Development of Tubular Chemical Reactor Models for Control Purposes

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A generalized nonlinear mathematical model for fixed-bed tubular chemical reactors with cooling is proposed. The model is suitable for simulation experiments. A strategy, focused on simplifying and adapting the "primary" model to control applications is shown. This procedure is driven through the so-called "pseudohomogeneous" form of the model until a final description which is linear and relatively simple. The resulting model is offered as a good basis for optimal control design. Some simulation events are included.

A permanent challenge for chemical process control engineers is mastering the problem of optimal control of nonlinear chemical processes. In spite of enormous quantity of work (see *e.g.* [1, 2]), having been done in this field, the results are still unsatisfactory. The reason of this can be found in inefficient process model identification and/or incorrect state estimation. Therefore, for a successful controller design, a precise process model development is of crucial importance.

One of widely used devices of chemical technology is the tubular chemical reactor. The object of our study is such a reactor with fixed-bed catalyst and cooling. For this system, a structured mathematical model is proposed on the bases of both, mass and heat balance equations. This "primary" model, represented by a system of partial differential equations, is nonlinear and relatively complex (MODEL 1). This has, however, an indispensable role in simulation of the system dynamic behaviour. By linearizing MODEL 1 according to the process operating curve, we get a linear model (MODEL 2). After its verification, such a model is suitable for analysis of system internal qualities and feedback state controller design. Under some simplifying assumptions the so-called pseudohomogeneous model (MODEL 3) can be derived. This is also nonlinear but simpler and, thus, it can be well applied when a large number of simulation events is needed. Finally, an appropriate version of adaptive model (MODEL 4) is proposed, such that a recursive least-squares identification method, operating on the process input-output measurement values, is used. MODEL 4 can serve as a good basis for discrete-time adaptive computer control of the reactor. Some selected simulation results are included to demonstrate the system static and dynamic behaviour.

THEORETICAL

Generalized Structured Model — MODEL 1

Under certain assumptions which are described in detail in [3], the mathematical model of a fixed-bed tubular chemical reactor with cooling, assuming that i_1 components of the reaction mixture take part in j_1 relevant reactions, takes the following form:

Mass balance equation

$$\frac{\partial c_i}{\partial t} + v\frac{\partial c_i}{\partial z} = -\sum_{j=1}^{j_1} r_{ij}(c_i, T_k)\ ;\ i = 1, 2, \ldots, i_1 \qquad (1)$$

Reaction gas heat balance equation

$$\frac{\partial T_g}{\partial t} + v\frac{\partial T_g}{\partial z} = \frac{P_{k1}(1-\varepsilon)}{\rho_g c_{pg} V_{k1}\varepsilon}\alpha_1(T_k - T_g) - \frac{4(1-b)}{\rho_g c_{pg} d_1 \varepsilon}\alpha_{23}(T_g - T_w) \qquad (2)$$

Catalyst heat balance equation

$$\frac{\partial T_k}{\partial t} = \frac{1}{\rho_k c_{pk}}\left[\sum_{j=1}^{j_1}(-\Delta H_j) r_j - \frac{P_{k1}}{V_{k1}}\alpha_1(T_k - T_g)\frac{4b}{d_1(1-\varepsilon)}\alpha_{23}(T_k - T_w)\right] \qquad (3)$$

Wall heat balance equation

$$\frac{\partial T_w}{\partial t} = \frac{4}{\left(d_2^2 - d_1^2\right)\rho_w c_{pw}}\left[d_1 b\alpha_{23}(T_k - T_w) + d_1(1-b)\alpha_{23}(T_g - T_w) - d_2\alpha_4(T_s - T_c)\right] \qquad (4)$$

The initial and boundary conditions are given as $c_i(z, 0) = c_{is}(z)$; $T_g(z, 0) = T_{gs}(z)$; $T_k(z, 0) = T_{ks}(z)$; $T_w(z, 0) = T_{ws}(z)$, and $c_i(0, t) = c_{i0}(t)$; $T_g(0, t) = T_{g0}(t)$, respectively.

Linearized Model — MODEL 2

Nonlinearities in MODEL 1 are represented by the Arrhenius reaction rate law

$$r_{ij} = k_{0ij} \exp(k_{ij}/T_k) \tag{5}$$

After introducing new variables in the deviation form

$$\Delta r_{ij} = r_{ij} - r_{ijs};\ x_1 = c_i - c_{is};\ x_2 = T_g - T_{gs};$$
$$x_3 = T_k - T_{ks};\ x_4 = T_w - T_{ws};\ u = T_c - T_{cs}$$

we can linearize MODEL 1 along the operating curve $T_{ks}(z)$ by developing eqn (5) into the Taylor's expansion. (Subscript s involved in the above expressions refers to the relating steady-state parameter values.)

This procedure results in a linearized model which can be expressed in the vector/matrix form

$$\frac{\partial \boldsymbol{x}}{\partial t} + \mathbf{V}\frac{\partial \boldsymbol{x}}{\partial z} = \mathbf{A}\boldsymbol{x} + \boldsymbol{B}\boldsymbol{u} \tag{6}$$

where **V** is a (4 × 4) singular matrix, **A** is a (4 × 4) constant matrix, and ***B*** is a constant column vector. The initial and boundary conditions are equal to zero.

Before applying model (6) to a given control or other problem, it should be verified in a certain neighbourhood of the operating curve.

"Pseudohomogeneous" Model — MODEL 3

If the time constant of eqn (4) is sufficiently small — which corresponds to a small wall heat capacity — this part of MODEL 1 can be neglected. Further, if the concentration responses are much more faster than those of the temperature, eqn (1) can be simplified to a static form. Moreover, if the following condition holds

$$\rho_c c_{pc} >> \rho_g c_{pg} \tag{7}$$

instead of T_k and T_g a new temperature term, the so-called "pseudohomogeneous temperature", T, can be introduced (see [4]).

Thus, the simplified reactor model takes the form

$$v\frac{\partial c_i}{\partial z} = -\sum_{j=1}^{j_1} r_{ij}\ ;\quad i = 1, 2, \ldots, i_1 \tag{8}$$

$$\frac{\partial T}{\partial t} + v\frac{\partial T}{\partial z} = a_1 \sum_{j=1}^{j_1} \left(-\Delta H_j\right) r_j + a_2 T + a_3 T_c \tag{9}$$

with initial and boundary conditions: $T(z, 0) = T_s(z)$; $c_i(0, t) = c_{i0}(t)$; $T(0, t) = T_0(t)$. Preferably, MODEL 3 is used for testing various control algorithms.

Input-Output Unstructured Model — MODEL 4

An up-to-date method of constructing a flexible process model suitable for optimal control design is applying a recursive identification procedure to the process input-output measurement values. The result is an adaptive discrete-time model, the coefficients of which are being adapted to the varying process parameters at each sampling period. The structure of the model is to be chosen *a priori*. In most of the applications, a model of the second or the third order is appropriate. An identification method which can be recommended for wide applications is the LDDIF method [5]. This is a modified recursive least-squares method based on LD factorization of the covariance matrix with directional forgetting. The resulting discrete-time model (MODEL 4) takes the form of a difference equation system

$$\mathbf{N}\boldsymbol{y} = \mathbf{M}\boldsymbol{u} + \mathbf{N}\boldsymbol{\varepsilon} \tag{10}$$

where **N** and **M** are polynomial matrices with argument d, the so-called shift operator. ε is a Gaussian zero-mean stochastic signal (white noise). The scheme of the adaptive model is illustrated in Fig. 1.

RESULTS

Large number of simulation events have been carried out for a real tubular chemical reactor with a given set of process parameters [4]. In the reactor, two relevant chemical reactions of the first order take place and the concentration profile of one dominant component is followed. In this paper, a few selected system dynamics courses are presented.

In Fig. 2, there is a comparison of the reactor steady-state behaviour computed using MODEL 1 (curves *1*) and MODEL 2 (curves *2*). As it shows, the linearized model corresponds well to the nonlinear one.

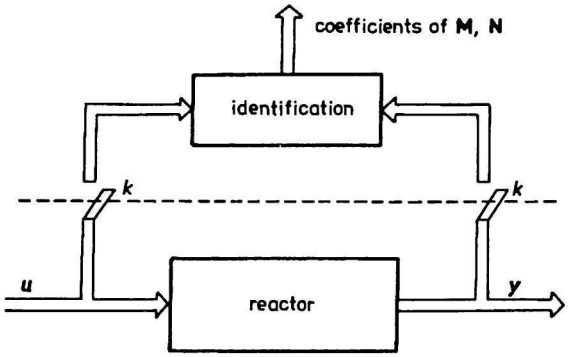

Fig. 1. The adaptive model configuration with sampling step k relating to eqn (10).

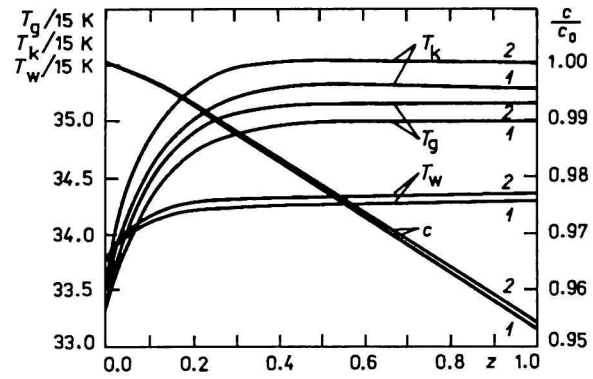

Fig. 2. Nondynamic process variable profiles computed according to the nonlinear (curves *1*) and linear model (curves *2*).

Figs. 3*a* and 3*b* are to demonstrate the process dynamics sensibility to the input variable T_c. When solving eqns (*1*) and (*2*), the system has to be discretized along the space variable and, thus, ten separate segments of the time-variant solutions are obtained. Results show that the admissible changes of T_c are approximately within the interval: $-30\ \mathrm{K} < \Delta T_c < 15\ \mathrm{K}$.

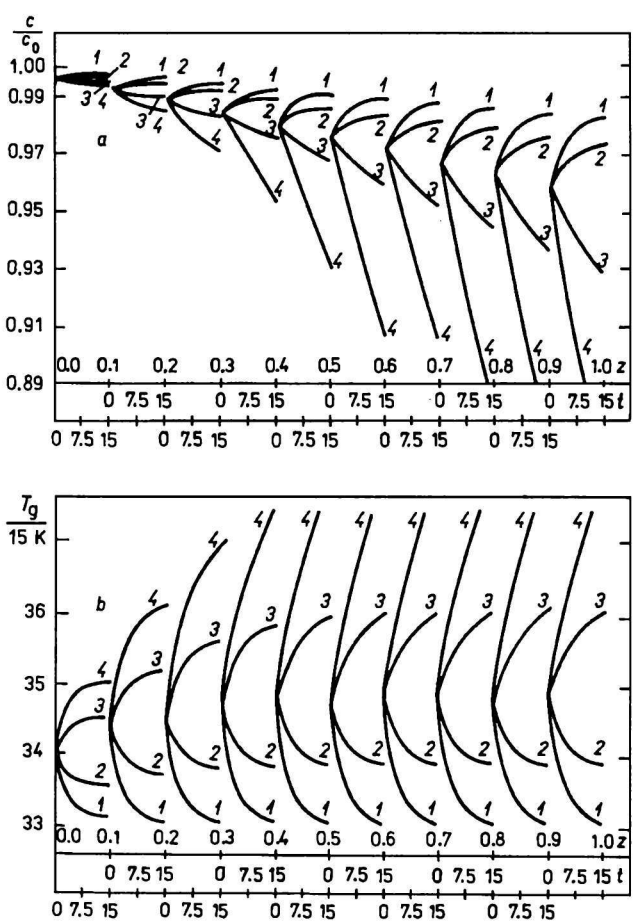

Fig. 3. Distributed dynamic responses of the concentration (*a*) and of the gas temperature (*b*). ΔT_c/K: *1*. – 20, *2*. – 10, *3*. – 10, *4*. – 20.

CONCLUSION

This contribution has been designed to be a guide in developing various forms of tubular chemical reactor models while different aims are followed. On the one hand, models which are well suited for precise simulation experiments may fail when used for control design purposes. On the other hand, models developed with control aims are often poor tools for conducting serious system analyses. A good compromise for both, simulation and control applications, seems to be a linearized form of MODEL 3.

SYMBOLS

t	dimensionless time	
z	dimensionless spatial variable	
k	discrete time	
c_i	concentration of the i-th component	kmol m^{-3}
T_k	catalyst temperature	K
T_g	reaction gas mixture temperature	K
T_w	reactor wall temperature	K
T	reactor inside (pseudohomogeneous) temperature	K
T_c	coolant temperature	K
v	gas flow rate	m^3 s^{-1}
i_1	number of reactants	
j_1	number of reactions	
r_{ij}	reaction rate for the i-th component and the j-th reaction	kmol m^{-3} s^{-1}
P_{k1}	surface area of a catalyst element	m^2
V_{k1}	volume of a catalyst element	m^3
b	coefficient	
α_1, α_{23}, α_4	heat transfer coefficients: catalyst—gas; reactor inside—wall; wall—coolant, respectively	kJ m^{-2} s^{-1} K^{-1}
ε	catalyst porosity	
ρ_g, ρ_k, ρ_w	density of reactant, catalyst, and wall, respectively	kg m^{-3}
c_{pg}, c_{pc}, c_{pw}	specific heat capacity of reactant, catalyst, and wall, respectively	kJ kg^{-1} K^{-1}
$(-\Delta H_j)$	heat of the j-th reaction	kJ kmol^{-1}
d_1, d_2	reactor tube inside and outside diameter, respectively	m
a_1, a_2, a_3	coefficients	
k_{0ij}, k_{ij}	reaction rate constants	
$\boldsymbol{x}$	vector of state variables, $\boldsymbol{x} = [x_1, x_2, x_3, x_4]^T$	
$\boldsymbol{y}$	vector of output variables	
$\boldsymbol{u}$	vector of input variables	
ε	Gaussian zero-mean stochastic signal	

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On the Role of Fermi and Coulomb Correlation in Pericyclic Reactions

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The recently proposed similarity approach to the systematic investigation of the changes of electron correlation during the chemical reactions was generalized by introducing the spin-resolved similarity indices allowing the separate investigation of correlation effects between electrons with parallel and antiparallel spins. The approach was applied to the investigation of several selected pericyclic reactions, both forbidden and allowed. The main attention was devoted to the evaluation of the relative role of Fermi and Coulomb correlation, especially from the point of view of the differences between the allowed and forbidden reactions.

Although the principal qualitative features of chemical reactions are usually satisfactorily described by simple MO methods based on the model of independent electrons, the achievement of quantitative agreement between the experimental and theoretical quantities usually requires the use of more sophisticated techniques taking into account the subtler effects of mutual coupling of electron motions, the so-called electron correlation. The manifestations of electron correlation in chemical reactivity are extremely heterogeneous and in addition to primary correcting effect on the heights of the activation and reaction energies *via* the so-called correlation energy, there is also a number of examples where the electron correlation affects also some other qualitative characteristics as *e.g.* the number and the nature of critical points on the potential energy hypersurface. As an example in this respect may serve some pericyclic reactions (the Diels—Alder reaction or 2 + 2 ethene dimerizations) for which the considerable differences in the predicted nature of PE critical points were reported [1—4].

Although the studies devoted to the systematic investigation of the influence of electron correlation on the character and the quality of the calculated theoretical quantities are rather numerous (for exhaustive review see *e.g.* [5]), the majority of these studies deal with this problem only from the point of view of the numerical investigation of the changes in the quality of the calculated results with increasing quality of the methods used.

In addition to this computational effort, there appeared recently also another kind of studies, attempting to analyze the correlation effects by means of simple qualitative models. The studies of this type are usually based on the analysis of second-order or pair density matrices [6—13]. As an example in this respect it is possible to mention *e.g.* the *Salem*'s study [11] dealing with the analysis of electron reorganization in allowed and forbidden pericyclic reactions in terms of pair correlation functions, or our own recent studies based on the analogous exploitation of the so-called second-order similarity indices [12, 13]. Since these indices are defined in terms of pair densities which inherently include the phenomenon of electron correlation, we proposed in one of our previous studies [12] to exploit these indices as a specific means for the study of correlation effects. As an example demonstrating the possibilities of the proposed similarity approach it is possible to mention *e.g.* the conclusions of recent studies [13, 14], confirming the close correspondence between the allowedness and/or forbiddeness of pericyclic reactions and the extent of electron correlation. In harmony with what could be expected, the role of electron correlation was found to be more important in forbidden reactions than in the allowed ones. In addition to this primary qualitative result, another in-