Accuracy of Mathematical Model with Regard to Safety Analysis of Chemical Reactors*

A. MOLNÁR, 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: attila@chtf.stuba.sk

Received 31 January 2002

Interest in discovering multiple steady-state solutions for reaction processes grew exponentially by the existence of the first computers. Modern process simulators can find multiple solutions only by the expenditure of much effort. Three mathematical models with different accuracy are introduced and a simple comparison of model's accuracy is made with regard to safety analysis of continuous stirred tank reactor. The first two models are based on standards in chemical reactor design; the third one is an internal model of CSTR in HYSYS simulation program. Furthermore, OLE automation interface is also used to access the existing physical property packages of HYSYS.

Chemical production in which chemical reactions take place at extreme condition (high temperature or pressure) requires a detailed analysis of possible dangerous situations, which may lead to industrial accidents with endangering of lives and health not only of workers, but also of civilians. From the viewpoint of operation safety, the attention should be focused on chemical reactors, especially multiple steady states, their characteristics; causes and ways of switching between them are of a great importance.

Liljenroth [1] first mentioned the existence of multiple steady states at the beginning of the 20th century. The study of multiple steady states of a continuous stirred tank reactor in which a single reaction occurs has been the subject of research of many authors. Many mathematical criteria have been proposed, but the usability of these analytical techniques and criteria is limited for simple situations [2—4]. A paper by *Heerden* [5] on autothermic reactors contains an argument for stability from the slopes of the heat generation and removal curves. For the first time, *Bilous* and *Amundson* [2] treated the reactor as a dynamical system. By using Lyapunov's method of linearization, a pair of algebraic conditions for local stability was given. The authors considered a scheme of two consecutive reactions and showed that up to five steady states might be expected under some conditions. Numerical continuation methods based on predictor-corrector procedure are used for solving complex system of equations these days [6, 7].

Process modeling often consumes a lot of time. Especially when the model requires new calculations with various initial conditions that must be entered manually. The integrated environment for chemical process simulation and design, like HYSYS, is a combination of stand-alone models, which helps users to take control of their time [8, 9]. The identification of multiple steady states of continuous stirred tank reactors by HYSYS is insufficient, even though this is the primary step when identifying the possible risky states of a reactor. The program can identify only some of the steady states (with expenditure of much effort). Moreover, neither the system stability nor the number of steady states could be predicted by means of HYSYS simulator [10, 11].

THEORETICAL

One of the qualitative characteristics of safety analysis is the accuracy of mathematical model. Numerous engineering equations have a form of nonlinear algebraic or differential equations, which may have one or more solutions. Omitting special kind of equations, one is not able to solve these equations without numerical or iterative calculations. During modeling or projection, a simplified model in its analytical form is often used. In most cases, the dependence of various characteristics of physicochemical parameters on temperature and composition is neglected, like thermal capacity, density, mixing heat, mixing volume, *etc.*

*Presented at the 29th International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 27—31 May 2002.

These parameters may have eminent influence on accuracy of the model and finally, these simplifications may lead to different results.

As mentioned above, the use of HYSYS for safety analysis has several constraints. Many users of HYSYS incline to use special algorithms and tools built for safety analysis. Still, they are mostly based on simple equations with insufficient accuracy. The benefit of HYSYS is in opened OLE technology, which includes also the OLE automation technology. This allows another program to use HYSYS as calculation engine. Benefit is that most of modern programming languages support OLE automation and open a way for re-using the code inside HYSYS. The internal structure of modeled system inside HYSYS is object-oriented; each object has specific properties and methods. These objects can be accessed through OLE interface and the properties can be read or changed, or some methods can be called. For example, from the Case's Flow sheet object (accessed through the "*Flow sheet*" property of the "*Case*"), new "*Process Streams*" and Unit "*Operations*" can be created; its properties changed, the process executed and calculated results read. In addition, the existing physical property package can be used. In this article, a comparison of two mathematical models is used to demonstrate the above-mentioned idea. The first model is based on standard equations used in chemical reactor design taken from a classical textbook of reaction engineering [12]. The second one utilizes the power of HYSYS through an OLE automation interface and enhances the equations of the first model.

General Model

In this section, the general form of equations describing the system of chemical reactions in continuous stirred tank reactor is discussed. Suppose R chemical reactions involving S species taking place in a continuous stirred tank reactor. Assuming ideal mixing of the reactor and constant volumetric flow rates of feeds, the material balance for any species in the system is

$$V_\mathrm{r}\frac{\mathrm{d}c_j}{\mathrm{d}t} = \dot{V}_0 c_{j0} - \dot{V} c_j + V_\mathrm{r}\sum_{i=1}^{R}\nu_{ij} r_i(c_1, \ldots, c_S, T)$$
$$j = 1, \ldots, S \qquad (1)$$

The enthalpy balance of the reactor can be as follows

$$V_\mathrm{r}\sum_{j=1}^{S} c_j c_{pj(T)}\frac{\mathrm{d}T}{\mathrm{d}t} = \dot{V}_0\sum_{j=1}^{S} c_{j0}h_{j(T_0)} - \dot{V}\sum_{j=1}^{S} c_j h_{j(T)} +$$
$$+ \dot{Q} + V_\mathrm{r}\sum_{i=1}^{R}(-\Delta_\mathrm{r}H_{i(T)})r_i(c_1, \ldots, c_S, T) \qquad (2)$$

$$\dot{Q} = UA(T_\mathrm{C} - T) \qquad (3)$$

$$n_\mathrm{C}c_{p\mathrm{C}}\frac{\mathrm{d}T_\mathrm{C}}{\mathrm{d}t} = \dot{n}_{\mathrm{C}0}(h_{\mathrm{C}0} - h_\mathrm{C}) - \dot{Q} \qquad (4)$$

$$h_{j(T)} = \int_{T_\mathrm{ref}}^{T} c_{pj}\mathrm{d}T \qquad (5)$$

Eqn (*4*) represents the enthalpy balance of cooling medium; in most cases, parameter T_C is assumed as a constant, or the exchanged heat $\dot{Q}$ is constant.

Modifying Models

The presented general model was accessed in two different ways. In the first model it was assumed that the coefficients of thermal capacity, reaction enthalpy, and volumetric flow rates do not depend on temperature and composition, and also the heat of mixing and mixing volume can be neglected. In steady state, the model was simplified into a form used as a standard at reactor design [12—14]

$$\dot{V}_0(c_j - c_{j0}) = V_\mathrm{r}\sum_{i=1}^{R}\nu_{ij} r_i(c_1, \ldots, c_S, T)$$
$$j = 1, \ldots, S \qquad (6)$$

$$\dot{V}_0\sum_{j=1}^{S} c_{j0}c_{pj}(T - T_0) - \dot{Q} =$$
$$= V_\mathrm{r}\sum_{i=1}^{R}(-\Delta_\mathrm{r}H_i)r_i(c_1, \ldots, c_S, T) \qquad (7)$$

The right-hand side of eqn (*7*) represents the heat generated; the left-hand side represents the heat exchanged with the environment. If one supposes that the thermal capacity, reacting volume, and volumetric flow rate into reactor are constant, and also the cooling is constant (*i.e.* the value of T_C is constant), the left-hand side of eqn (*7*) is drawn as a straight line (also called cooling line) and the right-hand side is drawn as a curve (called heating curve).

In the second model, the accuracy of the general model was enhanced so that the thermal capacities, volumetric flow rates, reaction heat, mixing volume, and mixing heat were assumed as functions of temperature and composition. Variation of these parameters with temperature and mixture composition was imported by OLE automation from flow sheet in HYSYS.

EXAMPLE

Hydrolysis of propylene oxide to propylene glycol in continuous stirred tank reactor was chosen as an example. The reaction is as follows

$$\mathrm{C_3H_6O} + \mathrm{H_2O} \rightarrow \mathrm{C_3H_8O_2}$$
$$\Delta_\mathrm{r}H^\circ = -90\ \mathrm{kJ\ mol^{-1}} \qquad (A)$$

Table 1. Parameters of the Reaction Mixture in the Simplified Model

	Water	Propylene oxide	Propylene glycol	Methanol
$c_p/(\mathrm{J\ mol^{-1}\ K^{-1}})$	76.15	116.10	179.7	76.83
$\dot{V} \cdot 10^3/(\mathrm{m^3\ s^{-1}})$	1.9732	0.41942	0	0.40143

c_p – molar heat capacity of component, $\dot{V}$ – volume flow rate of component.

The reactor with volume of 2.407 m^3 (liquid level 85 %) is fed with 5.934 mol s^{-1} of propylene oxide, 9.848 mol s^{-1} of methanol, and 110.33 mol s^{-1} of water. Methanol is added to improve the solubility of propylene oxide in water. The excess of water provides higher selectivity to propylene glycol and eliminates the consecutive reactions of propylene oxide with propylene glycol. The reaction is of the first order with respect to propylene oxide as a key component. The dependence of reaction rate constant on temperature is described by Arrhenius equation [12]

$$k = k_\infty \cdot \exp\left(\frac{-E}{RT}\right) = 4.7111 \times 10^9 \cdot \cdot \exp\left(\frac{-75362\ \mathrm{J\ mol^{-1}\ K^{-1}}}{RT}\right) \mathrm{m^3\ mol^{-1}\ s^{-1}} \quad (8)$$

The reactor is operated at atmospheric pressure and the cooling is constant, equal to 131.88 kW.

Frequent process in the examination of existence of multiple steady states is the bifurcation analysis. The continuation algorithm used here is a modification of Algorithm 502 by *Kubíček* [6]. Very important information is the location of the region where multiple steady states may occur and also the number of possible steady states and their stability. As the continuation parameter, the temperature of the reactor feed within the range from 297 K to 304 K was chosen.

RESULTS AND DISCUSSION

The values of constant parameters in the simplified model (thermal capacity, volumetric flow rates) are shown in Table 1. The heat of mixing and mixing volume were assumed to be zero.

In enhanced model, all the mentioned parameters were obtained from HYSYS database through OLE automation interface during the bifurcation analysis of this model. The results from the simplified and enhanced model were compared to the results obtained from two case studies made in HYSYS. The CSTR model used in case studies is generated internally in HYSYS by a black-box routine.

Fig. 1 compares the regions of multiple steady states obtained by simplified and enhanced model. Simplified model identifies the region of multiple steady states between 299 K and 302.4 K. In this region, the reactor can exhibit three steady states, from which two are stable and one is unstable. The stability

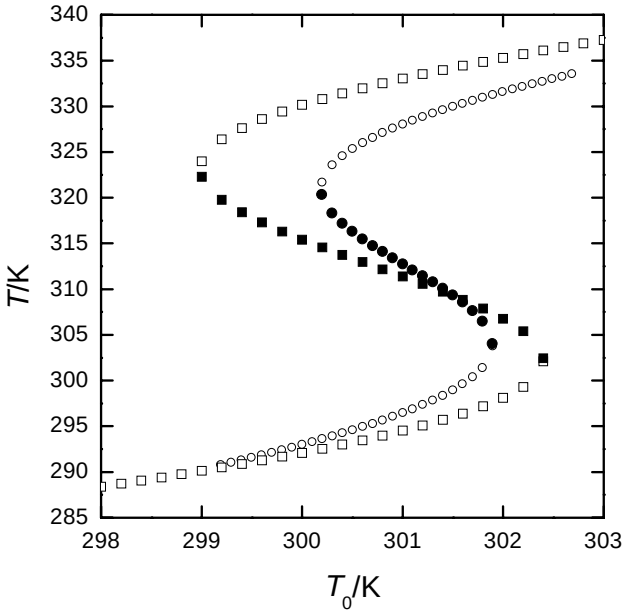

Fig. 1. Comparison of the regions of multiple steady states obtained by the simplified (squares) and by the enhanced model (circles). Stable steady states – (outline); unstable steady states – (solid).

of steady states can change only in the limit points. Outside of this region, only one stable steady state exists.

By solving the enhanced model, the multiple steady states occur in the temperature region from 300.2 K to 301.9 K. The region of multiple steady states in the case of simplified model is wider (approximately 3.4 K) than the region obtained for enhanced model (1.7 K). The difference in reactor's temperature in the limit points varies from 5 K to 8 K; also the achieved conversion varies from 6 % to 14 %. In real application, the mentioned differences may have eminent influence on the quality of the product or safe operation of a reactor, even if this reaction cannot be considered as highly exothermic.

Fig. 2 shows the incomplete bifurcation curve obtained from HYSYS. Because the HYSYS simulator was not able to identify the unstable steady states, only the stable ones are drawn. Two case studies, one with increasing and one with decreasing temperature of feed created the lower and upper branch. The lower branch starts with a steady state at low conversion (corresponding to lower reaction temperature) and with increasing temperature of feed ap-

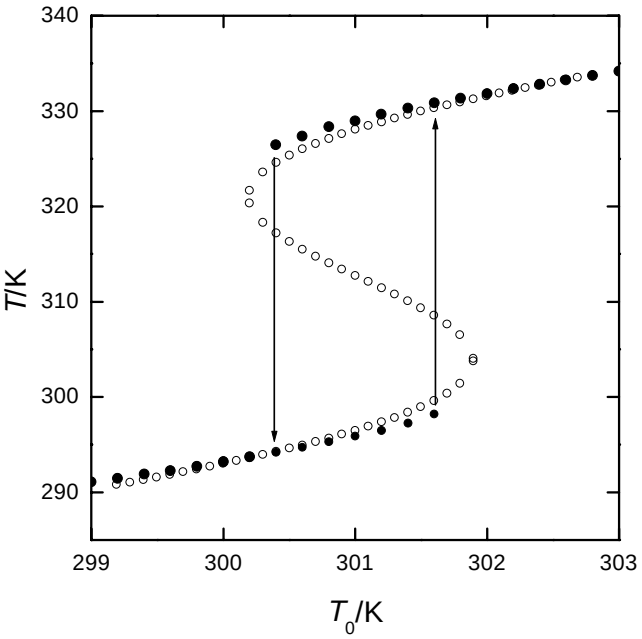

Fig. 2. Comparison of the regions of steady states obtained by the calculated enhanced model (outline) with the incomplete bifurcation curve achieved from two case studies solved with HYSYS (solid).

proaches the limit point. Once the feed temperature passes beyond the ignition point, the stable steady state moves to the upper branch, pronounced by increased reaction temperature and higher conversion. Opposite phenomenon, the reaction extinction can be seen when decreasing the feed temperature; just the limit point corresponds to lower value of feed temperature.

Fig. 2 presents also the comparison of data obtained by using the enhanced model and those calculated by HYSYS. Small differences of the identified stable steady states were found due to the higher accuracy of the enhanced model.

Comparison of selected steady states identified by the three models is presented in Table 2. The data obtained by simplified model exhibit an outstanding deviation from those achieved by solving the enhanced model and internal HYSYS model by case studies. In spite of it, the simplified model is often used in chemical reactor design and modeling. This can have unpredictable consequences in reactor operation. In industry, many reaction systems can give rise to multiple steady states with high thermal effects. The chosen example demonstrates the need for safety analysis of every reactor, even with simple reaction running.

Acknowledgements. This project was financed by the Grant VEGA 1/8112/01 of the Slovak Scientific Grant Agency. We would like to express our thanks to AEA Technology on account of the licence of network version of HYSYS simulation program.

SYMBOLS

A	heat exchange 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}
h	enthalpy	J mol^{-1}
$\Delta_r H^\circ$	reaction enthalpy	J mol^{-1}
k_∞	pre-exponential factor, dimension depends on kinetics	
k	reaction rate constant, dimension depends on kinetics	
n	hold-up	mol
$\dot{n}_C$	molar flow rate	mol s^{-1}
$\dot{Q}$	exchanged heat between the reactor and cooling medium	W
R	universal gas constant	J mol^{-1} K^{-1}
r	reaction rate	mol m^{-3} s^{-1}
T	temperature	K
t	time	s
V_r	reacting volume	m^3
$\dot{V}$	volumetric flow rate	m^3 s^{-1}
U	overall heat exchange coefficient	W m^{-2} K^{-1}

Table 2. Analysis of Steady States Identified by Simplified, Enhanced, and HYSYS Internal Models

T_0/K	Simplified model			Enhanced model			HYSYS model		
	N	T/K	X_A/%	N	T/K	X_A/%	N	T/K	X_A/%
300	3	292.11	10.33	1	293.0	11.97	1	293.26	11.68
		315.45	53.29						
		330.15	80.44						
301	3	294.52	12.92	3	296.49	14.90	2	295.90	14.82
		311.38	44.00		312.75	44.68		–	–
		333.04	83.91		328.08	77.48		328.99	78.61
302	3	298.11	17.69	1	331.59	82.08	1	331.59	82.33
		306.78	33.68						
		335.30	86.24						

T_0 – feed temperature, N – number of identified steady states, T – temperature in reactor, X_A – conversion of key component.

Greek Letters

ν stoichiometric coefficient

Subscripts

0 feed
C cooling medium

REFERENCES

1. Liljenroth, F. G., *Chem. Metall. Eng. 19,* 287 (1918).
2. Bilous, O. and Amundson, N. R., *AIChE J. 1,* 513 (1955).
3. Balakotaiah, V. and Luss, D., *Chem. Eng. Sci. 37,* 433 (1982).
4. Gobulitsky, M. and Schaeffer, D. G., *Commun. Pure Appl. Math. 32,* 21 (1979).
5. Heerden, C., *Ind. Eng. Chem. 45,* 1242 (1953).
6. Kubíček, M., *ACM Trans. Math. Software 2,* 98 (1976).
7. Holodniok, M. and Kubíček, M., *Appl. Math. Comput. 15,* 261 (1984).
8. Pongo, J. and Poras, W., *HYSYS Ref.*, Vol. *1.* Hyprotech, 1996.
9. Pongo, J. and Poras, W., *HYSYS Ref.*, Vol. *2.* Hyprotech, 1996.
10. Jelemenský, Ľ., Šoóš, M., and Markoš, J., *Dynamical Simulation of Safe Control of MTBE Reactive Distillation,* in *Proceedings of the 14th International Conference of CHISA,* Prague, Czech Republic, 2000.
11. Šoóš, M., Molnár, A., Purdeková, M., Markoš, J., and Jelemenský, Ľ., *Safety of Chemical Reactors,* in *Proceedings of the 26th International Conference of SSCHE,* Demänovská dolina, Slovak Republic, 1999.
12. Fogler, H. S., *Elements of Chemical Reaction Engineering.* 3rd Edition. Prentice-Hall, London, 1999.
13. Westerterp, K. R., Swaaij, W. P. M. V., and Beenackers, A. A. C. M., *Chemical Reactor Design and Operation.* 1st Edition. Netherlands University Press, Amsterdam, 1984.
14. Horák, J. and Pašek, J., *Design of Industrial Chemical Reactors from the Laboratory Data* (in Czech). Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1980.