STEADY STATES ANALYSIS AND DYNAMIC SIMULATION AS A COMPLEMENT IN THE HAZOP STUDY OF CHEMICAL REACTORS

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This paper discusses the relation between software tools primarily designed for mathematical modelling, simulation and investigation of chemical reactors and the common method for identification of hazard, the Hazard and Operability (HAZOP) study. We have tried to couple these tools with the HAZOP study. The principal objective was to present a new methodology for hazard investigation. In our work a multi-parameter analysis of a model system with exothermic reaction (hydrolysis of propylene oxide to mono-propylene glycol with consecutive reactions producing higher glycols) in two continuous-stirred tank reactors (CSTRs) in series with jacket cooling was used. In the first section a mathematical model of two CSTRs in series was formulated. The next step is safety analysis, including analysis of the multiplicity of steady states and their stability, study of safe operating, and conditions and trajectories, which can shift the reactors from one steady state to another steady state. Parametric studies of the failure of the reactants flow rate (propylene oxide and water) and of the cooling medium were also done. Finally, the results of safety analysis were reproduced and we tried to find all possibilities for utilization of these results in HAZOP studies.

Keywords: CSTR; HAZOP; nonlinear behaviour; multiple steady states; safety analysis; stability analysis.

INTRODUCTION

Hazard and operability studies (HAZOP) is a team-based brainstorming activity that systematically reviews a system representation and its operating procedure in order to identify potential safety related hazards (Fencott and Hebbron, 1995). Formal HAZOP review uses a list of key-words to examine each part of a facility to determine both the possible deviations and consequences of each mode of failure. Given a guideword and deviation produced by a theoretical cause, the consequences must then be determined. Each consequence is evaluated against frequency and severity. Finally, for each unacceptable consequence, corrective actions are evaluated (Kletz, 1999; AIChE/CCPS, 1995; Lees, 1996).

HAZOPs are normally carried out by a multi-disciplinary skilled team, but in some cases this team is not able to find relevant consequences, and corresponding corrective action. One feasible solution is designing software tools aimed at simulation and investigation of chemical reactors in virtual reality. In this article we present a safety analysis of two CSTRs in series. Our goal is to integrate the information obtained from dynamical simulation into HAZOP studies. In order to achieve this goal, two aspects should be considered.

The first aspect regards the mathematical modelling of chemical reactors (in our case a cascade of two CSTRs in series), including adequate kinetics and real operative conditions. As discussed by Paladino and Ratto (2000), in fact, when the systems under study involve complex mechanisms and coupled phenomena, very small errors and uncertainty do not have comparable effect on predictions, but they can complementary alter the results obtained. Therefore, the problem of model and parameter uncertainty cannot be neglected, when highly nonlinear systems are analysed, such as chemical reactors. Specifically the safety analysis of CSTR (CSTRs) includes some problems such as: identification of multiple steady states, analyses of the stability of this steady state, determination of conditions, which can shift the reactor from one steady state to another, identification of situations that could lead to unwanted reactor behaviour, and so on.

The second aspect involves a correct processing of the results, which are obtained during the mathematical
modelling and the safety analysis, and the finding of all possibilities for utilization of these results in HAZOP studies. In this part the guidewords are combined with the process parameter result in the deviations. The consequences of these deviations are determined as a result of mathematical modelling and safety analysis.

MA T H E M AT I C A L M O D E L

The mathematical model of two CSTRs consists of material balances of compounds, enthalpy balances of the reactor and enthalpy balances of the cooling medium (Froment and BischofT, 1990; Fogler, 1999). Additional equations can be used to enhance the accuracy of the basic model.

For each component \(i\) of \(S\) components, in the \(k\)th perfectly mixed continuous tank reactor with \(R\) reactions, the following mass balance equation can be written as follows:

\[
\frac{d c_i^{(k)}}{dt} = V_{R,k} \left( c_i^{(k-1)} - c_i^{(k)} \right) + V_{R,k} \sum_{j=1}^{R} v_{ij} r_{ij}^{(k)}
\]  

(1)

The reaction rate \(r\) of the \(j\)th reaction in the \(k\)th CSTR can be expressed by the following equation:

\[
r_{ij}^{(k)} = k_{ij} \prod_{i=1}^{S} c_i^{(k)}^{a_{ij}}
\]

(2)

The temperature dependence of the reaction rate constant is given by the Arrhenius equation

\[
k_{ij} = k_{ij}^0 e^{-E_j/R_T}
\]

(3)

The enthalpy balance of the \(k\)th reactor can be written in the following form:

\[
V_{R,k} \sum_{i=1}^{S} c_i^{(k)} c_{p,i}^{(k)} \frac{dT_k}{dt} = \sum_{i=1}^{S} V_{R,k} \left( c_i^{(k-1)} c_{i}^{(k+1)} (h_{i,k}^{(k+1)} - h_{i,k}^{(k)}) + Q_k + V_{R,k} \sum_{j=1}^{R} (-\Delta H_{r,j}^{(k)}) r_{ij}^{(k)}
\]

(4)

The system of equations is completed with the enthalpy balance of the cooling medium. In our model the cooling medium is flowing from the jacket of the first reactor through the jacket of the next reactor. The mathematical model for cooling is often simplified by assuming infinite flow rate of the cooling medium. However this leads to a wrong interpretation of the resulting data. In practice the flow rate of the cooling medium is not infinite, resulting in a temperature change between the inlet and outlet jackets. The following equations are used to enhance the accuracy of the system by taking into account this temperature change:

\[
N_{c,k} c_{p,k} \frac{dT_c}{dt} = \hat{q}_c (h_{c,k}^{(k-1)} - h_{c,k}^{(k)}) - \hat{Q}_k
\]

(5)

\[
\hat{Q}_k = \frac{(UA)h_k (T_{c,k}^{(k-1)} - T_{c,k}^{(k)})}{\ln(T_{c,k}^{(k-1)} - T_k)/(T_{c,k}^{(k)} - T_k)}
\]

(6)

Both the molar heat capacity coefficient of components and the components molar density are expressed as a polynomial function of temperature:

\[
c_{p,k} = \sum_{n=0}^{S} a_n T_k^n
\]

(7)

\[
\rho_k = \sum_{n=0}^{S} b_n T_k^n
\]

(8)

The reactor outlet volumetric flow rate is expressed as a function of the density of the mixture:

\[
\hat{\rho}_k = \left( \sum_{i=0}^{S} \rho_i \right)^{-1}
\]

(9)

\[
\hat{V}_k = \hat{\rho}_k \sum_{j=1}^{S} x_{ij} \rho_j
\]

(10)

The dependence of the reaction enthalpy on temperature is expressed in form of the Kirchhoff equation:

\[
\Delta H_{r,j}^{(k)} = \int_{T_{r,j}}^{T_k} c_{p,r,j} dT + \sum_{i=1}^{S} V_{ij} c_{p,ij} dT
\]

(11)

The initial conditions of equations (1)–(11) are defined as follows:

\[
t = 0: \quad c_{i,k}^{(0)} \quad T_k = T_k^{(0)} \quad T_{c,k} = T_{c,k}^{(0)}
\]

(12)

REACTION SYSTEM

As a model reaction, the exothermic reaction involving the hydrolysis of propylene oxide to mono-propylene glycol with consecutive reactions producing higher glycols was chosen. When catalysed by sulphuric acid, the reaction yielding mono-propylene glycol (R1) takes place at room temperature. Consecutive reactions (R2) and (R3) start at certain conditions, due to the presence of propylene oxide, forming di-, tri- and higher polypropylene glycols (Sullivan, 1993).

\[
\text{OH} - \text{CH}_3 \rightarrow \text{HO}-\text{CH}_2-\text{OH}
\]

(R1)

\[
\text{HO} \cdot \text{CH}-\text{CH}_2 \rightarrow \text{HO}-\text{CH}-\text{CH}_2-\text{OH}
\]

(R2)

\[
\text{HO} \cdot \text{CH}-\text{CH}_2 \rightarrow \text{HO}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{OH}
\]

(R3)

The kinetic parameters of the first reaction (R1) were taken from Fogler (1999). Information on the kinetics of consecutive reactions (R2) and (R3) is scarce. Therefore, the kinetic data of di- and tri-polypropylene glycols formations [reactions (R2) and (R3)] have been estimated assuming that the reaction rates ratio of the consecutive reactions with respect to the primary reaction (R1) is
commonly used.

The steady state (Holodnictk et al., 1986; Kubofek, 1976) is an eigenvalues of a linearized state equation in the vicinity of the steady-state point. This point is assumed stable only if the response to a small perturbation remains small as the time approaches infinity. Otherwise, the stationary solution is called unstable (Schmitz, 1974). A very known stability analysis (Van Heerden, 1953) is based on the comparison of heat generation and heat withdrawal curves, where the S-shape characteristic curve of the reactor gives the relation between the selected parameter and the output reaction temperature and the cooling curve gives the possible cooling characteristic in the same manner as the heating curve. Points, in which these two curves intersect, are possible steady state points. The stability of the steady-state point is indicated by the slopes of the tangent of each curve in the steady-state point. This point is assumed stable only in the case when the slope of the cooling curve is higher than the slope of the heating curve at the point of intersection. Such analysis is suitable only for simple reactions and cannot be applied to complex reaction systems with strong nonlinearities (Farr and Aris, 1986). Nowadays, local stability analysis, in which the stability is characterized by the eigenvalues of a linearized state equation in the vicinity of the steady state (Holodniok et al., 1986; Kubíček, 1976) is commonly used.

The analysis of multiple steady states was performed by means of a continuation algorithm, which is a modification of the CONT software presented by Marek and Schreiber (1991).

The next step in safety analysis of a CSTR (or a cascade of CSTRs) is the determination of conditions, which can shift the reactor from one steady state to another (e.g., from a steady state with good conversion to a steady state with worse conversion, or to a dangerous steady state above the practical stability limit). This state is usually caused by changes in the operating conditions. For example, input feed composition, input feed temperature or flow rate and temperature of the cooling medium (Paladino and Ratto, 2000). These changes can be continuous with several gradients, step or impulse. For safety analysis, it is very important to also have knowledge about the trajectory from one steady state to another. The next problem is the identification of states that could lead to unwanted reactor behaviour. Such states could be for example an oscillatory regime of the reactor or a state, which causes the practical stability limit to be crossed. The practical stability limit is presented for example by the boiling point of the reaction mixture, reactor material stability or start up of undesirable reactions, and so on. By performing simulations of the reactor dynamics, one could answer questions about unwanted reactor behaviour and conditions, which can shift the reactor from one steady state to another.

Furthermore, parametric studies on the failure of the reactants flow rate (propylene oxide and water) and the flow rates of the cooling medium have been performed. The reason is that during normal reactor operation the flow rate of the feed may vary, provoking undesirable changes in stability and reactor output. Parametric studies of a failure of the cooling medium are also very important, because hydrolysis of propylene oxide to mono-propylene glycol with consecutive reactions producing higher glycols is a highly exothermic reaction.

**SAFETY ANALYSIS**

The first step in the safety analysis of a CSTR (or a cascade of CSTRs) is the identification of multiple steady states and their stability. The multiplicity of steady states is expressed as the number of different sets of state variables at which the change of all state variables with time is zero for a fixed set of conditions or parameters (Schmitz, 1974). In other words, different conversion can be reached under the same conditions (Molnár et al., 2003). The number of steady states is related to the number of running chemical reactions in the order of equation 2n + 1, in which n is the number of independent reactions (Balakotaiah and Luss, 1982). However, this assessment is valid for the first cascade reactor, for the next cascade reactors, multiple steady states are observed in comparison with the first cascade reactor.

Stationary solutions are considered to be stable if the response to a small perturbation remains small as the time approaches infinity. Otherwise, the stationary solution is called unstable (Schmitz, 1974). A very known stability analysis (Van Heerden, 1953) is based on the comparison of heat generation and heat withdrawal curves, where the S-shape characteristic curve of the reactor gives the relation between the selected parameter and the output reaction temperature and the cooling curve gives the possible cooling characteristic in the same manner as the heating curve. Points, in which these two curves intersect, are possible steady state points. The stability of the steady-state point is indicated by the slopes of the tangent of each curve in the steady-state point. This point is assumed stable only in the case when the slope of the cooling curve is higher than the slope of the heating curve at the point of intersection. Such analysis is suitable only for simple reactions and cannot be applied to complex reaction systems with strong nonlinearities (Farr and Aris, 1986).

**CASE STUDY**

Propylene oxide and water were fed into the first cascade member as two separate streams. The inflow temperature of both streams was 299.15 K and the reactor pressure was approximately 2 MPa. At standard operating conditions, the molar flow rate of propylene oxide was 13 mol s⁻¹ and the molar flow rate of water was 6.8 mol s⁻¹. Two 1 m³ reactors were cooled with a jacket; the cooling medium, water, was fed into the first cascade member at a temperature of 288.15 K with a flow rate of 105 mol s⁻¹. The cooling medium was flowing from the jacket of the first reactor to the jacket of the second reactor. However, due to the high quantity of heat evolved by the reactions, the parameter UA of the cooling system was set to 10 kW K⁻¹.

Under these conditions, the main product was di-propylene glycol and the reactors were operated at stable steady state at a temperature of 470 K (first cascade member) and 425.7 K (second cascade member), respectively.

The temperature in the reactors should not exceed 503.15 K, the point of practical stability limit. Reaching this temperature would result in a large amount of reaction mixture being evaporated.
RESULTS AND DISCUSSION

Possible deviations during the HAZOP study are generated by rigorous questioning, prompted by a series of standard 'guidewords' applied to the intended design. (Kletz, 1999). After the guideword is coupled with the parameter, a deviation is generated. The next step in the HAZOP study is to look for potential consequences. In some cases, when complex consequences are generated, there is the application of mathematical modelling in order to find its consequences. Furthermore, mathematical modelling may also lead to the detection of some new or a more specific deviation.

Another important application of mathematical modelling is in the investigation of systems under abnormal situations (failure of reactant, step change of reactant flow rate, and so on). The results from these simulations are essential for the definition of the operator's strategy under normal and abnormal conditions.

The safe operation of a reactor is limited by several factors and these practical limitations must be taken into account during the safety analysis. An important question for practical application is the effect of cooling or feed failure. For this purpose, the molar flow rate of propylene oxide (first reactant), water (second reactant) and the molar flow rate of the cooling medium have been chosen as the parameters of interest, all three having an eminent influence on safe reactor operation.

Analysis of Propylene Oxide Flow Rate (First Reactant)

During the reactor operation, the feed flow rate may vary, invoking undesirable changes in the output of the reactor and its operation stability. The solution diagrams of temperature as a function of propylene oxide flow rate for two CSTRs in series [see Figure 1(a) and (b)] indicate, which deviation from the normal operating point can lead to unwanted situations, i.e., oscillatory, or unstable reactor regime.

The operation point of the first cascade member [Figure 1(a)] is located on the extensive stable branch, far from the regions of oscillatory regimes. Only an unwanted increase of the flow rate of propylene oxide will shift the operation point above the practical stability limit (above 503 K). The molar flow rate of propylene oxide in the operation point is 13 mol s$^{-1}$ and the reactor temperature at this point is 470 K. However at the molar flow rate of 13 mol s$^{-1}$ a lower stable steady state is possible. This may occur by an unwanted situation during the reactor operation. The temperature at this steady state is 298 K and the conversion is very low.

The operation point of the second cascade member [Figure 1(b)] is also located on the extensive stable branch. However, an unwanted increase in the flow rate of propylene oxide will shift the operation point into the oscillatory region. In this reactor, further steady states are above but also under the operation point. These can be evoked by unwanted situations. The temperature in the lowest steady state is 307 K and again the conversion is too low.

Dynamic simulation of an instantaneous failure of the propylene oxide flow

The analysis of the solution diagrams of the parameter—propylene oxide flow rate [Figure 1(a) and (b)] implies, that a small change of the propylene oxide flow rate does not cause the crossing of the practical stability limit. But, what happens in the case when the guideword is 'No'? The generated deviation would be: 'No flow of propylene oxide'. This sort of deviation can be investigated by dynamic simulation. Though the investigation of a different long failure of the propylene oxide flow rate by dynamic simulation is very simple, the acquired information is very complex.

Duration of the failure of propylene oxide flow rate significantly influences the temperature trajectory in all reactors in series. For a two minute long failure of the propylene oxide flow rate (Figure 2), the temperature trajectories change. At first, the temperature in both reactors falls, then the temperature grows sharply to the above operation temperature, and finally returns to the operation value. In this case the practical stability limit is not crossed.

The practical stability limit is crossed at a four minute failure (Figure 3). In this case, the temperature of the first cascade member increases so rapidly that the practical stability limit is exceeded. After crossing the practical

![Figure 1](image_url)

Figure 1. (a) Solution diagrams of temperature of the first cascade member as a function of propylene oxide flow rate. (b) Solution diagrams of temperature of the second cascade member as a function of propylene oxide flow rate. (Thick curves, stable steady state; thin curves, unstable steady state; dashed horizontal line, the practical stability limit; solid circles, limit points; empty circles, Hopf bifurcation points; white square, normal operation point of the reactor.)
stability limit, a large amount of reaction mixture is evaporated and a dangerous situation may occur.

An 8 minute failure of propylene oxide was simulated. In this case the practical stability limit was not crossed and both cascade reactors shifted to the lower steady state (see Figure 4). This situation is not dangerous, but unfavourable, because conversion is too low. This steady state is indicated on the solution diagrams of the parameter—propylene oxide flow rate [Figure 1(a) and (b)].

Thus, if the failure of propylene oxide is shorter than two minutes, the practical stability limit is not crossed and the temperatures in the reactors return to operation values. If the failure of propylene oxide is between 4–8 minutes, the practical stability limit is crossed, which may lead to a dangerous situation. However, if the failure is longer than 8 minutes, both cascade members shift to the lower steady state and the practical stability limit is not crossed. Knowledge concerning these temperature trajectories and reactors behaviour is important for the plant operator.

because of the need of an appropriate reaction in this situation. The deviation ‘No flow of propylene oxide’ in the HAZOP study should be defined more specifically with reference to the duration of failure, because different action would be necessary for different durations of failure.

Analysis of Water Flow Rate (Second Reactant)

Fluctuations of the flow rate of water are also dangerous for the safety of the process. Water is a key component for reaction (R1) and the amount of water in the system has a dominant influence on the yield of consecutive reactions (R2) and (R3); therefore the HAZOP study and mathematical modelling of a possible failure must analyse this fault. By means of mathematical modelling we can investigate the position of the operating point of both cascade members. Solution diagrams of the temperature of two CSTRs in series as a function of the water feed flow rate are depicted in Figure 5(a) and (b).

The operation point of the first cascade member [Figure 5(a)] is located near the Hopf bifurcation point, which indicates the boundary of the oscillatory region. A sudden decrease in the flow rate of water will move the operation point into this region. This state evokes oscillations of the temperature and concentrations in the reactor. In the case of large-scale oscillation, the practical stability limit can be crossed or the reactor can be switched into a lower steady state (both cases are an unfavourable state). On the contrary, on the right hand side of the operating point (when the water flow rate is higher), there are no oscillatory or unstable regions.

The operation point of the second cascade member [Figure 5(b)] is closely located near the oscillatory region as in the case of the first cascade member. Moreover, in this case, a multiple number of limit points and regions of oscillatory regimes are located on the left hand side of the operating point. Operation within these states can take place at flow rates lower than the defined operating conditions.
Figure 5. (a) Solution diagrams of temperature of the first cascade member as a function of water flow rate. (b) Solution diagrams of temperature of the second cascade member as a function of water flow rate. (Thick curves: stable steady state; thin curves: unstable steady state; dashed horizontal line: the practical stability limit; solid circles: limit points; empty circles: Hopf bifurcation points; white square: normal operation point of the reactor.)

Simulation of a step change of the water flow rate

The analysis of solution diagrams of the parameter—water flow rate [Figure 5(a) and (b)] implies, that a small increase in the water flow rate does not cause crossing of the practical stability limit. A different situation occurs, if the water flow rate is changed to a lower value. We hence investigated the case, when the deviation ‘lower flow rate of water’ was generated.

If a step change of some parameter occurs, the reactors are forced to find a new steady state. A different steady state can cause different behaviour of cascade reactors. In some cases the practical stability limit can be crossed.

At first, we simulated a step change of the water flow rate from 6.8 mol s⁻¹ to 6.3 mol s⁻¹ (Figure 6). In this case both cascade reactors were in an oscillatory regime, but the practical stability limit was not crossed.

When the water flow rate was changed to 6 mol s⁻¹ (Figure 7), the amplitude of oscillation rapidly increased with time. In this case the ratio of the water flow rate to the flow rate of propylene oxide was insufficient. Hence, consecutive reactions (R2) and (R3) were dominant. Since these reactions are significantly exothermic, the production of heat was too high and the practical stability limit was crossed.

Finally, we simulated a larger step change of the water flow rate to a value of 5 mol s⁻¹ (Figure 8). For this case, the practical stability limit was not crossed, because the cascade members shifted to a lower stable steady state. These stable steady states can be found in the solutions diagrams [see Figure 5(a) and (b)]. This situation is not dangerous, but undesired, because the amount of water in the system is too small and the rate of reaction (R1) and consecutively of reactions (R2) and (R3) is very low.

Though only one deviation was generated, several possible consequences were found by the dynamic simulation, according to the extent of the decrease in the water flow rate. The simulation thus reveals the importance of keeping the water flow rate at a constant operation value, because very small changes in this parameter would cause that the reactors move to oscillatory regimes and the practical stability limit may be crossed. Knowledge of this is very important not only for the operator, but also for the
HAZOP team, in charge of determining the corrective actions for each unacceptable consequence.

Analysis of the Cooling Medium Flow Rate

Two parameters are used to control the cooling of the reactor: the flow of the cooling medium and its inflow temperature. The last parameter, which has been investigated in this study, is the flow of the cooling medium. In our model the cooling medium flows from the first reactor to the second. Failure of the cooling medium thus influences both cascade members. Solution diagrams for the cooling medium flow rate are shown in Figure 9(a) and (b). Our attention was once again focused on the location of the operating points.

The operation points of both cascade members are located near the Hopf bifurcation point. On the right hand side of the operation points several limit points and regions of oscillatory regimes can be found. More limit points and regions of oscillatory regimes are shown in the solution diagram of the cooling medium flow rate for the second cascade member. Operation within these states can take place only at flow rates higher than the normal ones. In such a situation, the reactors will enter the oscillatory regime with different amplitude of oscillations. When the oscillations are large, the temperature could potentially cross the practical stability limit, even though the flow rate of the cooling medium is higher.

In the case of a rapid or gradual decrease of the cooling medium flow rate, the temperature in the first reactor will start rising following the branch of steady states. In this case, the second cascade member can shift to higher steady state or follow the branch of steady state on which the operation point is located. However, in the case of both reactors, the practical stability limit will be crossed, at a certain value of the flow rate.

Simulation of a step change of the cooling medium flow rate

The analysis of the solution diagrams [Figure 9(a) and (b)] of the parameter—cooling medium flow rate—reveals that a decrease in the cooling medium flow rate causes the practical stability limit to be crossed primarily, because the cooling medium flow rate is insufficient to provide enough cooling.

We thus have investigated the case, when the deviation was ‘lower flow of the cooling medium’. A step change of the cooling medium flow rate from 105 mol s\(^{-1}\) to 80 mol s\(^{-1}\) was simulated, 80 mol s\(^{-1}\) being the lowest cooling medium flow rate at which the practical stability limit is not crossed (Figure 10). Any cooling medium flow rate lower than 80 mol s\(^{-1}\) causing the practical stability limit to be crossed as is insufficient to cope with the rate of heat production of the exotherms.

If the investigated deviation is ‘higher flow of the cooling medium’ it could be expected, that at normal conditions, the temperature in both cascade reactors would decrease with increased flow of the cooling medium.

The solution diagrams [see Figure 9(a) and (b)] indicate an oscillatory behaviour, if the cooling medium flow rate is higher than the standard operating value. However, the dimension of oscillations is not discernible from these diagrams. If there is a bigger step change of the cooling
medium, say to 120 mol s\(^{-1}\) (see Figure 11), the temperatures in both reactors oscillate with a great amplitude and the temperature in the first cascade member crosses the practical stability limit.

When an even bigger step change to 150 mol s\(^{-1}\) was simulated (see Figure 12), the temperatures in both reactors decreased, without crossing the practical stability limit. The lower steady states on the stable branches are found for both cascade members.

Some important conclusions drawn from the changes in the cooling medium flow rate are: the practical stability limit will be crossed, if the cooling medium flow rate is lower than 80 mol s\(^{-1}\), due to insufficient cooling. If the flow rate of the cooling medium is increased to higher than the safe point value, the temperature in both reactors will oscillate with a large-scale amplitude and the practical stability limit may be crossed.

**CONCLUSIONS**

In the present paper, we tried to show a new methodology for the hazard identification. The basis of this methodology is the integration of software tools primarily designed for the safety analysis of chemical reactors into the HAZOP study. This integration is useful for identification of consequences for some deviations, for the suggestion of corrective actions. A dangerous situation can be pre-empted for suggestion of corrective actions. Moreover, the integration of mathematical modelling into the HAZOP study may potentially lead to the detection of some unexpected deviations.

An important aspect of the safety analysis is the knowledge of the existence of multiple steady states and their stability, connected with transient behaviour of the reactors. In the present work a multi-parameter analysis of an exothermic reaction (hydrolysis of propylene oxide to mono-propylene glycol with consecutive reactions producing higher glycols) is reported. Parametric studies of a failure of the reactants flow rate (propylene oxide and water) and the flow rate of the cooling medium were done. We have investigated the steady state multiplicity for all three parameters and observed an influence of these multiplicities on the reactors behaviour during dynamic simulations.

The first investigated parameter was the reactant (propylene oxide) flow rate and our attention was focused on the deviation 'no flow of propylene oxide'. We have shown, that duration of the failure has a dominant influence on the behaviour of the reactors. A different duration of failure causes different consequences implying that different actions need to be suggested by the HAZOP team.

During investigation of the second parameter—the flow rate of the reactant water—the deviation 'lower flow of water' was interesting. When a step change was made, the reactors were forced to find a new steady state. Solutions diagrams gave some information about the multiplicity of steady states and the unstable or oscillatory regimes of the steady states. The dynamic simulation of a lower flow rate of water gave rise to an oscillatory
The third investigated parameter was the cooling medium flow rate. In this case the deviations ‘lower flow of the cooling medium’ and ‘higher flow of the cooling medium’ were investigated. When the cooling medium flow rate was decreased, the temperature in the reactor rose, following the branch of steady states. The practical stability limit was crossed, when the cooling medium flow rate was lower than 80 mol s\textsuperscript{-1}. An anomalous situation takes place when the cooling medium is higher than the intended design. Two outcomes were found depending on the size of the increase of the flow rate. When the flow rate of cooling medium was increased to 120 mol s\textsuperscript{-1}, the operating point crosses the oscillatory region and the temperature oscillates with a great amplitude and the practical operating point crosses the oscillatory region and the temperature limit is crossed. However, an increase to 150 mol s\textsuperscript{-1} did not result in oscillatory behaviour and the practical stability limit was not crossed. This anomalous behaviour is again connected with multiplicity, oscillatory and unstable character of steady states. Therefore this information is very important for the HAZOP team for suggestion of effective corrective actions.

### NOMENCLATURE

- \(A\): area, m\textsuperscript{2}
- \(a\): reaction order in equation (2)
- \(a\): coefficient in equation (7)
- \(b\): coefficient in equation (8)
- \(c\): molar concentration, mol m\textsuperscript{-3}
- \(c_p\): molar heat capacity, J mol\textsuperscript{-1} K\textsuperscript{-1}
- \(E\): activation energy, J mol\textsuperscript{-1}
- \(h\): molar enthalpy, J mol\textsuperscript{-1}
- \(\Delta H\): heat of reaction, J mol\textsuperscript{-1}
- \(\Delta H^{0}\): heat of reaction at reference temperature \(T_{ref} = 298\) K
- \(k\): reaction rate constant, m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}
- \(k^{*}\): pre-exponential factor, m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}
- \(n\): molar flow rate, mol s\textsuperscript{-1}
- \(N\): accumulation of fluid, mol
- \(Q\): heat flow rate, J s\textsuperscript{-1}
- \(r\): molar rate of chemical reaction, mol m\textsuperscript{-3} s\textsuperscript{-1}
- \(R\): gas constant, J mol\textsuperscript{-1} K\textsuperscript{-1}
- \(S\): number of reactions
- \(S_{n}\): number of components
- \(t\): time, s
- \(T\): temperature, K
- \(U\): overall heat transfer coefficient, J s\textsuperscript{-1} m\textsuperscript{-2} K\textsuperscript{-1}
- \(V\): volume of reactor/reaction mixture, m\textsuperscript{3}
- \(V_{o}\): volumetric flow rate, m\textsuperscript{3} s\textsuperscript{-1}
- \(x\): component molar fraction

**Greek symbols**

- \(\nu\): stoichiometric coefficient
- \(\rho\): molar density, mol m\textsuperscript{-3}

### References


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