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Mathematical model of a chemical reactor—useful tool for its safety analysis and design

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Abstract

A large number of industrially important reactions with vast heat release is carried out in multiphase reactors (heterogeneously catalyzed reactors, gas–liquid reactors, reactive distillation (RD), etc.). From safety point of view, they represent the most dangerous operational units in the chemical industry. The possibility of hazard identification of such reactors by applying the HAZOP procedure using a mathematical model is discussed. The role of model complexity in safety analysis is also described. Two case studies are presented and analyzed: RD in CSTR and fixed bed catalytic reactor.

Keywords: Chemical reactors; Safety analysis; HAZOP study; Mathematical modeling; Nonlinear dynamics; Multiphase reactions

1. Introduction

Chemical reactors with exothermic reactions represent the most dangerous operational units in the chemical industry. Safety analysis of reactors performance should be done in each step of their design and construction. Some considerations related to the safety analysis of chemical reactors using their mathematical models were presented in our previous paper (Molnár et al., 2005).

HAZOP is one of the best and most rigorous techniques for hazard identification in a chemical plant. The HAZOP procedure formally examines step by step all equipment as well as deviations from its normal operation conditions and considers what faults can appear. The HAZOP report includes all the deviations, their causes, consequences in equipment performance, analysis of such consequences, implemented protection (active and/or passive), and resulting suggestions (Kletz, 1999; Lees, 1996). HAZOP is a time-consuming and labor—intensive activity. It is widely used in the chemical industry, and therefore the HAZOP results provided by the computer code may be understandable for all of the interested people. In the last ten years a lot of research efforts was dedicated to intelligent systems for automating the HAZOP analysis (e.g. Mushtaq and Chung, 2000). The main advantages of such approach are:

(1) greatly reducing the time and effort required in HAZOP;
(2) making the study more smooth and detailed;
(3) minimizing the influence of human factors.

Doing the HAZOP analysis of a reactor, appropriate deviations from the normal operation point have to be created. The main task of the HAZOP analysis is to find reasons for such deviations and to deduce their consequences on the reactor performance.

Usually, the HAZOP analysis does not consider duration and amplitude of deviations generated during the reactor operation. Using an appropriate mathematical model, the extent of deviations may be easily incorporated and possible consequences investigated.

The aim of this paper is to present a combination of the standard identification method, like HAZOP with mathematical modeling. Such a linkage has the potential to become a very practical and robust tool for safety analysis. To develop a mathematical model of a real industrial reactor with all

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particular processes, which take place in the reactor, is quite impossible without any simplified assumptions at present. However, a simple model with too many presumptions would be very far from the reality.

In this paper, by using two case studies (continuous stirred tank reactor with distillation and heterogeneous fixed bed catalytic reactor), we will try to demonstrate the basic principles of the safety analysis, based on the combination of mathematical modeling together with utilization of the HAZOP methodology.

2. Modeling of a chemical reactor for safety analysis

Mathematical models of multiphase chemical reactors are represented by a large system of specific equations with a large number of parameters. Thus, solution of these models requires an accurate estimation of all these parameters and an appropriate numerical algorithm for the solution of model equations. Due to a wide variety of the reactor types, their construction and operational constrains, an universal simulation software has not been available up to now. The main tasks which may be solved for safety analysis purposes by a mathematical model are formulated in the paper of Molnár et al. (2005).

In deriving a model of a chemical reactor, two aspects have to be considered:

- Each mathematical model, based on the knowledge of parallel and consecutive elementary processes proceeding inside the reactor, is developed by taking into account some simplifications and assumptions. The model is valid only in the framework of these applied presumptions. A dramatic change of the performance conditions (e.g. increase of temperature in the catalytic bed) could lead to a negation of the applied assumptions and the model will not longer be entirely adequate.
- By increasing the complexity of the model, the number of its parameters is being increased too. The problem is the accuracy of these parameters, the range of the performance conditions of their validity and the possibility of extrapolation out of this range. This fact may strongly influence the prediction of reactor behavior by a mathematical model generating HAZOP deviations.

3. Case study 1—RD in a CSTR with total condenser

As a model system, the following simple reaction system was chosen:

$$CH_3OH + (CH_3)_2C = CH_2 \rightleftarrows (CH_3)_3COCH_3, \qquad (R1)$$

where isobutene (IB) reacts with methanol (MeOH) to form methyl-tertiary butyl ether (MTBE) in the presence of 1-butene as an inert. The reaction is catalyzed by a strong ion-exchange resin. The reaction rate equation, the reaction rate constant and the temperature dependence of the equilibrium constant are given by Rehfinger and Hoffmann (1990).

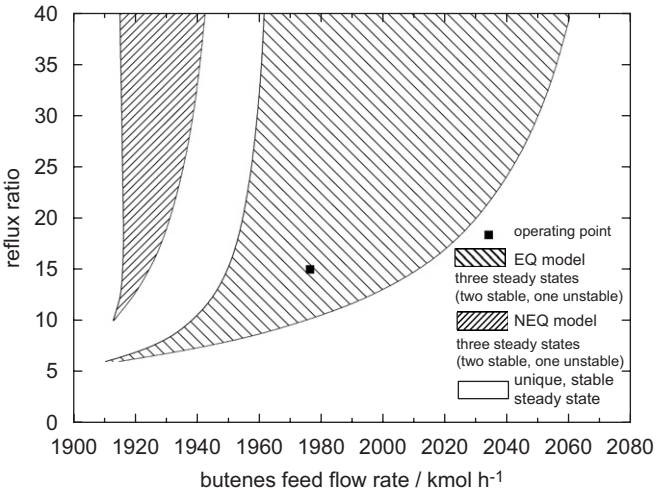

Fig. 1. Bifurcation diagram in the parametric plane butenes feed flow rate vs. reflux ratio.

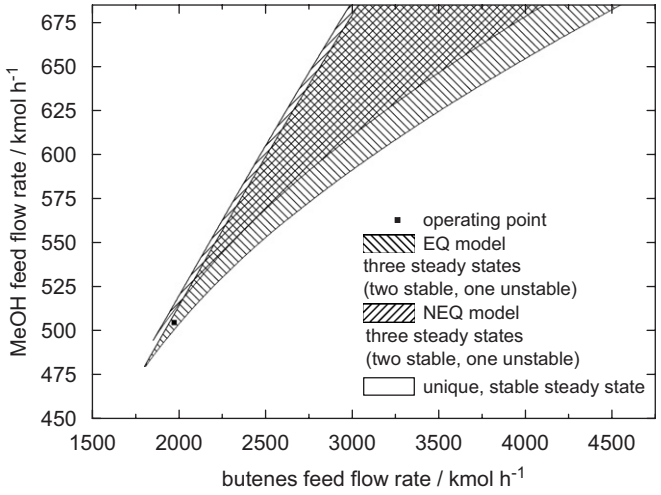

Fig. 2. Bifurcation diagram in the parametric plane butenes feed flow vs. methanol feed flow rate.

For modeling RD, two distinctly different approaches are possible (Taylor and Krishna, 2000):

- The equilibrium (EQ) model, which assumes that the streams leaving the reactor are in equilibrium with each other.
- The non-equilibrium model (NEQ), which assumes equilibrium only at the vapor–liquid interphase. In this case description of the interphase heat and mass transfer is necessary.

Using the continuation algorithm CONT (Holodniok et al., 1986), identification of the multiple steady states locus in two parametric planes predicted by the EQ model and the NEQ model was done as it is presented in Figs. 1 and 2. In the parametric plane—butenes feed flow rate vs. reflux ratio (Fig. 1)—extensive differences of the multiplicity locus might be distinguished using different models. On the other hand, in the parametric plane—butenes feed flow rate vs. MeOH feed

flow rate (Fig. 2)—multiplicity regions are overlaid on a large scale.

If the operating point of the reactor is localized as it is indicated in Fig. 1 by black square, the NEQ model does not predict any multiplicity in a wide range of both parameters around this operating point. Then, after the occurrence of some fluctuations of both the reflux ratio and/or the butenes feed flow and their following eliminations, the NEQ model will turn the reactor back to the original operating point, but the EQ model can predict the new steady state with different reactor output.

If the feed flow rate of butenes has been chosen as parameter of interest, in the solution diagram of MeOH conversion in the reactor as a function of the butenes feed flow rate, differences of the multiplicity locus were predicted by the EQ model and the NEQ model (Fig. 3). For the given operating butenes feed flow rate (dashed line in Fig. 3), the EQ model predicted three steady states, but the NEQ model only one steady state.

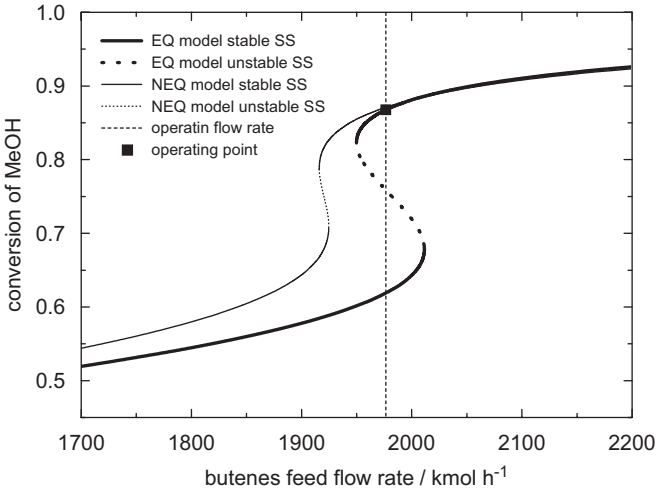

Fig. 3. Solution diagram conversion of methanol vs. butenes feed flow rate.

The presence of multiple steady states could strongly influence the reactor behavior during disturbances of input parameters, in our case butenes feed flow rate, when its very fast decrease was simulated (HAZOP deviation: “less flow”). After returning the butenes flow rate to the operating value, the system described with the EQ model was stabilized to the lower stable steady state with low conversion of methanol. However, the reactor described by the NEQ model will turn back to the original steady state (see Fig. 4).

4. Case study 2—Fixed bed catalytic reactor with parallel reactions

The selected system is a simplified reaction model for partial oxidation of ethylene to ethylene oxide in a fixed bed catalytic reactor according to the following reaction scheme:

$$O_2 + 2C_2H_4 \rightarrow 2C_2H_4O, \tag{R2}$$

$$O_2 + \frac{1}{3}C_2H_4 \rightarrow \frac{2}{3}CO_2 + \frac{2}{3}H_2O. \tag{R3}$$

The kinetic data have been adopted from the work of Westersterp and Ptasinski (1984), the operating conditions, reactor geometry and the transport parameters are reported by Labovský et al. (2006). The reaction takes place in an excess of ethylene.

Both reactions are exothermic. The activation energy and reaction enthalpy of the second reaction are higher than those for the first reaction. It means, that an increase of temperature will accelerate the rate of reaction (R3) with an increase of temperature in the reactor and decrease of the selectivity to the desired product. A one-dimensional heterogeneous model with axial dispersion was used. External heat and mass transfer between the fluid and the solid phase was assumed. However, internal diffusion and heat transfer inside the catalyst particle were neglected.

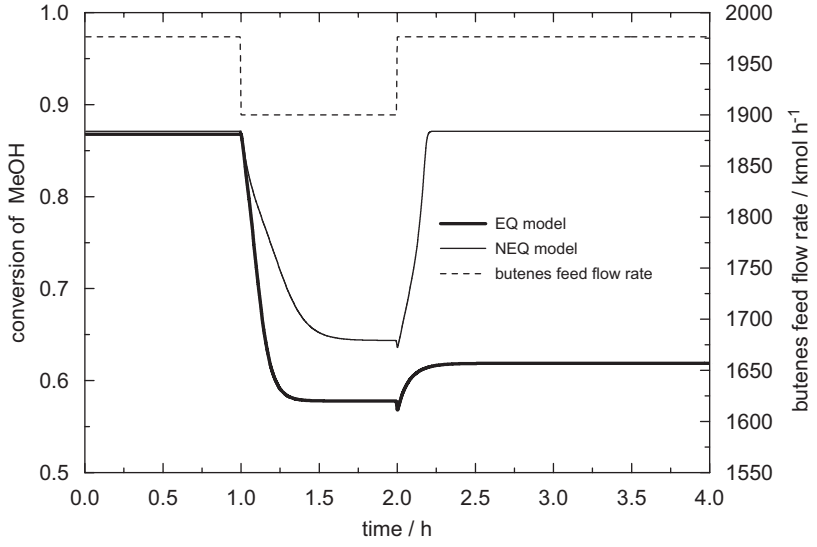

Fig. 4. Conversion changes in the reactor after a step change of the butenes feed flow rate.

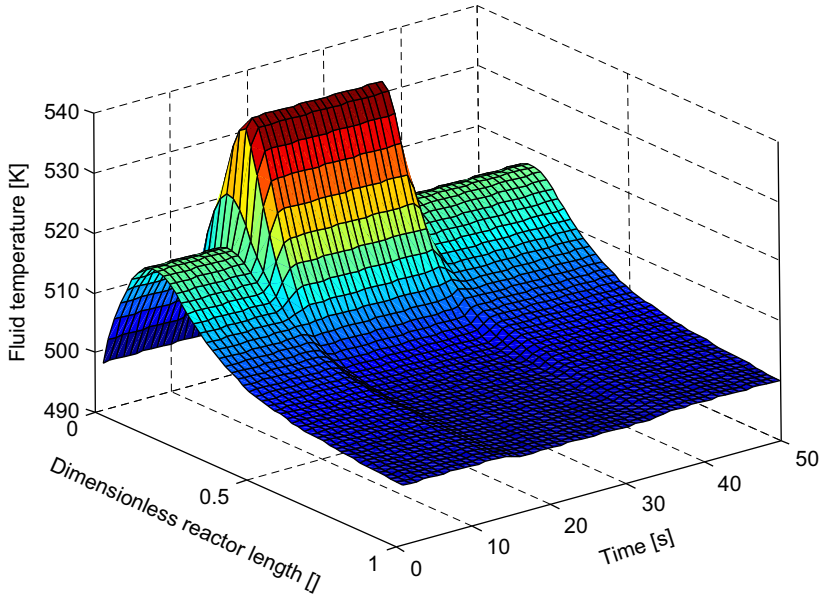

Fig. 5. Time and space temperature profiles in the reactor after the step increase of the inlet oxygen flow into the reactor (HAZOP deviation: higher inlet oxygen flow).

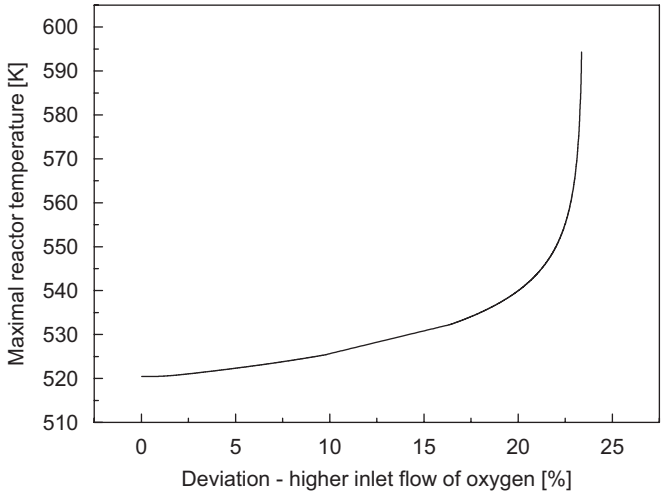

Fig. 6. Temperature in the hot spot as a function of oxygen inlet flow deviations.

The selected reaction system can be considered as a very fast system according to the previous case study. In Fig. 5 the time and space temperature profiles in the reactor are shown after a fast (step) increase of the input oxygen flow rate (HAZOP deviation: "higher inlet oxygen flow"). After the oxygen inlet flow has been turned back to the normal operating value, the reactor is turned back to the original steady state. From Fig. 6 it is possible to deduce, that the critical value for the higher oxygen inlet flow deviation is about +20% from the normal operating point, when the temperature in the hot spot is about 20 °C higher than that at normal operation. An increase of the oxygen content in the feed flow (higher than 20%) can cause an uncontrolled rise of the temperature in the hot spot—a possible run away effect.

Table 1
Possible generated consequences of the deviation from normal "*inlet oxygen flow*"

Deviation	Consequence
"No inlet oxygen flow" and "Lower inlet oxygen flow"	Not dangerous, but a technological problem, conversion is equal to zero or too low
"Higher inlet oxygen flow"	May be dangerous if the deviation is higher than 20%—possible run-away

As it has been already mentioned, information about the maximal temperature in the reactor is only a small part of the necessary information for the examination of the reactor safety. However, it is possible to extract and translate some partial information to the purposeful HAZOP consequences. With the utilization of the heuristic interpretation of the dynamic results it is possible to generate the consequences of three deviations of the "inlet oxygen flow" summarized in Table 1.

5. Conclusions

The HAZOP analysis of a chemical reactor integrated with its mathematical model could be a very useful tool not only for the working apparatus, but also in all steps of its design. The use of a mathematical model allows not only to generate the deviations from the normal operation conditions, but also to analyze the time duration of these deviations and the time profile of the device response. The results of these simulations are essential for the definition of the operator's strategy under normal and abnormal conditions, because of the need of an appropriate reaction in this situation.

A reliable prediction of equipment behavior during the deviations from the normal operation conditions is impacted by the selection of an adequate mathematical model. This is demonstrated in the first case example. Reactive distillation (RD) processes may exhibit a wide variety of multiple steady states and subsequent dynamic phenomena. Mohl et al. (1999) have shown that the multiple steady states found for a RD column (e.g. Jacobs and Krishna, 1993) have the same genesis as the multiplicity for a continuous stirred tank reactor. In our study of RD, two of possible modeling approaches for RD in a CSTR with total condenser (EQ and NEQ models) were used.

The EQ model is simpler and requires a less number of parameters. On the other hand, the assumption of equilibrium between vapor and liquid streams leaving the reactor could be difficult to fulfill, mainly when some perturbations of process parameters occur. The NEQ model takes into account interphase mass and heat transfer resistances, what leads to a more realistic description of the system. However, it is important to point out, that prediction of the reactor behavior by the NEQ model is strongly dependent on the quality of parameters, which describe interphase mass and heat transfer resistances.

Prediction of consequences for the HAZOP deviation "lower molar flow of the key component" by EQ and NEQ models (see Figs. 3–4) gives different answers. It is very difficult to make a decision whose approach is true. Because the NEQ model is more exact and precious, it seems to be more reliable than the EQ model. On the other hand, the indeterminacy and inaccuracy of a huge number of model parameters which are strongly dependent on the reactor construction and operation conditions require enhanced care and practical experience when the simulation results are analyzed.

The same situation is the event of the fixed bed reactors. For its modeling more complicated mathematical models can be used, e.g. two-dimensional models, models accounting the intraparticle resistance, etc. On the other hand, these model refinements require the knowledge of a larger number of parameters. The final quality of the simulation results is strongly dependent on these parameters.

All of the HAZOP deviations together with their consequences present a wide multidimensional view on the reactor safety. This information can directly serve for the examination of the reactor safety, or can be used as a robust basis for a subsequent ordinary HAZOP study.

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