NUMERICAL SIMULATION OF A CATALYTIC REACTION DYNAMICS IN A KINETIC REGION

Karel KLUSÁČEK

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

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The method of numerical simulation of a catalytic system dynamics with lumped parameters is reported. Appropriate balance equations have been derived and suitable calculation procedures are discussed. Numerical example of simulation of the catalytic methanol dehydration dynamics is presented and calculated relaxation curves are compared with experimental data obtained earlier.

In recent years, nonstationary kinetic studies have attracted increasing attention. In these studies, dynamic response of a laboratory reactor to defined disturbance of the steady state has been examined[1]. Numerical simulation of dynamic behaviour makes it possible to evaluate information wealth of planned experiments and to confront calculated responses with experimental data. The frequently used types of laboratory reactors are a differential reactor (that gives rapid information) and an ideally mixed reactior (that enables to make experiments over broad range of conversions). Balance equations of both types are the same and thus the same calculation procedures can be used in both cases. The problem of simulation represents the solution of sets of ordinary differential (balance) equations that describe the dynamics of the catalytic system modelled.

The aim of this work was to derive generally the sets of appropriate balance equations and to discuss applicable calculation procedures. Furthermore, numerical example of calculation of the methanol dehydration dynamics (the response of a laboratory reactor to jump change in inlet composition) will be reported and its comparison with experimental data[2] reported earlier will be performed.

Balance Equations

In the reactor represented schematically in Fig. 1, there proceeds only one reaction between p reaction components A_i that involves k elementary steps

$$\sum_{i=1}^{p} a_{ij} A_i = 0 , \quad j = 1, \ldots, k . \tag{1}$$

The stoichiometric coefficient of components A_i in the j-th step, a_{ij}, is positive for products and negative for reactants in the j-th elementary step (an eventual

inert has this coefficient equal to zero). Let us suppose that p component reaction system consists of n gaseous components (including an inert) and of $(p-n)$ components on catalyst surface (including free active centres). The rate of formation $\mathscr{R}_i$ of any component A_i is described by Eq. (2)

$$\mathscr{R}_i = \sum_{j=1}^{k} a_{ij} r_j , \quad i = 1, \ldots, p , \tag{2}$$

where r_j is the rate of the j-th elementary step.

The balance of reaction components in the bulk phase of the reactor gives n differential equations for time changes of partial pressures p_i (Eq. 3)

$$(V/\boldsymbol{RT})\,(\mathrm{d}p_i/\mathrm{d}t) = F_v^0 c_i^0 - F_v c_i + W\mathscr{R}_i , \quad i = 1, \ldots, n , \tag{3}$$

where V is the free volume of the reactor and c_i^0 and c_i are the molar concentrations of components A_i in the reactor inlet and reactor outlet, resp., for which the relation for the total molar concentration c has the following form

$$\sum_{i=1}^{n} c_i^0 = \sum_{i=1}^{n} c_i = c . \tag{4}$$

Taking into account the relation for the total pressure P

$$\sum_{i=1}^{n} p_i = P = \text{const} . \tag{5}$$

only $(n-1)$ equations (3) are independent.

Balance equations (3) contain the flow on the reactor outlet F_v which can be determined only with difficulty. This quantity can be expressed by the volume flow on the reactor inlet F_v^0.

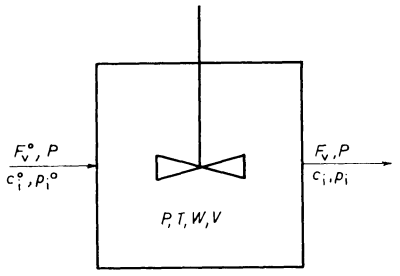

FIG. 1
Scheme of the reactor

With respect to the validity of Eqs (*4*) and (*5*), the summation of n equations (*3*) leads to the expression

$$(V/RT)\sum_{i=1}^{n}(dp_i/dt) = F_v^0 c - F_v c + W\sum_{i=1}^{n}\mathscr{R}_i \qquad (6)$$

from which

$$F_v = F_v^0 + (W/c)\sum_{i=1}^{n}\mathscr{R}_i\,. \qquad (7)$$

Combination of Eqs (*3*) with Eq. (*7*) gives n balance equations for gaseous components A_i in the form

$$(V/RT)(dp_i/dt) = F_v^0(c_i^0 - c_i) - W[(c_i^0/c)\sum_{i=1}^{n}\mathscr{R}_i - \mathscr{R}_i] \qquad (8)$$

$$i = 1, \ldots, n$$

of which only $(n-1)$ ones are again independent. Therefore, one of differential equations (*8*) can be replaced (*e.g.* that for component A_n) by the equation

$$(dp_n/dt) = -\sum_{i=1}^{n-1}(dp_i/dt)\,. \qquad (9)$$

Balance of the components adsorbed on catalyst surface (and of free centres) provides another $(p-n)$ balance equations for time changes of surface concentrations q_i

$$(dq_i/dt) = \mathscr{R}_i\,, \quad i = n+1, \ldots, p. \qquad (10)$$

As it holds that

$$\sum_{i=n+1}^{p} q_i = L\,, \qquad (11)$$

where L is the total concentration of active centres, only $(p-n-1)$ equations (*10*) are independent and one of them (*e.g.* that for component A_p) can be replaced by the equation

$$(dq_p/dt) = (dL/dt) - \sum_{i=n+1}^{p-1}(dq_i/dt)\,, \qquad (12)$$

where (dL/dt) stands for the possible time change of the total concentration of active centres (*e.g.* irreversible occupation of the centres by the product or formation of further active sites, *etc.*). If the total concentration of active centres on catalyst surface remains constant, (dL/dt) equals to zero.

The set of balance equations is complemented by initial conditions

$$\text{for } t = 0 \qquad \begin{aligned} p_i &= p_i(0)\,, \quad i = 1, \ldots, n \\ q_i &= q_i(0)\,, \quad i = n + 1, \ldots, p\,. \end{aligned} \tag{13}$$

The value of L can be obtained from independent measurements (*e.g.* from measurements of surface acidity in the case of acidic catalyst or merely from adsorption data). The relations for rate of formation ($\mathscr{R}_i$; $i = 1, \ldots, p$) follow from model concepts about a given reaction. The other quantities in the set of balance equations (*8*)–(*10*), (*12*) can either be determined directly or they result from numerical simulation (p_i, q_i). The solution of the set at fixed time interval gives time profiles of partial pressures of reaction components on the reactor outlet that can be compared with experimental data, and time profiles of the concentrations of reaction components on the catalyst surface.

Solution of Set of Balance Equations

The set of balance equations (*8*)–(*10*), (*12*) describing the catalytic system dynamics has to be solved numerically. Classical explicit methods of numerical integration, represented *e.g.* by Runge–Kutt procedures, usually fail to give reasonable results. The reason is a significant "stiff" character of the set (*8*)–(*10*), (*12*) which is caused by very different (by several orders of magnitude) rate constants of single elementary steps. In recent years, numerical calculation method for solution of these problems went through rapid development[3–5]. On testing these methods, the most generally applicable procedures have turned out to be a semiimplicit method reported by Michelsen[6] and a nonlinear explicit method proposed by Kubíček[7].

Numerical Example

For purposes of illustration, we present here the numerical simulation of the catalytic methanol dehydration on an ion exchanger catalyst at 140°C and atmospheric pressure

$$2\,CH_3OH \rightarrow (CH_3)_2O + H_2O \tag{A}$$

that was studied also experimentally[2].

From kinetic results obtained by Thanh, Setínek and Beránek[8] it follows that the reaction (*A*) proceeds *via* the following sequence of elementary steps

$$A + 2\,S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} XS + YS$$

$$A + 2S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} XS + YS \qquad (B)$$

$$XS + YS \xrightarrow{k_2} Z^*S + S$$

$$Z^*S + XS + YS \longrightarrow E + WS + 2S$$

$$WS \underset{k3'}{\overset{k3}{\rightleftharpoons}} W + S .$$

Methanol (A) adsorbs on active centres (S) with dissociation to nonequivalent fragments (XS, YS). The rate determining step is an irreversible surface reaction which involves initial formation of an active intermediate (Z*S) which reacts in very rapid and irreversible step with another two fragments to produce nonadsorbed dimethyl ether (E) and adsorbedwater (WS). The final step is desorption of water (W). The reaction mixture can contain also an inert (N_2).

Let us designate gaseous components as

$$A \equiv A_1 ; \quad E \equiv A_2 ; \quad W \equiv A_3 ; \quad N_2 \equiv A_4 .$$

As folows from the set (*B*), concentrations of fragments XS and YS on catalyst surface must be identical (they are symetrically formed and consumed) and thus also they can be balanced as one component („adsorbed methanol"). The balance of adsorbed active intermediate product Z*S has not to be made, as its concentration on catalyst surface is essentially nearly zero during all the process. After introduction further symbols

$$XS \equiv A_5 ; \quad YS \equiv A_5 ; \quad WS \equiv A_6 ; \quad S \equiv A_7$$

expressions (*8*) for the rate of formation $\mathscr{R}_i$ have the following form

$$\begin{aligned}
\mathscr{R}_1 &= 2(k_1' q_5^2 - k_1 p_1 q_7^2) \\
\mathscr{R}_2 &= k_1 q_5^2 \\
\mathscr{R}_3 &= k_3 q_6 - k_3' p_3 q_7 \\
\mathscr{R}_4 &= 0 \\
\mathscr{R}_5 &= 4[k_1 p_1 q_7^2 - q_5^2(k_1 + k_1')] \\
\mathscr{R}_6 &= k_2 q_5^2 + k_3' p_3 q_7 - k_3 q_6 \\
\mathscr{R}_7 &= 4(k_1' q_5^2 - k_1 p_1 q_7^2) + 3k_2 q_5^2 + k_3 q_6 - k_3' p_3 q_7 .
\end{aligned} \qquad (14)$$

Provided that $(\mathrm{d}L/\mathrm{d}t) = 0$, balance equations (*3*), (*9*), (*10*), and (*12*) can be formulated as

$$(V/\boldsymbol{RT})(\mathrm{d}p_1/\mathrm{d}t) = (F_v^0 c_1^0 - F_v c_1) + W\mathscr{R}_1$$

$$(V/\boldsymbol{RT})(\mathrm{d}p_2/\mathrm{d}t) = (F_v^0 c_2^0 - F_v c_2) + W\mathscr{R}_2$$

$$(V/\boldsymbol{RT})(\mathrm{d}p_3/\mathrm{d}t) = (F_v^0 c_3^0 - F_v c_3) + W\mathscr{R}_3 \qquad (15)$$

$$(\mathrm{d}p_4/\mathrm{d}t) = -\sum_{i=1}^{3}(\mathrm{d}p_i/\mathrm{d}t)$$

$$(\mathrm{d}q_5/\mathrm{d}t) = \mathscr{R}_5$$

$$(\mathrm{d}q_6/\mathrm{d}t) = \mathscr{R}_6$$

$$(\mathrm{d}q_7/\mathrm{d}t) = -\sum_{i=5}^{6}(\mathrm{d}q_i/\mathrm{d}t).$$

Balance equations for gaseous components include the total volume flow on the reactor outlet, F_v, which can be expressed according to Eq. (7) by the relation

$$F_v = F_v^0 + (W/c)\sum_{i=1}^{3}\mathscr{R}_i. \qquad (16)$$

By substitution for F_v according to Eq. (*16*), the first three equations of the set (*15*) acquire the form which is formally identical with Eq. (*8*).

The total concentration of active centres $L = 520$ μmol/g and rate constants of elementary steps (*B*)

$$k_1 = 1{\cdot}48 \,.\, 10^{-3} \text{ g/μmol kPa s}$$

$$k_2' = 1{\cdot}0 \qquad \text{g/μmol s}$$

$$k_2 = 1{\cdot}49 \,.\, 10^{-3} \text{ g/μmol s}$$

$$k_3 = 1{\cdot}0 \qquad \text{l/s}$$

$$k_3' = 3{\cdot}14 \,.\, 10^{-2} \text{ l/kPa s}$$

were obtained from stationary kinetic data[2].

The set of balance equations (*15*) has been solved by using a nonlinear explicit method proposed by Kubíček[7] for the case where at time $t = 0$ the composition of the inlet flow to the reactor was changed by jump from pure nitrogen ($p_1^0 = p_2^0 = p_3^0 = 0$; $p_4^0 = 100$ kPa) to pure methanol ($p_1^0 = 100$ kPa; $p_2^0 = p_3^0 = p_4^0 = 0$). The initial conditions for gaseous components have the form (*17*)
for $t = 0$

$$p_1 = p_2 = p_3 = 0 \qquad (17)$$

$$p_4 = 100 \text{ kPa}$$

and for surface concentrations
for $t = 0$

$$q_5 = q_6 = 0 \qquad (18)$$

$$q_7 = 520 \text{ μmol/g} .$$

Calculated response of the ideally mixed flow catalytic reactor to the above inlet concentration jump is represented graphically in Fig. 2*a*,*b*. The values of the parameters used for numerical simultation are as follows

$$T = 413 \text{ K} , \quad V = 4{\cdot}5 \text{ cm}^3 , \quad F_v^0 = 0{\cdot}2 \text{ cm}^3/s , \quad W = 1 \text{ g} .$$

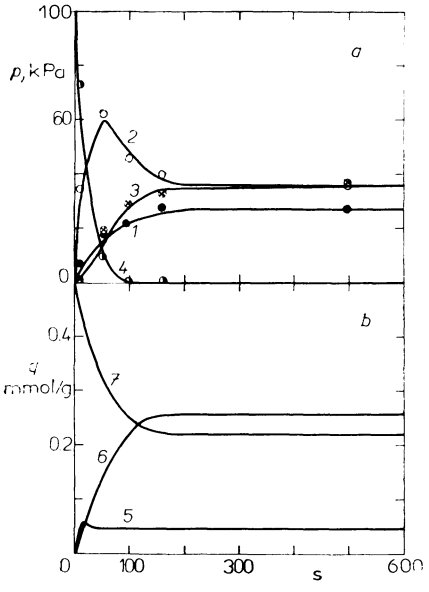

FIG. 2

The time profiles of partial pressures (*a*) and surface concentrations (*b*) after jump change in the composition of the input from pure nitrogen to pure methanol. Calculated partial pressures: *1* methanol, *2* dimethyl ether, *3* water, *4* nitrogen; experimental points[2] ● methanol, ○ dimethyl ether, ⊗ water, ◐ nitrogen. Surface concentrations: *5* methanol, *6* water, *7* free centres

Immediately after nitrogen has been replaced by methanol in the inlet flow to the reactor, the partial pressure of dimethyl ether rapidly increases (Fig. 2*a*). The time course of the not adsorbing dimethyl ether provides direct information about the rate of consumption of methanol by the reaction. Initially, the adsorbed water formed by the reaction blocks only small portion of active centres (Fig. 2*b*), and the rate of methanol consumption increases. After attaining maximum (approximately in 60 s), the rate of methanol consumption (and thus also partial pressure of dimethyl ether) begins to decrease due to the increasing coverage of the catalyst surface by water. In about ten minutes, the catalytic system reaches new steady state.

For comparison, Fig. 2*a* shows also experimental points[2] that represent the composition of the reaction mixture in the ideally mixed reactor during relaxation period. The agreement between experiment and calculation can be regarded as good and the proposed mechanism of dehydration of methanol (*B*) as adequate to the real process that is taking place on catalyst surface.

DISCUSSION

In the present work we have derived the set of differential balance equations that describe the dynamics of a simple catalytic system in kinetic region. Numerical solution by classical integration procedures (*e.g.* of Runge–Kutte type) has led in some cases to difficulties not easy to overcome, that were caused by very different rate constants of single elementary steps of catalytic reaction (so called stiff character of the system). On testing a series of integration procedures, the most generally applicable has turned out to be a semiempirical method by Michelsen[6] and a nonlinear explicit method proposed by Kubíček[7].

In this work we present also an example of formulation of balance equations and the results of numerical simulation for the response of the ideally mixed laboratory reactor to the jump change in composition of the inlet flow. The applicability of the kinetic model tested is documented by confrontation with the experimental data obtained earlier[2].

Similar simulation calculations can be performed also for other proposed mechanisms of the reaction (*A*) and for another types of steady state disturbances (*e.g.* concentration pulse and others). Also the value of W/F_v^0 can be changed, making it possible to achieve different conversions. Characteristic parts of the responses (*e.g.* maximum) can be confronted with experimental data, and by this way, the validity of suggested reaction mechanisms can be verified. Information obtained from numerically simulated dynamics of catalytic reaction can thus contribute significantly to the rational planning of experiments and to the reduction of their number.

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