

## SAFETY ANALYSIS OF CHEMICAL REACTORS

ATTILA MOLNÁR, JOZEF MARKOŠ, ĽUDOVÍT JELEMENSKÝ

*Dep. of Chemical and Biochemical Engineering, Faculty of Chemical Technology,  
Slovak Technical University, Radlinského 9, Bratislava, Slovakia.  
E-mail: attila@chtf.stuba.sk, markos@cvt.stuba.sk, jelemen@chtf.stuba.sk*

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### 1. INTRODUCTION

Modern trends in reactor design or reactor parameter revision make use of software tools primarily designated for simulation. A proper engineering tool for design and simulation studies is HYSYS. The safety analyses provided by these tools are mostly insufficient.

From the view of the operation safety, the attention should be focused on chemical reactors. In many reactors highly exothermic reactions are running. Therefore, the rate of heat generation and cooling possibilities are the most significant criterions of design. The number of reactors where the main specification is the safe operation is low. Many reactors were designed by "scale-up" method and were run without safety analysis.

Chemical production in which chemical reactions take place at extreme conditions (high temperature and pressure), require a detailed analysis of possible danger situations, which may lead to industry accidents with menace of lives and health not only of workers, but also of civilians. The Directive 96/82/EC on the control of major-accident hazards determines the duties of the operators of chemical productions to identify the potential danger that may result from their activities. Individual accent lays on the analysis of danger that may result from chemical reactions performed not only at standard conditions, but also at undesirable situations. The accident in Seveso, Italy in 1976, showed the implications, which may result from darkness about the existence and conditions of subsidiary reactions. [Lees, 1996].

Safety criterions of modern design of equipment are not evaluated during the whole design process, but only within specific decision steps. Identification of risky states during design process can significantly reduce or completely remove its occurrence. About 25% of accidents in chemical industry took place due to mistakes in design and at least 30% of mentioned accidents were evincible [Lees, 1996].

#### 1.1. Historical review

The study of multiple steady states of a stirred tank reactor in which a single reaction occurs has been the subject of much research of many authors<sup>1</sup>. The existence of more than one chemical reaction makes the system complicated, thus the analytical solution of this system is becoming very complex.

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<sup>1</sup> System of equations is relatively simple and therefore the information can be obtained easily.

The first mention of the existence of multiple steady states and the associated stability phenomena was made by [Liljenroth, 1918]. A paper on autothermic reactors contains an argument for stability from the slopes of the heat generation and removal curves [Heerden, 1953]. For the first time [Bilous and Amundson, 1955] treated the reactor as a dynamical system, and by using Ljapunov's method of linearization, a pair of algebraic conditions for local stability was given. They had touched a topic of a consecutive reaction scheme  $A \rightarrow B \rightarrow C$  and had shown that up to five steady states might be expected under some conditions.

Mathematical methods for solving complex systems of equations were developed [Kubíček, 1976, Kubíček, 1983, Holodniok and Kubíček, 1984, Holodniok and Kubíček, 1984, Holodniok, Klíč, et. al., 1986, Marek and Schreiber, 1991]. The study of multiple steady states, stability and dynamics of reactive distillation are the topics of the recent years.

## 2. PROGRAM HYSYS

Process modeling that cannot be simply calculated, often consumes a lot of time. Especially in that cases when the model requires new calculations with various initial conditions that must be entered manually. Using an integrated engineering package like HYSYS, all the required applications work within common integrated environment. The true integrated environment has a number of advantages [Pongo and Poras, 1996]:

1. All information are shared, rather than transferred among applications,
2. All applications use common thermodynamic models,
3. All applications use common flow sheet topology,
4. User only need to learn one interface
5. User can switch between modeling applications at any time, gaining the most complete understanding of the process

The integrated environment is a combination of all models with data and therefore it is simply to design a steady state model, perform optimization, carry out some sizing and costing calculations, to do some dynamic modeling to determine appropriate control strategies. Finally, we might perform some on-line modeling using actual plant data for "what-if" studies.

### 2.1. Safety analysis by HYSYS

From some points of view, the utilization of HYSYS for safety analysis of continuous stirred reactor is not suitable. The identification of multiple steady states with HYSYS is not sufficient, even though this is the primary step when identifying the possible dangerous states of a reactor [Purdeková, 1999, Kvinta, 2000]. The program can identify only some of the steady states of the reactor, but neither the stability nor the number of steady states [Kvinta, 2000]. The advantages of the program are in dynamic regime, which is suitable for on-line simulations of properties not visible in steady state. Benefits are in monitoring the jumps between steady states, but there are some limitations in the starting conditions of reactor startup [Purdeková, 1999].

### 3. MATHEMATICAL MODELING OF CSTR

#### 3.1. Material balance

Suppose we have  $R$  chemical reactions taking place between  $S$  species in a continuous flow stirred tank reactor. Let  $v_{ij}$  be the stoichiometric coefficient<sup>2</sup> of the  $j$ -th species in the  $i$ -th reaction. Let  $r_i$  be the rate of the  $i$ -th reaction<sup>3</sup> defined so that  $v_{ij} \cdot r_i$  gives the rate of production of the  $j$ -th species in the  $i$ -th reaction.

Assuming that the reactor is ideally mixed and the volume flow of feed is constant<sup>4</sup>, the material balance which describe the system is in form

$$\tau \frac{dc_j}{dt} = c_{j0} - c_j + \tau \sum_{i=1}^R v_{ij} \cdot r_i(c_1, \dots, c_S, T), \quad j = 1 \dots S$$

$$t = 0: \quad c_j = c_j^0 \quad T = T^0 \quad (1)$$

The startup of reactor depends on choice of initial conditions of concentrations and temperature [Purdeková, 1999].

#### 3.2. Enthalpy balance

A curve of generated heat and a line of cooling are using the same simplifications as the enthalpy balance. We can omit the enthalpy balance of cooling fluid.

$$\tau \cdot \sum_{j=1}^S c_j \cdot c_{pj} \cdot \frac{dT}{dt} = \sum_{j=1}^S c_{j0} \cdot c_{pj} \cdot (T_0 - T) + \frac{U \cdot A}{\dot{V}} \cdot (T_c - T) + \tau \cdot \sum_{i=1}^R (-\Delta_r H_i) \cdot r_i \quad (2)$$

The right hand side of equation (2) represents the heat exchange and the heat of chemical reactions. The heat of reactions copies the curve of heat generation. The heat exchange copies the cooling line. We can consider that the parameters of heat exchange are constants and in this case, the heat exchange copies the cooling line [Westerterp, Swaaij, et. al., 1984, Fogler, 1992].

Neglecting the dependence of some coefficients on temperature or composition may markedly touch the precision of the calculated steady state and consequently the calculated steady state moves. On the other hand, sometimes this is the only way to get approximative results.

#### 3.3. Multiple steady states

The points of intersection of the curve of heat generation and the cooling line give us the temperature at which the reactor can be operated at steady state. Depending on selected parameters the cooling line and the heating curve may intersect in one or more points. In case of more reactions, the number of steady states is increasing [Carberry and Varma, 1987].

<sup>2</sup> By convention, the stoichiometric coefficients are taken to be positive for products, negative for reactants, and zero for inert.

<sup>3</sup> Dependence of reaction velocity on temperature is described by Arrhenius equation.

<sup>4</sup> We need another equation to describe the change of volume of the reaction mixture.

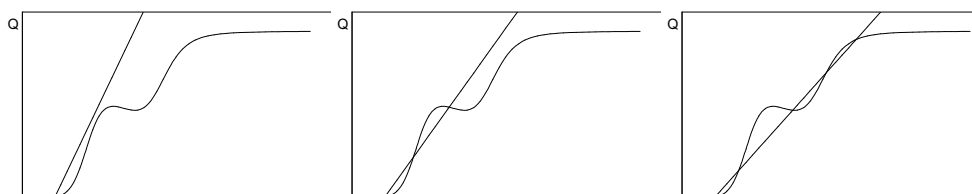


Fig. 1: Variations of steady states in case of two parallel reactions in the following form:  $A \rightarrow B \rightarrow C$  and  $A \rightarrow D$ . The changing parameter is the overall coefficient of heat exchange.

Appropriate changes of these parameters can change the number and position of steady states (Figure 1). The existence of multiple steady states is a characteristic phenomenon for continuous stirred reactors and involves serious danger mostly for exothermic reactions that must be operated in some of lower steady state [Horák and Pašek, 1980, Westerterp, Swaaij, et al., 1984].

### 3.3.1. The number of steady states

For systems with a simple reaction scheme there is a possibility of analytical solution [Schneider, Aris, et. al., 1973, Cohen and Keener, 1976, Farr and Aris, 1986]. In these days, the existing computation power allows us to study the problem from different point of view and search the multiple steady states numerically. The simplest method is the mapping of the desired interval of parameters. There are also some other methods that allow us to predict intervals where multiple steady states can occur [Hlaváček and Rompay, 1981, Kubíček, 1983, Holodniok and Kubíček, 1984, Holodniok, Klíč, et al., 1986].

### 3.3.2. Stability of steady states

The common usage of the words multiplicity, stability and sensitivity in the literature is according to the following definitions [Schmitz, 1974]: the multiplicity of steady states is the number of different sets of state variables at which the time rate of change of all state variables is identically zero for a fixed set of conditions or parameters. A steady state is stable if perturbations within an arbitrary small neighborhood surrounding the state die away to zero. If even the smallest of such perturbations grows, the steady state is unstable. Even though the steady state is stable, we don't have any information about the way of getting steady, even if it reaches the steady state.

Very simple definition of stability was mentioned [Heerden, 1953]. The stability can be determined by comparing the slopes of the cooling line and the tangent of the heat-generating curve at the point of steady state.

The region of asymptotic stability surrounding the potential steady state is defined as a set of initial conditions, from which the system of trajectories are asymptotically approaching the steady state [Sabo and Dranoff, 1970]. In common, in the case of more steady states, each steady state is surrounded by such region. The imaginary border called separatrix then surrounds the largest area of asymptotic stability [Berger and Perlmutter, 1965].

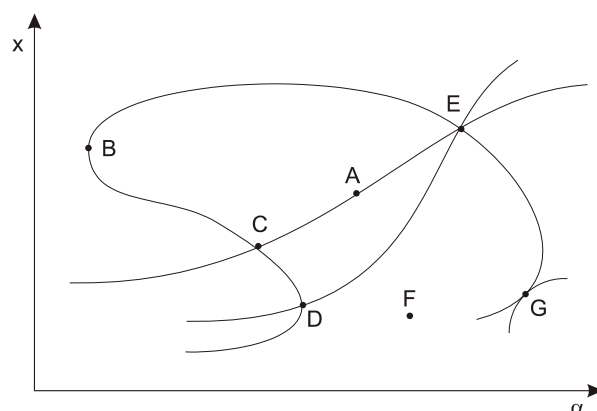
The stability of steady states can be obtained from analyzes of differential equations of material and enthalpy balances. For nonlinear systems the stability of solution is characterized by eigenvalues  $\lambda_1 \dots \lambda_n$  of the linearized matrix of differential equations. Some characterization of stability condition is in table 1, more about possible odds in [Holodniok, Klíč, et al., 1986].

**Tab. 1**

<i>Characterization of the stability of steady states by eigenvalues</i>			
	$Re(\lambda_i) < 0$	$Re(\lambda_i) > 0$	$Re(\lambda_i) = 0$
$Im(\lambda_i) = 0$	Stable node	Unstable node	
$Im(\lambda_i) \neq 0$	Stable oscillating focus	Unstable oscillating focus	Hopf bifurcation

### 3.4. Dependence of solution on parameters

A region with one steady state qualitatively differs from the region with more steady states. A suitable algorithm for evaluation of the dependence of the solution of a system of equations on the parameter  $\alpha$  can draw single solutions into branches. Each branch ends in a branching point, where the system qualitatively changes with the change of parameter  $\alpha$ . Qualitative changes like these are real bifurcations (fig. 2).



*Fig. 2: Branches and types of bifurcation points: A – regular point, B – limit point, C – double bifurcation point, D – limit bifurcation point, E – triple bifurcation, F – isolated point, H – cusp.*

A parameterization with respect to the arc length of the solution locus seems to be a powerful technique which overcomes the difficulties with branching points [Kubíček, 1976, Kubíček, 1983, Holodniok and Kubíček, 1984, Holodniok and Kubíček, 1984, Holodniok, Klíč, et al., 1986, Marek and Schreiber, 1991]

The algorithm can be simply extended by another parameter  $\beta$  to draw a bifurcation diagram in the space of these two parameters. We can calculate all the limit and bifurcation points for each chosen value of parameters  $\alpha$  and  $\beta$ . Then, we can assume that these points are dependent on parameter  $\beta$  and draw the branches in the parametric space  $\alpha$ - $\beta$ . Each region is characterized with the same number of solutions. Crossing the branch line, the number of solution changes with

two (Fig. 8). We can use the same way to construct the curve of bifurcation points to obtain information about the stability of branching points.

### 3.5. Dynamic regime

At the reactor startup, it is very important to know the initial conditions and the way the reactor reaches the steady state [Purdeková, 1999]. For example, a significant overshoot in temperature may cause a reactant or product to degrade or the overshoot may be unacceptable for safe operation [Westertep, Swaaij, et al., 1984, Fogler, 1992]. If either case were to occur, we would say that the system exceeded the practical stability limit (Fig. 6).

The time dependence of concentration or temperature, or the concentration-temperature phase diagram is used to determine the trajectory manifesting how the reactor reaches the steady state. Following figures shows some basic characteristic signs like monotonous fixing (Fig. 3), oscillatory behavior of concentrations or temperature (Fig. 4), or a limit cycle (Fig. 5).

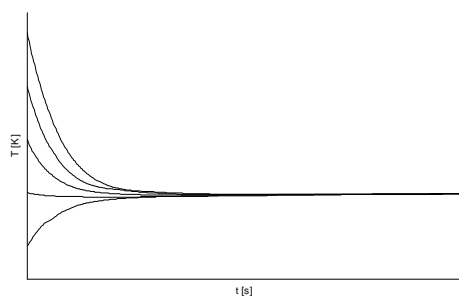


Fig. 3: Approach to steady state. Steady state is a node.

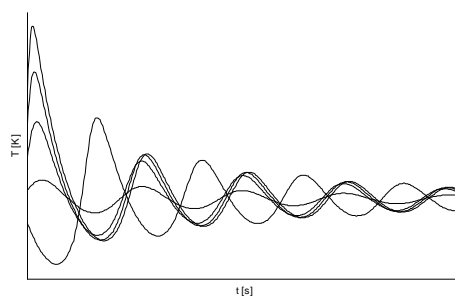


Fig. 4: Approach to steady state. Steady state is focus with damped oscillations.

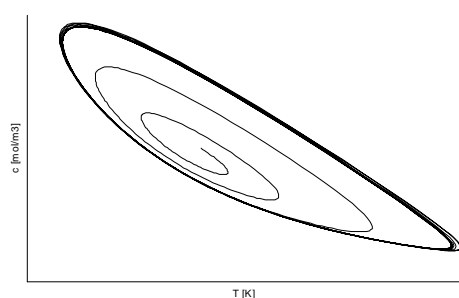


Fig. 5: Phase diagram of limit cycle approaching from inside (the steady state will be never reached). This state is characterized by twisting the trajectory around the steady state.

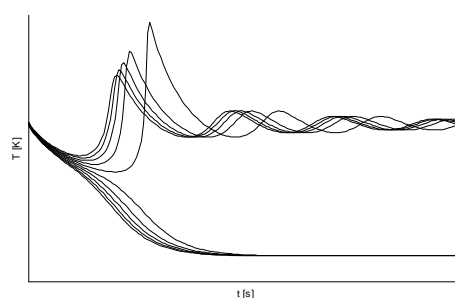


Fig. 6: Approaching various steady states and exceeding the practical stability limit. All the trajectories start withing close interval. Trajectories ending in uppers steady states are crossing a maximum and ends in focus. Lower steady state is a node.

#### 4. CONCLUSION

The safety analysis of chemical reactors is necessary. Most of the software engineering tools do not provide a deeper safety analysis of the designed units. This problem is mostly solved by transfer of achieved information into another application, which is capable to perform these analyses. As available literature has shown, many authors were concerning with dynamic behavior of continuous stirred tank reactors with one single chemical reaction. In real conditions, there are reactors with various parallel and consecutive reactions with various heat generation. Some of them may become significant during unacceptable conditions (fails in technological regime, significant changes of inlet variables, etc.). With the respect to complexity of safety analysis (information sources of physical and chemical properties of reacting mixtures, equilibrium, etc.), our goal is to create an interface that would allow us to work with professional engineering software like HYSYS.

A narrow analysis of HYSYS showed some possibilities to enhance the provided information with extended safety analysis by using the large HYSYS database. Within the integrated simulation environment a new client program should utilize large databases of the hosting program and perform safety analysis of stirred tank reactor at various conditions, like startup, shutdown, influence of changes in input variables on the reactor regime (ignition, blowout, runaway etc). The safety analysis should contain steps of identifying the steady states and their stability, causes and ways of switching between steady states and parametric sensitivity.

#### 5. LIST OF USED SYMBOLS

##### Symbols of Latin alphabet

A	Area	$m^2$
c	Molar concentration	$mol.m^{-3}$
$c_p$	Molar heat capacity	$J.mol^{-1}.K^{-1}$
E	Activation energy	$J.mol^{-1}$
$\Delta_r H$	Heat of reaction	$J.mol^{-1}$
k	Homogenous reaction velocity, dimension depends on kinetics	
$k_\infty$	Pre-exponential factor in the Arrhenius equation for homogenous reaction; the dimension depending on kinetics	
Q	Heat flow	$J.s^{-1}$
r	Molar rate of production	$mol.m^{-3}.s^{-1}$
R	Gas constant	$J.mol^{-1}.K^{-1}$
t	Time	s
T	Temperature	K
U	Overall heat transfer coefficient	$W.m^{-2}.K^{-1}$
$V_r$	Volume of reactor/reaction mixture	$m^3$
V	Volume flow	$m^3.s^{-1}$

### Greek symbols

$\alpha$	Parameter
$\beta$	Parameter
$\nu$	Stoichiometric coefficient
$\tau$	Space time

s

### Subscript

0	Inlet variables (T, c)
c	Coolant (T)
i	Index of reactions (r, R)
j	Index of compounds (c, c <sub>0</sub> )

### Superscript

0	Initial conditions
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