CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong
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ISBN 978-88-95608-30-3; **ISSN** 2283-9216

DOI: 10.3303/CET1439170

Modelling the Dynamical Regimes of Mass Transfer in Cascades of Through-Reactors

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The paper deals with the technique for modelling and computer simulating the multiplicity and stability types of stationary regimes in chemical through-reactors and for calculating the mass transfer efficiency with allowing for the phenomena of irreversibility and thermodynamic imperfectness in systems where dynamical wave regimes can arise. The rate characteristics for certain kinetic models, which can be applied to different kinds of systems characterized by formation of transient regimes with moving concentrate fronts and oscillators have been considered.

1. Introduction

Multi-stage reactions and the imperfection of reaction-diffusion systems in chemical reactors can substantially affect the formation of the technological process regime (Ni et al., 2009). In complex multi-stage chemical systems the multiplicity of steady-states (Barkanyi et al., 2013), oscillational regimes in autocatalytic reactors (Dateo et al., 1982) and in the bromate-cerium-malonic acid systems (Field et al., 1972), and regimes of wave concentrate waves (Brener and Musabekova, 2006) can be observed. Thus these factors should be taken into account when modelling the transport phenomena in a chemical apparatus of different types, for example, jetloop-reactors (Behr and Becker, 2009) or cascades of bath reactors (Wang et al., 2011). At the same time, despite a lot of important works (Berezowski, 2011) and the outstanding monograph (Holodniok et al., 1984), several problems remain to be worked out insufficiently. We believe those are the problems of how the irreversibility of some stages of complex multi-stage reactions and the imperfectness of thermodynamic system can affect the dynamical behavior of the system (Russo et al., 2002). The goal of this work is to consider the technique for modelling and computer simulating the multiplicity and stability types of stationary regimes in chemical through-reactors and for calculating the mass transfer efficiency with allowing for the mentioned above phenomena of irreversibility and thermodynamic imperfectness in systems where dynamical wave regimes can arise (Brener and Musabekova, 2006). So, the paper deals with the methodology for calculating rate characteristics for certain kinetic models, which can be applied to different kinds of systems characterized by formation of transient regimes with concentrate moving fronts and oscillators (Carvajal et al., 2012). Several models of great generality describing the nonlinear physics-chemical systems have been identified. The study of such systems creates prerequisites for the establishment of methods suitable for calculating a wide class of systems and reactors (Jesus et al., 2013).

2. Theoretical details

The model systems such as "Brusselator", the system of Belousov-Zhabotinsky reaction and a few of autocatalytic systems of second and third order have been considered. The model “Brusselator", which is investigated first under the guidance of I.R. Prigogine, simulates many real complex multistep reactions occurring in industrial reactors. Kinetics of this system is described by the following system of equations (Dateo et al., 1982):

Please cite this article as: Kalbayeva A., Kurakbayeva S., Zhidebayeva A., Musrepova E., 2014, Modelling the dynamical regimes of mass transfer in cascades of through-reactors, Chemical Engineering Transactions, 39, 1015-1020 DOI:10.3303/CET1439170

$$A\xrightarrow{k_1}X,\ B+X\xrightarrow{k_2}Y+D,\ 2X+Y\xrightarrow{k_3}3X,\ X\xrightarrow{k_4}E. \tag{1}$$

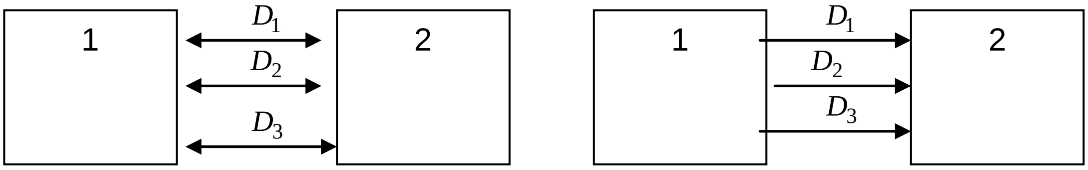
In reality, some of the stages in the reaction medium "Brusselator " may be reversible, what complicates the kinetic equations and their analysis. Since this case is not well described (Holodniok et al., 1984), in this work the two special cases are investigated: the reversibility of the last stage of the reaction and reversibility of the two reaction stages of the above system:

$$Y+D\xrightarrow{k_5}B+X, E\xrightarrow{k_6}X. \tag{2}$$

The Belousov-Zhabotinsky system, described first by the example of oxidation of malonic acid in the medium catalysed by ions of transition metals, is a classic example of a system with self-oscillatory kinetics. For the study we selected the kinetic scheme (Holodniok et al., 1984), which is modified with the possibility of reversibility of the fourth stage

$$A+Y\xrightarrow{k_1}X+P,\ X+Y\xrightarrow{k_2}2P,\ A+X\xrightarrow{k_3}2X+2Z,\ 2X\underset{k_6}{\overset{k_4}{\leftrightarrow}}A+P,\ B+Z\xrightarrow{k_5}hY. \tag{3}$$

The flow structure is represented as a cascade of two reactors of perfect mixing (Hua et al., 2004) with mutual mass transfer (Figure 1).



a) Cascade with recycles

b) Cascade without recycles

Figure 1 Cascades of chemical reactors with mutual mass transfer

The corresponding systems of kinetic equations, provided the resulting inflow and outflow of intermediate reactants are zero, and the concentration of the incoming components are kept constant, have the form. For the "Brusselator" system:

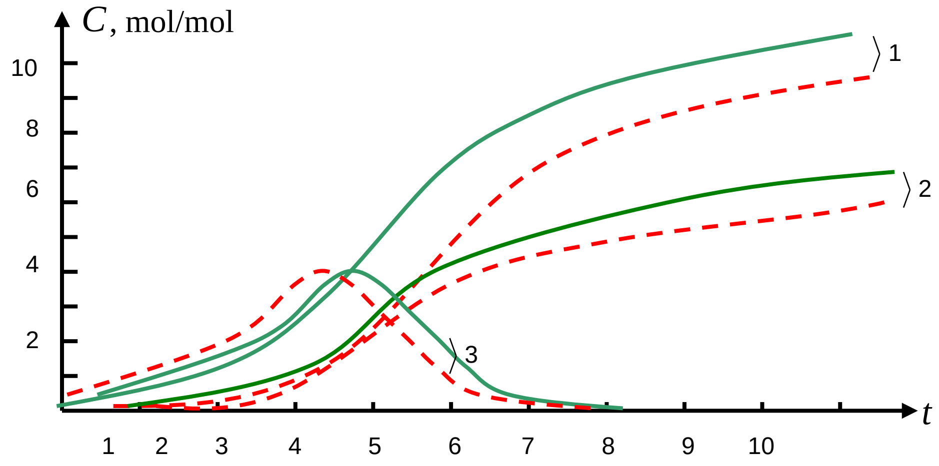
$$\begin{aligned}
&dX_1/dt=k_1A_1-k_2BX_1-k_4X_1+k_3X_1{}^2Y_1+k_5\mathring{A}_1+D_{11}(X_2-X_1),\\
&dY_1/dt=k_2BX_1-k_3X_1{}^2Y_1+D_{21}(Y_2-Y_1),\\
&dE_1/dt=k_4X_1-k_5E_1+D_{31}(E_2-E_1),\\
&dX_2/dt=k_1A_2-k_2BX_2-k_4X_2+k_3X_2{}^2Y_2+k_5\mathring{A}_2+D_{12}(X_1-X_2),\\
&dY_2/dt=k_2BX_2-k_3X_2{}^2Y_2+D_{22}(Y_1-Y_2),\\
&dE_2/dt=k_4X_2-k_5E_2+D_{32}(E_1-E_2).
\end{aligned} \tag{4}$$

For the Belousov-Zhabotinsky system

$$\begin{aligned}
&dX_1/dt=k_1A_1Y_1-k_2X_1Y_1+k_3A_1X_1-2k_4X_1{}^2+D_{11}\left(X_2-X_1\right),\\
&dY_1/dt=-k_1A_1Y_1-k_2X_1Y_1+hk_5BZ_1+D_{21}\left(Y_2-Y_1\right),\\
&dZ_1/dt=2k_3A_1X_1-k_5BZ_1+D_{31}\left(Z_2-Z_1\right),\\
&dZ_2/dt=2k_3A_2X_2-k_5BZ_2+D_{32}(Z_1-Z_2)\\
&dX_2/dt=k_1A_2Y_2-k_2X_2Y_2+k_3A_2X_2-2k_4X_2{}^2+D_{12}(X_1-X_2),\\
&dY_2/dt=-k_1A_2Y_2-k_2X_2Y_2+hk_5BZ_2+D_{22}(Y_1-Y_2),
\end{aligned} \tag{5}$$

For the convenience of numerical experiments and interpretation of data, all of the rate constants of reactions k_i, transport coefficients D_{ij} and time t were arranged to the dimensionless form with the help of the relaxation time of the first stage $\tau_p = 1/k_1$, i.e. the dimensionless characteristics were determined according to the following scheme $t \to tk_1,\ k_i \to k_i/k_1,\ D_{ij} \to D_{ij}\,k_1$.

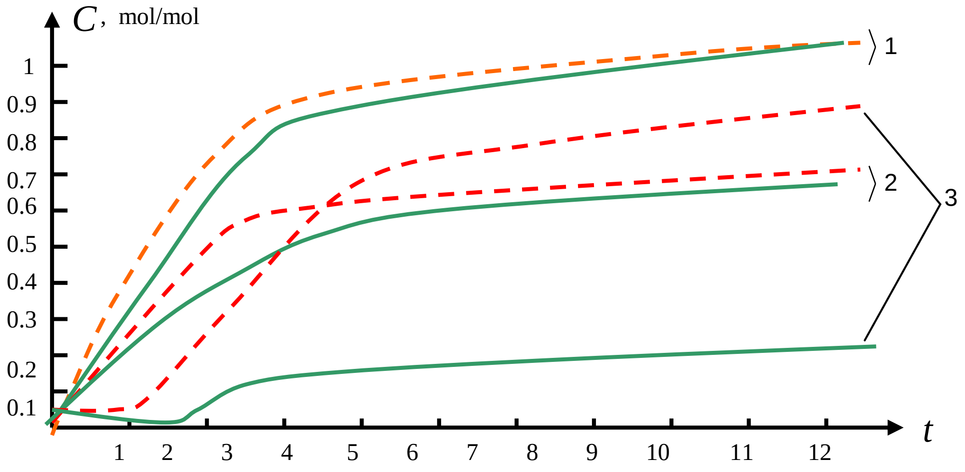
Some results of numerical experiments at the initial stabilization period are shown in Figures 2 and 3.



Dotted curve - first reactor; solid curve - the second reactor.

1 - the reaction product E_1; 2 - complex X_1; 3- complex Y_1

Figure 2 - Changes in the concentrations of reactants in the cascade of reactors with recycle System "brusselator"



Dotted curve - first reactor; solid curve - the second reactor.

1 - the reaction product Z_1; 2 - complex X_1; 3 - complex Y_1

Figure 3 - Changes in the concentrations of reactants in the cascade of reactors with recycle System "Brusselator"

Analysis of numerical experiment data shows that the concentration of active complex Y which is arising during the reaction in the "Brusselator" system has the maximum after some time from the beginning of the process, and then it begins to decrease with striving for a stable value. Dependences of concentrations of the intermediate complex X and the final product E on time are monotonous and they strive to stable values through the rather long time.

It is found that the partial decomposition of the final product under the rate constants of the decomposition reaction, comparable to constants of other stages, may withdraw the oscillating behaviour in the concentrations of intermediate complexes characteristic for “Brusselator". This confirms the importance of considering the reversibility of individual reaction stages in the analysis of the kinetics of the cascade of chemical reactors (Manenti et al., 2011).

With respect to the Belousov-Zhabotinsky reaction (Holodniok et al., 1984) the influence of recycle is manifested in establishing the stable characteristics of the reactor (i.e., concentrations of the major products of the reaction) in a shorter time.

It can be seen that with increasing of *k1* and *k2* the concentration of the component *Y* in the system increases and become practically stable at a time depending on the stoichiometric ratio of the last reaction stage. In the absence of the last stage (*h = 0*) , there exists a rapid exhaustion of the component in the system. The numerical experiment allows us to recommend this model for the calculation of complex chemical interaction processes in multicascade autocatalytic reactors.

3. Analysis of dynamical regimes

One-dimensional equation of convective diffusion of the main reaction product in tubular chemical reactors can be written as (Berezowski, 2011):

$$\partial C/\partial t + V\,\partial C/\partial x = D\,\partial^2 C/\partial x^2 + f(C). \tag{6}$$

The solution of equation (6) will be sought in the form of a traveling wave front with similar variable

$$\xi = x - vt. \tag{7}$$

A stationary point of the system is determined by the condition $y = 0$, $f(C_0) = 0$.

The kinetic function for the system of “Brusselator” type which contains an excess of acid with allowing for the basic process stages can be given as expression of third order.

$$f(C) = C(k_1 + k_2 C)(C_0 - C)$$

It can be shown that in this case the equilibrium state is a stationary point of the "saddle" type for any velocities of flow and wave front.

For bimolecular chemisorption with partially reversible reaction absorption of the target component the kinetic function has a second order.

$$f_1(C) = (k_2 - k_1 C)(C_0 - C), \tag{8}$$

where k_1, k_2 are the rate constants of the forward and reverse reactions, respectively.

Condition for the existence of stationary states of the "saddle" or "node" types has the form:

$$(V - v)^2 > 4D(-k_1 + k_2 C_0). \tag{9}$$

From (9) it follows that under the average velocity of reactants mixture less than critical velocity of the wave front the stationary point is stable.

The appropriate critical velocity of wave front reads

$$v^* = V + 2\sqrt{D(-k_1 + k_2 C_0)}. \tag{10}$$

Numerical results show that in the neighbourhood of the reactor inlet there is formed the concentration field corresponding to the soliton-like wave front. This phenomenon is fully consistent with the results of theoretical analysis and known experimental data (Hua et al., 2004, Dateo et al., 1982). According to the numerical experiment it can be defined the size of the initial site and the amplitude of oscillations.

4. Transient regimes in tubular through-reactors

Multiplicity of stationary states in the flowing reacting systems leads to the need for a detailed analysis of both the stability of each state and emerging in the vicinity of the unstable points periodic and transient regimes (Sierra et al., 2013). The estimates for calculating the required residence time in a separate diffusion cell for different systems which have a plurality of stationary states and oscillatory dynamical regimes, which should be used in the general system of equations taking into account the known structure of streams, have a great importance for calculating cascades of reactors (Hua et al., 2004.

Let us consider a model reaction scheme in which the main components and reactants are X, Y, and the first stage is autocatalytic

$$X + Y \xrightarrow{k_1} 2X\ , \quad X \xrightarrow{k_2} A,\ Y \xrightarrow{k_3} C. \tag{11}$$

Let us also suppose the reactor works with a continuous supply of the component Y with consumption speed q.

The detailed analysis of modes in this case gave the following results.

If $\frac{k_3}{k_2} \ge 1$ then for any q the stationary point is a stable node. Therefore the oscillating regime in this case does not arise. If $\frac{k_3}{k_2} < 1$ then there exists a range of speeds q for which the transient oscillating regime can be generated.

This range reads

$$\left(2k_2^2/k_1\right)\left[1-\sqrt{1-k_3/k_2}\right] < q < \left(2k_2^2/k_1\right)\left[1+\sqrt{1-k_3/k_2}\right]. \tag{12}$$

For this oscillatory transient regime the frequency of oscillation occurring ω and the logarithmic decrement ν can be determined as

$$\omega = \sqrt{2q/k_3 - 2k_2k_4/k_1k_3 - k_3k_4^2/4}\ , \tag{13}$$

$$\nu = -k_4/2 \tag{14}$$

The case of imperfectness of the reaction-diffusion system in the reactor with an autocatalytic reaction has been studied also. The expression for the phase velocity of the wave front, adjusted for non-perfectness can be written as follows:

$$c_{0r} = c_0 + \gamma\sqrt{k_1 D_i A}\ . \tag{15}$$

Here the parameter of imperfectness reads (Prigogine, 1957)

$$\gamma = 2\kappa\left(2\varepsilon_{AX} - \varepsilon_{AA} - \varepsilon_{XX}\right)Ak_1/k_2\ . \tag{16}$$

Here ε_{AX}, ε_{AA}, ε_{XX} are the parameters of molecular interactions (Prigogine, 1957)

The analysis shows that the rate of supply of reagents in chemical reactors not only controls the output of the reactor, but also may qualitatively change the set of stationary and transient regimes of their work. Typically, these changes relate only to the thermal operating conditions (Jesus et al., 2013), and other factors often are neglected in practice of calculation and design of chemical reactors.

5. Conclusions

It was shown that irreversibility of certain stages didn't change dynamics of chemical oscillations but led to decreasing or increasing the conversion depending on irreversibility of the concrete reaction stage. It was established that influence of recycle is manifested in stabilization of process parameters for all components in reduced time. Analysis of propagating models for non-linear concentration waves in tubular through-reactors with model diffusion-reaction systems has been carried out. Conditions for non-linear concentration wave fronts propagating in through-reactors in the cases of irreversibility or reversibility of one reaction stage have been obtained, and relations for parameters of the concentration wave front have been obtained too. The character of the influence of a non-perfectness of reaction-diffusion systems on the effective diffusion coefficient and dynamic regimes transfer parameters has been studied.

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