markoš, & Jelemenský, 2007b; Švandová, Markoš, & Jelemenský, 2006; Švandová, Markoš, et al., 2006; Švandová, Markoš, Jelemenský, & Molnár, 2005), which makes it a very time-consuming task requiring an expert in mathematical modeling, numerical mathematics and safety analysis. It is clear that the identification of hazards by means of mathematical modeling is dependent on the quality of the mathematical model as well as on the quality of the model parameters (Švandová, Labovský, Markoš, & Jelemenský, 2009; Švandová, Markoš, & Jelemenský, 2006; Švandová, Markoš, & Jelemenský, 2008). In addition, the results of safety analysis based on mathematical modeling are very often specific to a particular type of process and therefore it is very difficult (or even impossible) to apply them even for a similar chemical technology. It is also important to point out that mathematical modeling is not an alternative to standard hazard identification methods. The investigated reactor or distillation column must be considered in a very complex plant with interfering problems, e.g. equipment aging, human and organization factors and many other issues, which cannot be included in the mathematical model. Therefore, the process of safety analysis will always require the cooperation of engineers with different expertise even in case a very sophisticated mathematical model is used. Mathematical modeling is valuable for the identification of specific physical hazards and the standard methods are essential for the identification of interfering hazard.

Evaluation of the safety concerns all equipment and technology. In principle, unit operations repeated in multiple technologies can be distinguished and thus considerable information and experience related to such equipments and processes are required. As a rule, the nature of physical processes (e.g. pumping liquids, gas compression, distillation, etc.) is essentially the same and the procedures of safety evaluation are generally established and more or less standard. Another group of processes are associated with chemical transformation specific to the type of reactions taking place under different hydrodynamic and thermodynamic conditions, and which are usually associated with heat and mass transfer, possibly combined with separation processes (e.g. reactive distillation). Chemical reactors in which exothermic reactions take place are probably the key units considering safety. Many accidents in the near history point to the necessity of safety analysis of each chemical reactor, not only after its design but also during its operation, as well as in cases when one of the operating parameters is changed. Based on the statistics presented, the majority of accidents involving chemical interactions occurs in chemical reactors, (Sales, Mushtaq, Christou, & Nomen, 2007); therefore, chemical reactivity is an issue that must be taken into consideration at any stage of the process. To operate a chemical reactor in safe regime it is very important to have qualitative and quantitative knowledge about the limits of the control parameters, at which the reactor operates in a safe regime. Also, it is essential to identify the parameter values potentially leading to a dangerous situation or even to a breakdown of a chemical reactor. When a chemical reactor is operated in the vicinity of multiple steady states, importance of the determination of safe operation increases markedly. However, the information about the presence of multiple steady states is often missing.

Principal objective of the recent work is to summarize problems regarding model-based hazard identification in processes. The existence of the multiple steady states phenomena in an ammonia synthesis reactor is described in the first case study. The influence of the model complexity and model parameters uncertainty on the quality of hazard identification for a reactive distillation column for MTBE production is underlined in the second case study.

2. The first case study – ammonia synthesis reactor and the existence of multiple steady states

One of the most important steps in the process of safety analysis is to qualitatively and quantitatively describe the range between normal operating conditions and conditions at which reactor breakdown can occur. In the process of safety analysis it is very important to identify the boundary between normal operating and potentially hazardous conditions (high temperature, high pressure) which can lead to a breakdown of the reactor. Sometimes, very small disturbances in any process parameter can lead to undesirable hazardous situations. It is therefore very important to know the influence of all process parameters on the reactor behavior. As it was mentioned in (Labovský, Švandová, Markoš, & Jelemenský, 2008; Molnár, Markoš, & Jelemenský, 2005), one of the primary questions concerning safety analysis of chemical units is the knowledge of the existence of multiple steady states. In general, multiple steady states are expressed as the number of different sets of state variables at which the time rate of the change of all state variables is zero for a fixed set of conditions or parameters (Molnár, Markoš, & Jelemenský, 2003). It means that the chemical unit can be operated in different regimes (temperature, conversion, selectivity etc.) under the same input conditions. From the safety analysis point of view, switching from one steady state to another one

caused by a small perturbance in an operating parameter can be very dangerous. Switching between two qualitatively different steady states can be accompanied by a significant change of the reactor pressure and/or temperature possibly resulting in a change of the reaction mixture state. Moreover, the situation can be much more dangerous when the disturbance in the control parameters causes an instability or oscillatory behavior (limit cycles).

Probably the most known accident of an industrial reactor, where the sustained oscillations were recorded, occurred in Germany in 1989. Detail information on this accident can be found in Mancusi, Merola, Crescitelli, and Maffettone (2000), Morud and Skogestad (1998) underlined the importance of a complex operability analysis of a desired reactor. Another example of the description of the attractors, both static and dynamics, in an industrial ammonia reactor operating under typical operating conditions can be found in (Mancusi, Maffettone, Gioia, & Crescitelli, 2001). The mentioned industrial ammonia reactor was operated without feedback control and after a rapid change of the internal reactor pressure, caused by a temporary decrease of fresh feed flow, the reactor became unstable and the recorded temperatures started oscillating with a period of about 6 min and an amplitude of about 200 °C. After the incident it was observed that this kind of oscillations tends to occur more frequently and also for smaller disturbances (Morud & Skogestad, 1998). As it was already mentioned, the accident occurred after a fast decrease of the reactor pressure. In the work Morud and Skogestad (1998) the reader can find a very detail analysis of the reactor pressure on the behavior of the ammonia synthesis reactor. In the following case study, the focus was set on another important control parameter – feed temperature.

Ammonia is produced in a fixed-bed reactor which is schematically depicted in Fig. 1. The reactor consists of three beds, where the fresh feed is quenched to every bed, to adjust optimal temperature profile.

A steady state solution diagram of the outlet temperature from each of the reactor segments as a function of feed temperature is depicted in Fig. 2. The solution diagram exhibits a maximum of three steady states (in the range of 220–270 °C) and shows that the normal operating point (marked with a diamond) is located in the region of multiplicity. Therefore, in case of a failure of the inlet temperature control, switching between individual steady state branches can be expected. Moreover, the operating point is located very close to the Hopf bifurcation points (empty circles). A decrease of the feed inlet temperature causes a slight decrease of the temperature in each reactor segment, following the upper (stable) branch. If the inlet temperature crosses the Hopf bifurcation points (empty circles), the reactor enters the dynamic regime, where oscillations can be expected. In case of a further decrease of the feed inlet temperature (to approximately 220 °C – full squares) the reactor stabilizes in a new stable steady state. This stable state is however characterized by a very low reaction rate and therefore low ammonia conversion.

Although the information provided by steady state analysis is essential for the examination of the process safety, it not always answers all questions coupled with safety analysis (How the perturbances of a control parameter affect the reactor behavior? Which trajectory will be followed during the transition from one steady state to another? Will the operator have enough time to perform some corrections and return the reactor operation into safe conditions?). Dynamic simulation of a chemical reactor can provide answers to most of these questions. As an example of such simulation, the following series of figures (Fig. 3) describes the responses of the ammonia synthesis reactor to step changes in the feed temperature. For simplicity, the reactor outlet temperature is the only monitored parameter. In Fig. 3a, a step change of fresh feed

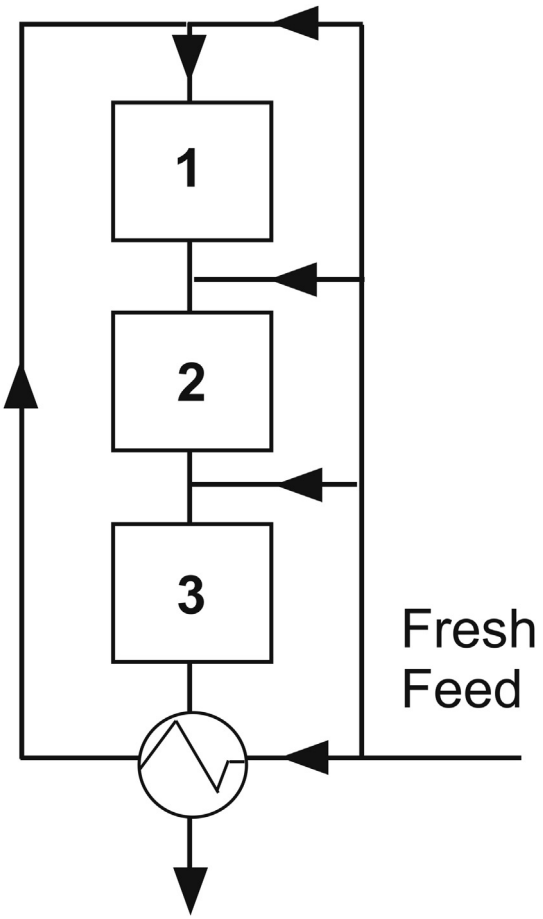

Fig. 1. Schematic description of an ammonia synthesis reactor.

temperature from the designed value of 250 K–240 K was simulated.

The reactor was relatively quickly stabilized in a new stable steady state. Seventy minutes later, when the feed temperature was

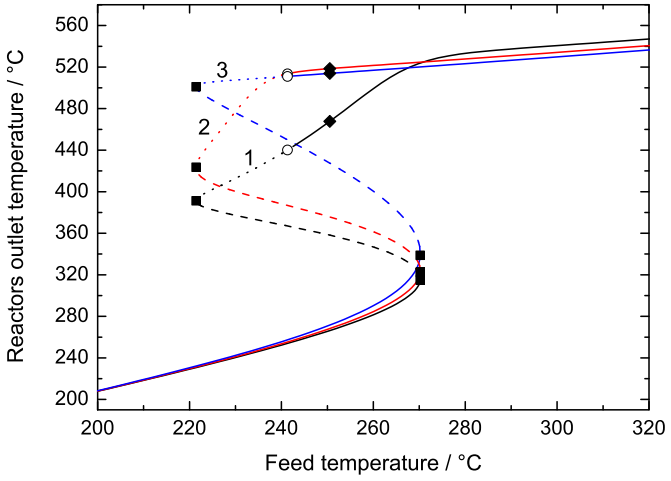

Fig. 2. Solution diagram of reactor segments outlet temperature (1. segment – black line, 2. segment – red line, 3. segment – blue line) as a function of feed temperature (diamonds – normal operating point, empty circles – Hopf bifurcation point, full squares – limit, dashed lines – unstable steady states). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

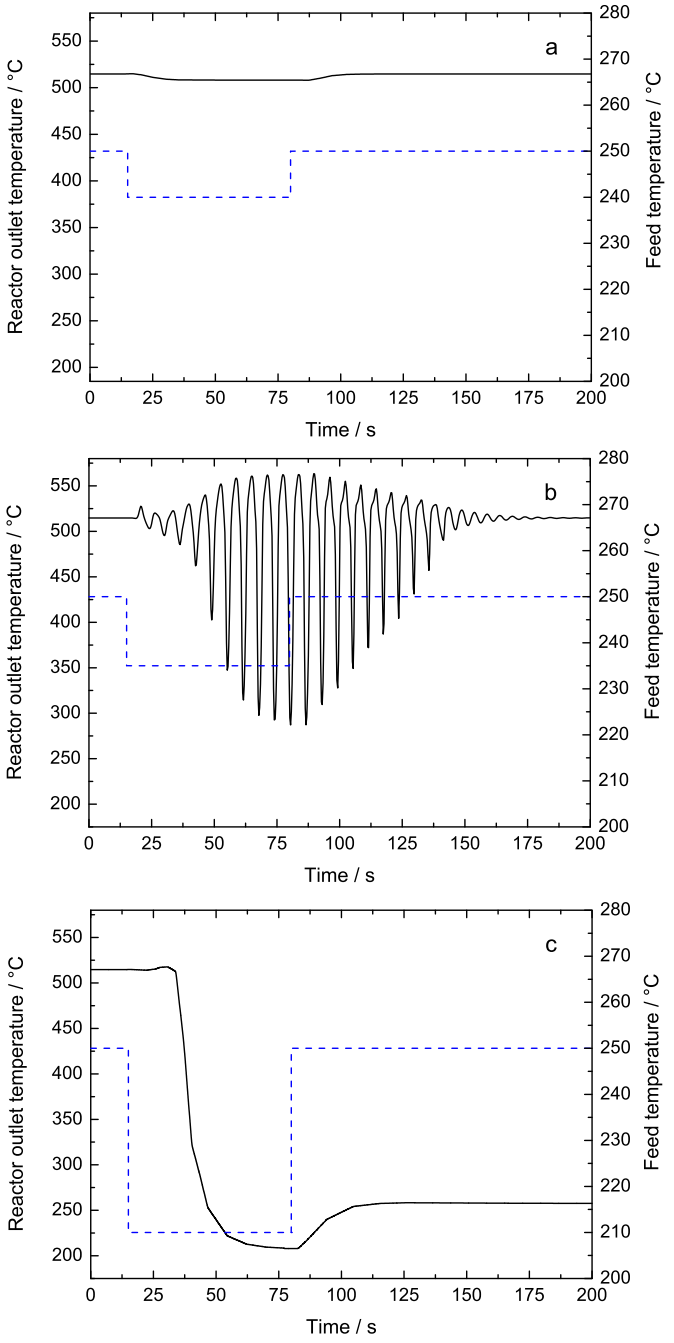

Fig. 3. Effect of a reactor response to the failure of inlet feed temperature simulated as step change from the operating value to 240 °C (a), 235 °C (b), and 210 °C (c) (solid lines – reactor outlet temperature, dashed lines – reactor feed temperature).

restored to the operating value, the system returned to the initial state. In case of a larger amplitude of the failure (step change of fresh feed temperature from 250 °C to 235 °C), oscillatory behavior of the reactor temperature was observed (Fig. 3b). This was caused by crossing the Hopf bifurcation point (see Fig. 2). In this case, the outlet reactor temperature was changing very quickly with an amplitude larger than 200 °C. When the failure of feed temperature exceeded 40 °C (inlet temperature decreased bellow 210 °C), the reactor behavior was changed dramatically. The reactor was switched to a steady state located on the lower solution branch. This led to significant decrease of the reactor outlet temperature and ammonia production. Moreover, after returning the feed temperature to the original operating value (time 80 min in Fig. 3c), the reactor remained in the lower steady state and a new reactor startup was required.

The previous analysis is focused on the failure of a single parameter. In case of real units, an accident is usually coupled with a concurrent failure of several parameters. The analysis of the simultaneous failure of a higher number of parameters is much more complicated. This is ever more significant when the objective of the analysis is to identify parameter regions, where multiple steady states or oscillations may occur. An example of a parallel failure of two parameters is presented in Fig. 4. Information gained from the bifurcation diagram depicted in Fig. 4 should be used to predict a set of unsafe situations. In this case, the reactor pressure and the feed temperature entering the reactor were chosen as the parameters of interest. Both parameters have a significant influence on the safe operation of the reactor (as it was already mentioned above). The regions of multiplicity and oscillation regimes shown in this diagram provide detailed information about the location of the limit points and of the Hopf bifurcation points allowing thus the investigation of the reactor basic behavior after simultaneous fault of the control parameters. From these results it follows that it is important to identify the safe operation conditions to achieve a safe operation of a reactor.

3. The second case study – reactive distillation column for MTBE production

3.1. Model complexity

Currently there is a huge collection of mathematical models and techniques for the description of the dynamic behavior of process engineering units. In general, mathematical models of chemical reactors are represented by a large system of specific equations with a large number of parameters (Labovský, Švandová, Markoš, & Jelemenský, 2007a). From the safety analysis point of view, the accuracy and complexity of a mathematical model can be considered to be the most important qualitative characteristics of its efficiency in the field of risk identification. To underline the importance of choosing an adequate mathematical model, an example of two different approaches to reactive distillation modeling is given.

Based on Taylor and Krishna (2000), reactive distillation is a multifunctional reactor concept which combines distillation separation with a chemical reaction. These processes have often better conversion and selectivity and lower capital and operating costs than the corresponding reactor followed by separation technology. Based on literature (Kooijman & Taylor, 1995, 2000; Taylor & Krishna, 1993, 2000), there are two distinctly different approaches to reactive distillation modeling: equilibrium (EQ) and nonequilibrium (NEQ) models. The EQ model is based on the assumption that between liquid and gaseous streams leaving each tray, equilibrium can be expected. To describe the EQ model, for each tray MESH equations are used. The term **MESH** is an abbreviation of the main types of equations used in the model (**M**aterial balances, equations of phase **E**quilibrium, **S**ummation equations and **H**eat balances). In case of the NEQ model, each of the phases is described by its own material and energy balances relationships. To complete the mathematical model, these balances need to be coupled with energy and material balances around the interface. Compositions on the phase interface are related through known equilibrium relations, and therefore they have to be determined as an integral part of the complete column simulation. The model is referred to as the **MERSHQ** model and it is formed by the following types of equations: **M**aterial balances, **E**nergy balances, **R**ate

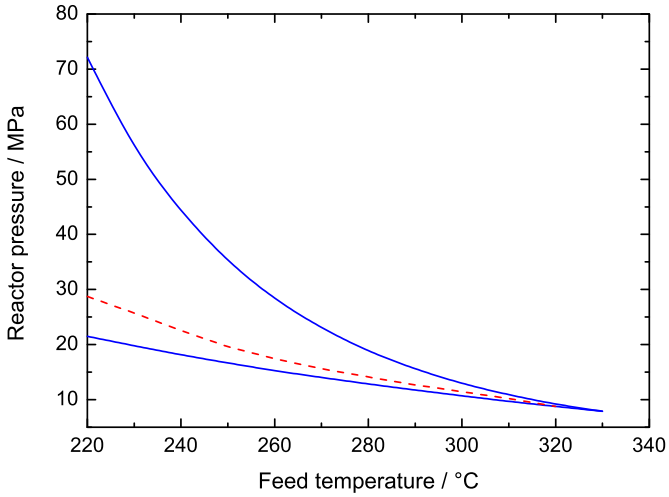

Fig. 4. Bifurcation diagram in the parametric plane feed temperature and reactor pressure. The region of multiple steady states is between the solid lines. Dashed line represents the border of the Hopf bifurcation points.

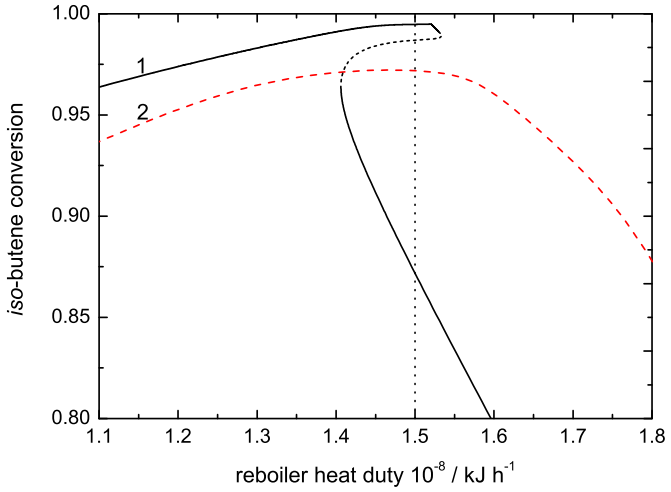

Fig. 5. Conversion of isobutene vs. reboiler heat duty solution diagrams predicted by equilibrium (1) and nonequilibrium (2) models.

equations, **S**ummation equations, e**Q**uilibrium relations for each stage and **H**ydraulic equations.

To describe the interphase heat and mass transfer in the liquid phase, the Maxwell–Stefan theory was used (Krishna & Wesselingh, 1997; Krishnamurthy & Taylor, 1985a, 1985b). Based on this theory, the interphase heat and mass transfer rates were estimated. Binary mass transfer coefficients were obtained based on the Zuiderweg empirical correlation (Zuiderweg, 1982).

In this investigation, Methyl Tertiary Butyl Ether (MTBE) production was chosen as the model system. MTBE production is based on the reaction of methanol with isobutene in an exothermic and reversible reaction, where strong ion exchange resin is used as the catalyst. This system is relatively known for its tendency to exhibit multiple steady sates. The existence of multiple steady states was for the first time described by Jacobs and Krishna (1993). Also several theoretical works indicate the existence of multiple steady state (Hauan, Hertzberg, & Lien, 1997; Jacobs & Krishna 1993; Sales, Mushtaq, Christou, & Nomen, 2007; Singh, Singh, Kumar, & Kaistha, 2005; Sudibyo & Aziz, 2012). An approach, based purely on steady-state analyses, for synthesizing effective control structures for a reactive distillation column for MTBE and the impact of steady-state multiplicities on the control structure design is highlighted in (Singh, Singh, Kumar, & Kaistha, 2005). The control strategy of a reactive distillation system for the synthesis of MTBE in case of multiplicity occurrence is investigated in (Wang, Wong, & Lee, 2003). The nonlinear dynamic behavior of the reactive distillation columns for the production of MTBE and TAME and the rigorous experimental verification of steady-state multiplicity in a pilot plant reactive distillation column for the production of TAME are presented in work (Mohl, Kienle, Gilles, Rapmund, Sundmacher, & Hoffmann, 1999).

For the purposes of the case study, the column configuration corresponds to that described by Jacobs and Krishna (1993). The column was formed by two rectifying stages, eight reactive stages (which were charged with the catalyst), five stripping stages, a total condenser and a partial reboiler. The overpressure in the column was maintained on a constant value of 1000 kPa. Methanol and the mixed butenes were fed to the 10th stage of the column.

The mixed butenes stream contained a mixture of isobutene and 1-butene. Molar flow rate of fresh methanol was 775 kmol h^{-1} and the mixed butanes were fed at the molar rate of 1976 kmol h^{-1}. In the presented case study, reflux rate, set to the value of 7 was used and the reboiler heat duty was set to 1.5×10^8 kJ h^{-1}. Solution diagram for a system in which the reboiler heat duty was the investigated parameter is depicted on (Fig. 5).

It is important to point out that, based on the diagram, there are three steady states in the region of the operating value of the reboiler heat duty (1.5×10^8 kJ h^{-1}) for the equilibrium model (EQ) but only one steady state for the nonequilibrium (NEQ) model. For each of the steady states, significantly different values of isobutene conversion are predicted. Only two of the predicted, the higher and lower, steady states are considered as possible operating states of the RD column. The prediction of the more complex NEQ model is quantitatively very similar to that of the EQ model in the region of the upper stable steady state. On the other hand, the presence of multiple steady states predicted by the EQ model, has potential to significantly influence the RD column dynamic behavior in case of the reboiler heat duty failure. Moreover, in case of stronger disturbances of the reboiler heat duty, very different predictions of the RD column behavior in comparison with that predicted by the NEQ model can be expected. This can be documented on the following series of dynamic simulations, where disturbances of the reboiler heat duty were studied using both models. At the time of 1 h, the reboiler heat duty was suddenly decreased (Fig. 6a) and increased (Fig. 6b) from the operating value. The operating value of the reboiler heat duty (1.5×10^8 kJ h^{-1}) was re-established one hour later. After returning the reboiler heat duty from 1.2×10^8 kJ h^{-1} to the operating value (Fig. 6a), both model approaches predicted that the column will continuously return to its original steady state (characterized by high isobutene conversion). A different column behavior is depicted in Fig. 6b, where the reboiler heat duty was increased from the operating value (1.5×10^8 kJ h^{-1}) to 1.8×10^8 kJ h^{-1}. After returning the reboiler heat duty back to the operating value, a qualitatively different behavior of the EQ and NEQ models can be considered. In case of the NEQ model, the conversion returned back to the designed value. However, when EQ was used to describe the column behavior after the failure caused by the heat duty perturbance, the reactive distillation column was stabilized in the other (lower) steady state. Significant disagreement in the column prediction by the EQ and NEQ approaches, indicated by the presented results, underlines the need to very carefully consider the complexity of the model and the quality of the input parameters used in the simulation, especially in the situations, when the mathematical model is used for the purpose of a safety analysis.

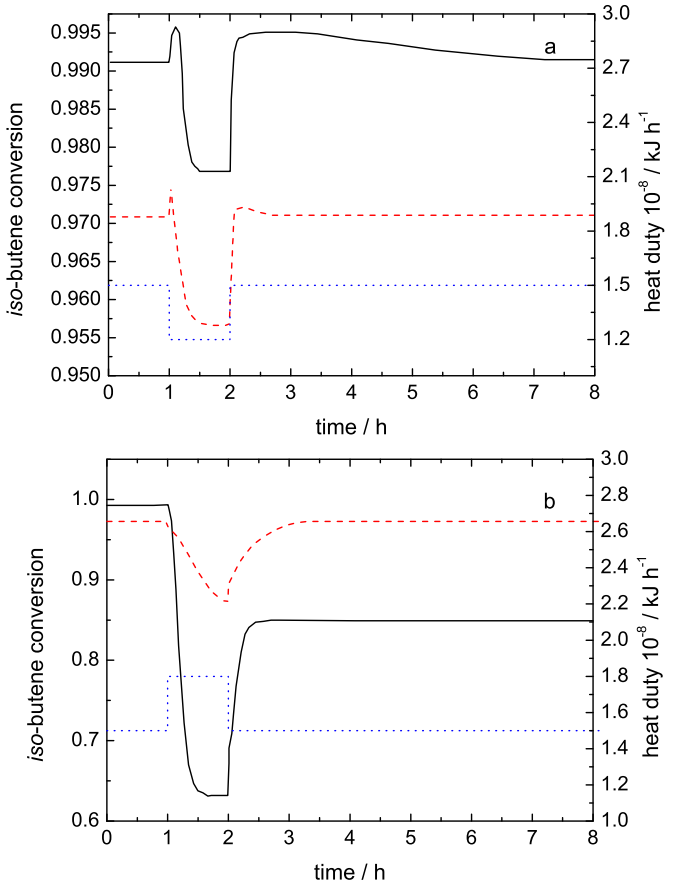

Fig. 6. Isobutene conversion changes predicted by the EQ (solid line) and NEQ (dashed line) models caused by a step decrease (a) and increase (b) of the reboiler heat duty (dotted line) from the operating value and back. Duration of deviations: 1 h.

3.2. Model parameters uncertainties

Almost all mathematical models of chemical reactors require the knowledge of physical (e.g., viscosity, density, heat capacity), kinetic (e.g., activation energies, reaction enthalpy), mass or heat transfers (e.g., diffusion coefficients, thermal conductivity) parameters. By increasing the complexity of the model, the number of its parameters also increases. Most of these parameters were taken from literature and/or other databases, they are very often estimated based on empirical correlations, and less often are they measured. The problem of the accuracy of these parameters cannot be neglected. During each case study, attention should be paid to the verification of the validity of these parameters in the range of interest and also to the verification of the possibility of parameters extrapolation behind this range. There are many methods for uncertainty assessment, which have been successfully applied in the field of chemical reactor modeling and safety analysis (Hauptmanns, 2007, 2008; Laššák, Labovský, & Jelemenský, 2010; Švandová, Labovský, Markoš, & Jelemenský, 2009; Švandová, Markoš, & Jelemenský, 2008).

For example, accuracy of the nonequilibrium stage model (described in the previous Section 3.1) seems to be limited mainly by the accuracy of the correlations used to estimate the mass transfer coefficient and the interfacial area (Švandová, Labovský, Markoš, & Jelemenský, 2009). To estimate the binary mass transfer coefficients, empirical or semi empirical correlation are very often used. These correlations depend on the chemical and physical properties of the liquid and gaseous phases. Geometry of the tray and packing type are also very often included in the mentioned correlations. The following case study is focused on the reactive distillation column simulation with the NEQ model approach. An RD column was used to produce MTBE. The NEQ model requires the estimation of the binary mass transfer coefficient. In the presented case study, four different correlations were selected and the RD column behavior was investigated for each of these correlations. Chosen correlations are summarized in Table 1 (formally marked as Model 1–4). Gas diffusion coefficients were estimated based on the correlations of Fuller, Schettler, and Giddings (1966) and diffusion coefficients in the liquid phase were computed based on Wilke and Chang (1955).

Table 1
Summarization of four correlations used for the estimation of the mass transfer coefficient chosen for this case study.

Model number	Mass transfer coefficient correlation
1	AICHE (AICHE, 1958)
2	Chan–Fair (Chan & Fair, 1984)
3	Chen–Chuang (Chen & Chuang, 1993)
4	Zuiderweg (Zuiderweg, 1982)

To investigate the impact of different correlations on the steady state behavior, the NEQ model of an RD column was used. The mixed butenes feed flow rate was chosen as the continuation parameter and the product purity was examined (MTBE mole fraction in bottom flow). Based on Fig. 7, three of the four correlations used in the presented case study show the possibility of multiple steady states. On the other hand, when the mass transfer coefficients were calculated by Model 4, no multiplicity was reported in the wide range of butenes feed flow rate considered. Very interesting results were obtained using Models 1 and 2, which both predicted continuous relation of the conversion, however with an isolated solution (isolas). From Fig. 7 it is also clear that the failure of the investigated parameter (in case of Models 1–3) leads to significant changes in the RD dynamic behavior. A very different prediction of the RD column behavior in comparison with Model 4 can be expected.

It is important to point out that each uncertainty of the input parameters needed for the estimation of the mass transfer coefficient (diffusion coefficients in the liquid or vapor phases, surface tension, viscosity, density, etc.) can significantly influence the

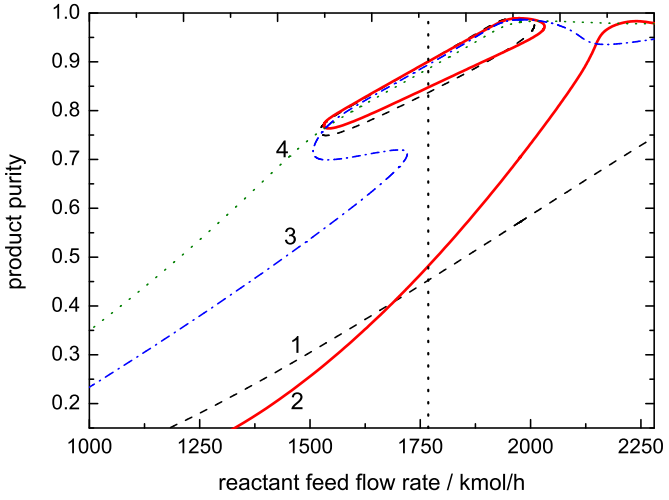

Fig. 7. Product purity vs. butenes flow rate solution diagrams (1 – dashed line – Model 1, 2 – thick solid line – Model 2, 3 – dash – dotted line – Model 3, 4 – dotted line – Model 4).

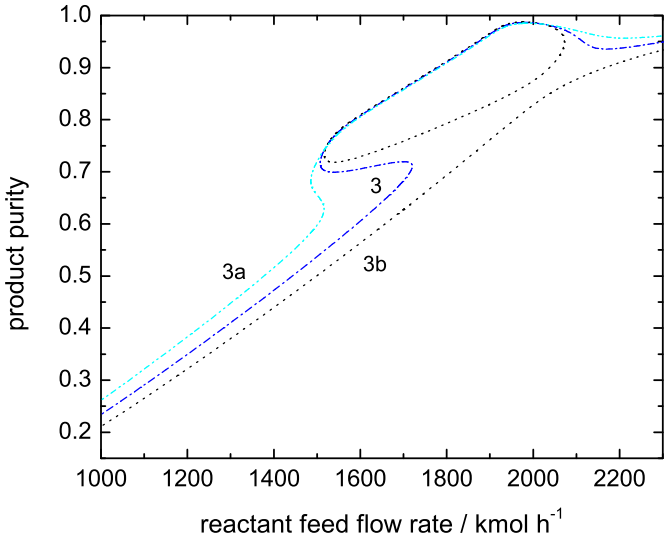

Fig. 8. Product purity vs. reactant feed flow rate solution diagrams predicted by Model 3 using different liquid phase diffusion coefficients, D^L, (3a – dash-dot-dotted line – $0.8 \times D^L$, 3 – dash-dotted line – $1 \times D^L$, 3b – dotted line – $1.2 \times D^L$).

general NEQ model steady state prediction. Fig. 8 shows the product purity dependence on the reactant feed flow rate calculated using Model 3, in which different values (±20%) of the diffusion coefficients in the liquid phase, D^L, were used. To estimate the diffusion coefficients in a dilute liquid mixture, the Wilke and Chang (1955) correlation corresponding to the dash dotted line (line 3) in Fig. 8 was used. To show the effect of the diffusion coefficient uncertainty on the NEQ models steady state prediction, a 20% decrease (line 3a in Fig. 8) and increase (line 3b in Fig. 8) of the calculated diffusion coefficients were assumed. From Fig. 8 follows that the influence of the liquid phase diffusion coefficients on the steady states prediction can be significant. The decrease of the diffusion coefficients led to significant reduction of the zone, where multiple steady states can be expected. Qualitatively different results can be expected for the increase of the diffusion coefficients, which caused the formation of an isolas closure and the creation of a multiplicity zone very similar to that predicted by Model 1 (i.e., the AIChE method, see Fig. 7) and Model 2 (i.e., the Chan–Fair method, see Fig. 7).

4. Conclusion

In the present paper, an attempt to formulate and discuss the guidelines for model based safety analysis in process industries was done. Model based hazard identification can prove to be a very useful tool in the field of safety analysis. It can be successfully applied for already existing units and also in all phases of unit design. It was shown that simulation of a chemical unit using an appropriate mathematical model and the nonlinear analysis theory can be a suitable tool for safety analysis. The presented approach requires utilization of mathematical modeling where both the steady-state analysis and the dynamic simulation are used. Simulations performed in dynamic mode enable a detailed investigation of the consequences of operating parameters failure. Another advantage of the model-based approach is the ability to analyze the consequences of the deviations in dependence on the time duration of the failure and to describe the time evolution of the device response to the parameter failure. On the other hand, steady state simulations are preferable when the device behavior needs to be investigated for a wide range of failures. The steady state approach allows identifying parametric zones, where shifting between qualitatively different steady states can be expected.

In the first case study focused on the investigation of multiple steady states, an industrial ammonia synthesis fixed-bed reactor was presented. It was also shown that an adequate mathematical model can predict oscillatory behavior of a real industrial reactor. However, the complexity of the mathematical model can significantly affect the prediction of the chemical unit behavior. In the second case study, the influence of the mathematical model complexity on the description of an RD column was investigated. The simpler EQ and the more complex NEQ model were analyzed using steady state simulations focused on the identification of multiple steady states. As the EQ model is relatively simpler it requires less model parameter; however, its main assumption – equilibrium between the liquid and gaseous phase is in many cases difficult to meet. The mass and heat transfer resistances, which are included in the NEQ model, make this model more complex. On the other hand, the distillation column behavior becomes very strongly dependent on the quality of the NEQ model parameters, which often depends on the equipment design. Based on the presented results, it is clear that different levels of model complexity lead to more or less different predictions of the RD column dynamic behavior. It was also confirmed that different correlations for the mass transfer coefficient estimation cause qualitatively different prediction of the RD column behavior. Moreover, it is important to note that each uncertainty of an input parameter needed for the mass transfer coefficient calculation (diffusion coefficients in the liquid or vapor phases, surface tension, viscosity, density, etc.) can significantly influence the general NEQ model steady state prediction.

Acknowledgments

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0355-07.

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