HAZOP Analysis of CSTR with the Use of Mathematical Modelling*

Z. ŠVANDOVÁ, J. MARKOŠ**, and Ľ. JELEMENSKÝ

Department of Chemical and Biochemical Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-812 37 Bratislava
e-mail: jozef.markos@stuba.sk

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Modelling of a homogeneous continuous stirred tank reactor (CSTR) with a simple exothermic reaction for the computer-based HAZOP analysis is discussed. Using an appropriate mathematical model of CSTR, steady-state analysis (including analysis of multiplicity of steady states and their stability) and description of the dynamics behaviour of the reactor can be done. After generation of the parameter deviations in a chosen node, the steady-state solution diagram provides corresponding consequences of such failure. Dynamic simulation offers an answer to the time response of the reactor to the generated deviations. Moreover, it is possible to study also the influence of deviation duration on the reactor performance. Here, only one parameter, molar flow of the one of reactants, and its deviations from the normal operating point were investigated.

Many accidents of chemical reactors involving exothermic reactions called for the necessity of safety analysis in each step of their design. There are numerous basic questions, which have to be answered. A summary of these questions could be found elsewhere [1—4].

HAZOP is one of the best and most rigorous techniques for hazard identification in a chemical plant. The HAZOP procedure step by step formally examines all equipments of an enterprise as well as deviations from the equipment 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 [2—4].

The HAZOP algorithm can be successfully applied not only for existing plants, but also for new designed technologies and equipment. On the other hand, there exists one essential drawback of the HAZOP study, the possibility that hazards and dangerous scenarios may be overlooked. For more complicated units or reactors the discussion with a plant staff is often confusing and the causes of faults remain unclear, as the team of specialists accomplishing the HAZOP analysis does not have enough experience with the considered process. To gain information about the possible consequences of some deviations is often impossible, or the obtained information is wrong. This situation led to the development of computer-based approaches for hazard identification.

Recently, some considerations related to the safety analysis of chemical reactors and the use of mathematical model of chemical reactor for such analysis were presented [1]. In this paper, the hazard identification was applied on a continuously stirred tank reactor (CSTR) with a simple exothermic reaction. The analysis is based on application of the HAZOP procedure integrated with a mathematical model with the aim to determine the reactor response on deviations from normal operation conditions.

THEORETICAL

Mathematical model of a reactor consists of material balances of components, enthalpy balances of the reactor, and the cooling/heating media. Complexity of the model reflects the level of knowledge about the system considered [5] and its form depends on the purpose of its utilization [1, 6, 7].

Steady-state simulation and analysis of the possible multiple steady states and their stability, ignition-extinction analysis, parametric sensitivity analysis, run-away conditions, are represented by a system of nonlinear algebraic equations

$$F(\boldsymbol{X}, \boldsymbol{\alpha}, \boldsymbol{X}^{\mathrm{f}}) = 0 \qquad (1)$$

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**The author to whom the correspondence should be addressed.

Table 1. Model Parameters of CSTR with a Single Exothermic Reaction and the Reactor Steady-State Operation Condition

Reaction kinetics	
Pre-exponential factor, $k^{\infty}/(\mathrm{m^3\ mol^{-1}\ s^{-1}})$	96 000
Activation energy, $E/(\mathrm{J\ mol^{-1}})$	75 362
Heat of reaction, $\Delta_r H^{\mathrm{ref}}_{298}/(\mathrm{J\ mol^{-1}})$	−91 360
Reactor parameters, $\boldsymbol{\alpha}$	
Reactor volume, $V_R/\mathrm{m^3}$	2
Cooling medium temperature, $T^{\mathrm{f}}_{\mathrm{CM}}/\mathrm{K}$	288.15
Cooling medium molar flow rate, $F^{\mathrm{f}}_{\mathrm{CM}}/(\mathrm{mol\ s^{-1}})$	150
Overall heat-transfer coefficient, $U/(\mathrm{kJ\ s^{-1}\ m^{-2}\ K^{-1}})$	1.65
Heat-exchange area, $A/\mathrm{m^2}$	6.7
Reactor inlet conditions, $\boldsymbol{X}^{\mathrm{f}}$	
Molar flow rate of reactant A, $F^{\mathrm{f}}_{\mathrm{A}}/(\mathrm{mol\ s^{-1}})$	10
Molar flow rate of reactant B, $F^{\mathrm{f}}_{\mathrm{B}}/(\mathrm{mol\ s^{-1}})$	6
Temperature of inlet streams, $T^{\mathrm{f}}/\mathrm{K}$	299.15
Reactor outlet conditions, $\boldsymbol{X}$	
Reactor and outlet stream temperature, T/K	358.08
Cooling medium outlet temperature, $T_{\mathrm{CM}}/\mathrm{K}$	322.60
Outlet stream volumetric flow rate, $V/(\mathrm{m^3\ s^{-1}})$	8×10^{-4}
Outlet stream composition, $c_{\mathrm{A}}/(\mathrm{mol\ m^{-3}})$	5571
$c_{\mathrm{B}}/(\mathrm{mol\ m^{-3}})$	514
$c_{\mathrm{C}}/(\mathrm{mol\ m^{-3}})$	6965
Conversion of the reactant B	93.1 %

where $\boldsymbol{X}^{\mathrm{f}}$, $\boldsymbol{X}$, and $\boldsymbol{\alpha}$ represent the vectors of reactor inlet and outlet conditions and the vector of reactor parameters, respectively.

Dynamic simulation for the reactor start-up (analysis of initial conditions, safe way from the initial point to the desired steady state) and shut-down procedure, analysis of the effect of the process parameter fluctuations (continuous, step, impulse) on the reactor behaviour, could be modelled using a system of ordinary differential equations

$$\frac{\mathrm{d}\boldsymbol{X}}{\mathrm{d}t} = G(\boldsymbol{X}, \boldsymbol{\alpha}, \boldsymbol{X}^{\mathrm{f}}) \qquad (2)$$

with the following initial conditions

$$t = 0: \quad \boldsymbol{X} = \boldsymbol{X}^0 \qquad (3)$$

t being the time and $\boldsymbol{X}^0$ the vector of reactor outlet conditions at an initial steady state.

Detailed mathematical model of the CSTR, in which a simple exothermic reaction is carried out, could be found elsewhere [1].

For the purpose of the HAZOP analysis of CSTR (the flow diagram is schematically shown in Fig. 1), all streams related to the reactor (nodes) were investigated. For example, in a chosen node the parameter values (temperature, molar/volumetric/mass flow rate, composition, pressure, *etc.*) at normal operation conditions were identified. Using the guidewords (more, less, no, reverse...) appropriate deviations were created. For the molar flow rate of the component A in the stream A there are these deviations: more flow, less flow, no flow, reverse flow. 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. However, what exactly does the deviation "less flow" mean: 90 % or 20 % of the usual operation value? The deviation occurs as an immediate (step) decrease of the flow lasting 10 min or more, or is it only an impulse? Is this decrease continuous with some rate? Answers to these questions may be obtained by using an appropriate mathematical model. In such model the extent of deviations may be easily incorporated and possible consequences investigated.

Let us consider a CSTR working in a stable, safe steady state, in which a simple second-order exothermic reaction takes place according to the scheme

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} \qquad (A)$$

The steady-state characteristics of the outlet stream, $\boldsymbol{X}^0$, are given as a response to the reactor characteristics and characteristics of the streams fed into the reactor (see Table 1). In this study two inlet streams

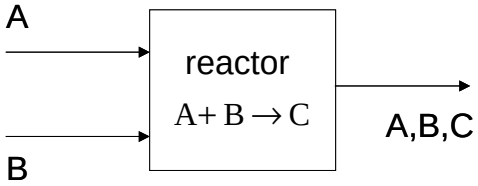

Fig. 1. Schematic flow diagram of the CSTR.

representing the pure reactants and one outlet stream were considered, according to the scheme shown in Fig. 1. The physical and chemical properties of components and mixtures correspond to the conditions, at which propylene glycol (C) is produced from water (A) and propylene oxide (B).

RESULTS AND DISCUSSION

As explained above, the HAZOP analysis is quite complex and time-consuming. Therefore, only one parameter, the inlet molar flow rate of the reactant A, and its deviations from the normal operation value are analyzed and discussed here.

The first step of the safety analysis is the identification of a locus of multiple steady states and examination of their stability. This parametric analysis was performed by the continuation algorithm, which is a modification of the CONT software presented in [8—10]. For given reactor parameters (Table 1), the solution diagram of temperature in the reactor as a function of the molar flow rate of the reactant A is presented in Fig. 2. Let us consider that the normal operating point of the reactor is represented by the white square in Fig. 2, *i.e.* for $F_{\mathrm{A}}^{\mathrm{f}} = 10$ mol s^{-1} the temperature in the reactor is 358.08 K and the conversion of the component B is equal to 93.1 %.

The solution diagram indicates an extensive oscillatory region on the left-hand side from the operating point and another oscillatory and unstable region on the right-hand side, where multiple steady states were identified (see Fig. 2).

Further, deviations of the molar flow rate of the reactant A and their consequences for the CSTR operation were investigated. The analysis was focused on the time profile of the reactor performance after the deviation occurred. Moreover, identification of the states leading to a hazard reactor behaviour, *i.e.* crossing of the practical stability limit, was carried out. Practical stability limit could be represented *e.g.* by the reaction mixture boiling point, reactor material stability or start-up of undesirable reactions, *etc.*

As mentioned above, the chosen node for HAZOP analysis was the reactor feed stream of the component A and the studied parameter, its molar flow rate. The designed steady-state operation value of this parameter was 10 mol s^{-1}. The influence of changes of the component A input stream on the reactor performance was investigated.

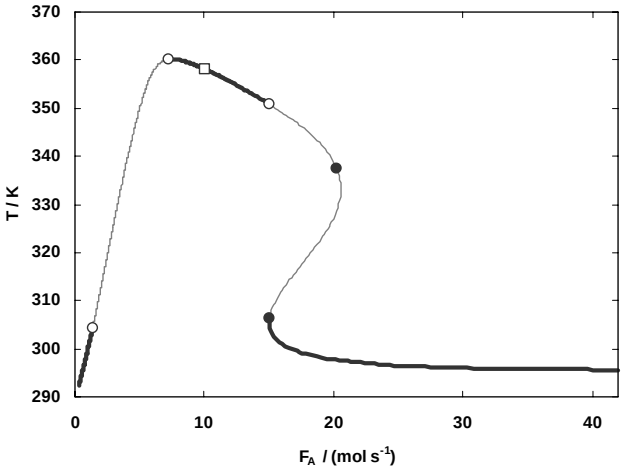

Fig. 2. Solution diagram of the temperature of CSTR as a function of the flow rate of reactant A: stable steady state – thick solid line, unstable steady state – thin solid line, limit points – solid circles, Hopf bifurcation points – empty circles, reactor normal operation point – white square.

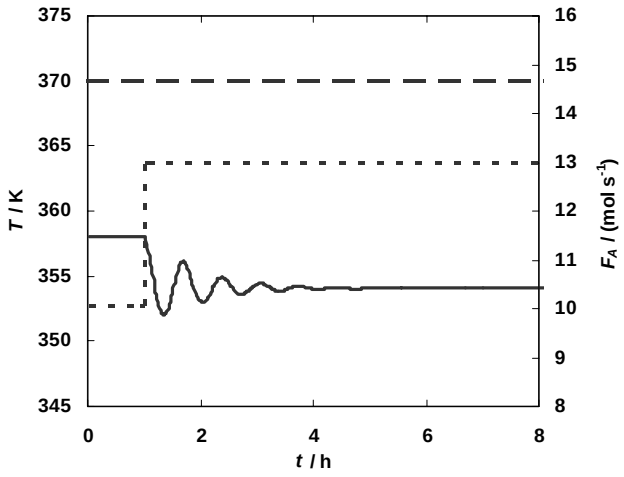

Fig. 3. Step-up change of the flow rate of reactant A from the value of 10 to 13 mol s^{-1}: reactor temperature – solid line, reactant A flow rate – dotted line, practical stability limit – dashed line.

If a step change of the reactant A molar flow from 10 to 13 mol s^{-1} was considered (*i.e.* the value by 30 % higher than the normal operation one), attenuated oscillations of the reactor temperature were observed and a new stable steady state (reactor temperature 354.0 K, component B conversion 91.2 %) was achieved. During the transient state, the reactor practical stability limit was not crossed (Fig. 3).

For the value of the reactant A flow rate of 16 mol s^{-1}, the solution diagram (Fig. 2) indicated an oscillatory and unstable reactor behaviour. Dynamic simulation of the reactor performance showed (Fig. 4) that the reactor temperature oscillated with amplitude crossing the practical stability limit. The period

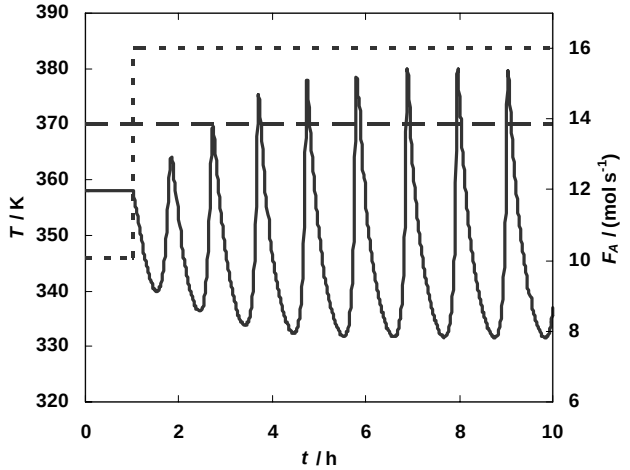

Fig. 4. Step-up change of the flow rate of reactant A from the value of 10 to 16 mol s^{-1}: reactor temperature – solid line, reactant A flow rate – dotted line, practical stability limit – dashed line.

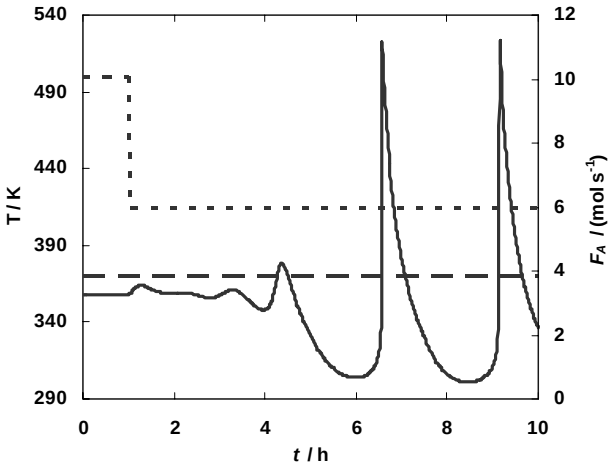

Fig. 6. Step-down change of the flow rate of reactant A from the value of 10 to 6 mol s^{-1}: reactor temperature – solid line, reactant A flow rate – dotted line, practical stability limit – dashed line.

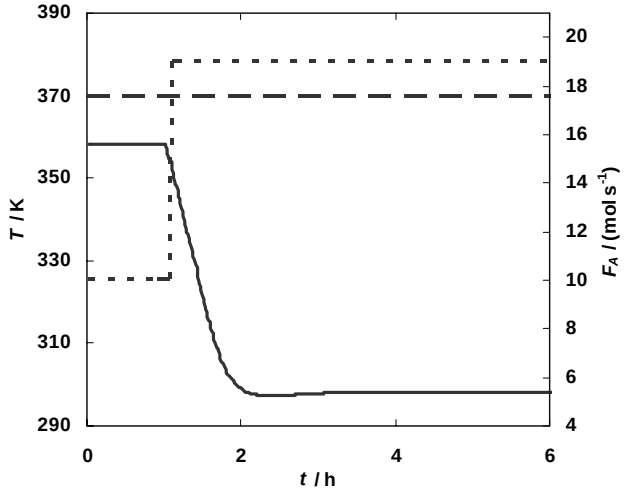

Fig. 5. Step-up change of the flow rate of reactant A from the value of 10 to 19 mol s^{-1}: reactor temperature – solid line, reactant A flow rate – dotted line, practical stability limit – dashed line.

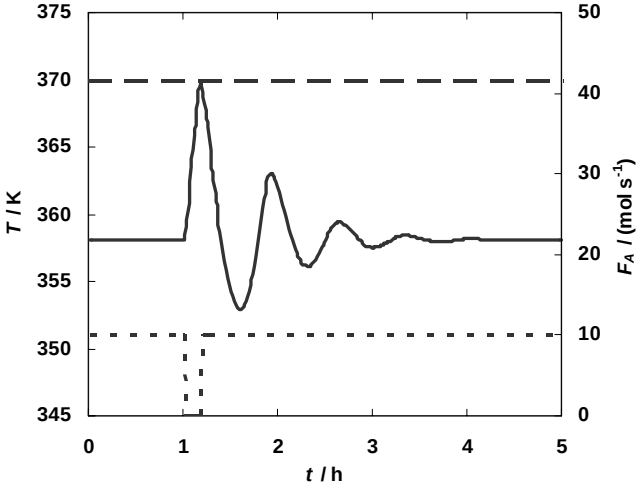

Fig. 7. Evolution diagram of a failure of the flow rate of reactant A for 10 min: reactor temperature – solid line, reactant A flow rate – dotted line, practical stability limit – dashed line.

of this oscillation was approximately one hour.

If the deviation of the reactant A molar flow rate was even higher, *e.g.* 19 mol s^{-1}, the reactor was switched to the lower stable steady state characterized by low temperature (298.2 K) and low conversion of the reactant B (9.7 %), see Fig. 5. Duration of the reactor extinction was about one hour. The reactor was switched to a safe steady state, without crossing the practical stability limit.

On the other hand, the reactant A molar flow rate of 1.5 to 7 mol s^{-1} corresponds to an oscillatory regime as indicated in the solution diagram (Fig. 2). In Fig. 6 such situation is demonstrated for the step change of the flow rate of the reactant A from 10 to 6 mol s^{-1}. When this deviation was imposed on the system, the reactor was working near the original steady-state conditions for a long time (more than 2 h). Later on, the reactor temperature started to oscillate and crossed the practical stability point.

Situation corresponding to "no flow" of the reactant A means that the continuous reactor becomes a semi-batch reactor containing certain amount of the reactant A with a continuous feed of the reactant B and a continuous outlet stream from the reactor.

Fig. 7 demonstrates consequences, when the reactant A flow was stopped for 10 min. At the beginning, the reactor temperature started rising and reached the practical stability limit. The temperature fell down prior to the reactant A flow rate was reestablished to its original value. At given conditions, the reactor tem-

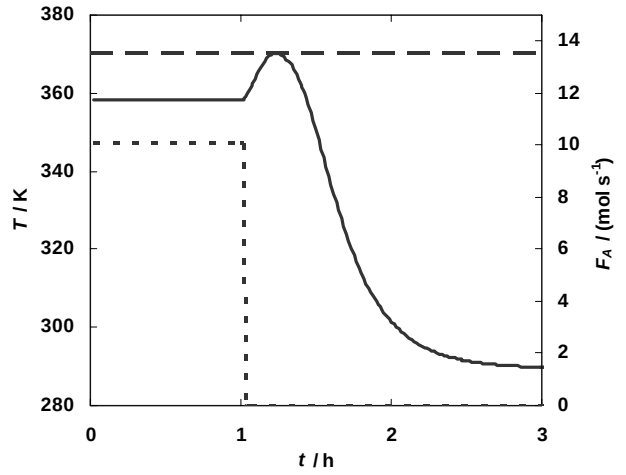

Fig. 8. Evolution diagram of a failure of the flow rate of reactant A: reactor temperature – solid line, reactant A flow rate – dotted line, practical stability limit – dashed line.

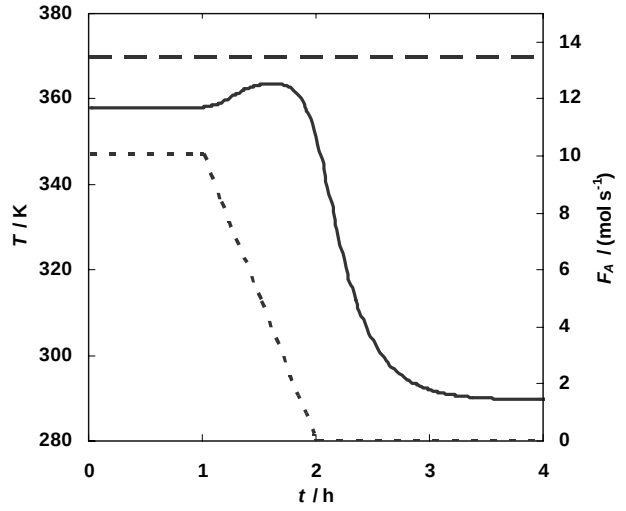

Fig. 9. Evolution diagram of the reactor shut-down by stopping the reactant A feed flow into the reactor: reactor temperature – solid line, reactant A flow rate – dotted line, practical stability limit – dashed line.

perature turned back to the normal operation point.

In the case that the reactant A flow rate was suddenly switched off (Fig. 8), the reactor temperature approached the practical stability limit very quickly. Then, after a few minutes, the temperature decreased again and the reaction was stopped. A dangerous situation could be expected, when the reactor temperature reached the practical stability limit.

Fig. 9 shows the consequences, when the reactant A flow rate was gradually decreased during 1 h from the normal operation conditions to "no flow" state. It was found that this could be a good shut-down strategy to extinct the reactor, as the practical stability limit was not crossed. The reactor was completely shut down approximately one hour after the reactant flow rate was stopped.

Analogically it is possible to perform this type of analysis for other parameters (*i.e.* temperature, concentrations, and pressure) and for other nodes (feed of the reactant B, feed of the cooling media).

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SYMBOLS

A	heat-exchange area	m^2
c	molar concentration	mol m^{-3}
E	activation energy	J mol^{-1}
F	molar flow	mol s^{-1}
$\Delta_r H^{ref}$	heat of reaction at reference temperature	J mol^{-1}
k^∞	pre-exponential factor	m^3 mol^{-1} s^{-1}
T	temperature	K
U	overall heat-transfer coefficient	J s^{-1} m^{-2} K^{-1}
V	volumetric flow	m^3 s^{-1}
V_R	reactor volume	m^3

Subscripts

A, B, C	reactants
CM	cooling medium
R	reactor

Superscripts

f	feed

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