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UNSTEADY PROCESSES IN CATALYTIC REACTORS

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Volume 22 **Unsteady Processes in Catalytic Reactors**
by **Yu. Sh. Matros**

PREFACE

Technological progress in the chemical industry is largely determined by the development of new, highly efficient, large-scale production processes and by improvements to the operating schemes. The most important factor favouring the acceleration of technological progress is shortening of the period of introduction of scientific achievements into industry. The latter, in particular, is determined by the availability of methods by which one can predict the course of physico-chemical processes in apparatus of any design and dimensions. The main apparatus used in chemical production in most instances is a reactor, the performance of which affects the costs and the quality of the products obtained, the power required, labour productivity and capital investment.

Most frequently no methods of similarity theory can be used to predict the functioning of the process in an industrial reactor on the basis of laboratory experimental data because, as a rule, an industrial contact apparatus and a laboratory reactor are not similar. The theoretical principles and mathematical modelling methods for solving the problems of elaborating a chemical process, constructing contact apparatus, determining their optimal regimes and creating automatic control systems have been laid down by Boreskov, Zeldovich, Frank-Kamenetsky, Kafarov, Slinko, Amundson, Aris and others.

The heterogeneous catalytic reactor is a complex system, consisting of many parts. A detailed study of the structure of the inner connections in the reactor and an understanding of the main factors that determine the technological regime make it possible to build a model that imitates the essential aspects of the reactor's behaviour. The analysis of the mathematical model of a reactor helps to construct an optimally operating industrial contact apparatus and an automatic system to control it, thereby avoiding long and costly gradual development.

The general principles of the construction and analysis of mathematical models of fixed catalyst bed reactors operating under steady-state regimes are well known. In establishing the processes that occur on catalysts with time-variable activity, in starting and stopping the unit, in working under forced unsteady-state conditions and in solving the problems of an automatic control system synthesis, it is necessary to know the

dynamic properties of the reactor. Moreover, one should learn to create contact apparatus with the static and dynamic characteristics necessary for operation. An attempt is made in this book to solve this problem to some extent for fixed catalyst bed reactors.

Chapters 1-5 deal with the problems of constructing and investigating mathematical models. The problems set are solved on the basis of theoretical and experimental research on the elementary processes in a reactor and by revealing the main factors that determine steady- and unsteady-state processes. In Chapters 6-8 methods are expounded for creating highly efficient contact apparatus via the qualitative and quantitative analysis of mathematical descriptions of processes in reactors.

Chapter 9 considers the accomplishment of reactions of heterogeneous catalysis in forced unsteady-state conditions. This aspect, which can be briefly referred to as "unsteady-state catalysis", has been developing particularly rapidly in the last decade, and at the Institute of Catalysis of the Siberian Branch of the USSR Academy of Sciences it has grown into one of the main directions of theoretical and applied research. It is shown in Chapter 9 that the transition from conventional steady-state regimes to forced unsteady-state techniques of performing catalytic reactions often permits an increase in the efficiency of the processes.

The book is mainly based on research carried out at this Institute and is technologically oriented. In presenting the subject matter mathematical calculations have often been omitted while the physical sense of the results obtained from the study of mathematical models is always discussed.

The author is deeply indebted to his colleagues S. Bogdashov, G.A. Bunimovich, I.A. Zolotarsky, O.V. Kiselev, A.S. Noskov, V.A. Chumachenko and N.A. Chumakova for their assistance in preparing this book, and to T.N. Khandros for her selfless assistance in the preparation of the manuscript for publication. The author also thanks V.P. Kobkov for his assistance in the time-consuming translation of the book from Russian into English.

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CONTENTS

Chapter 1

A MATHEMATICAL MODEL OF THE REACTOR

1.1 PRINCIPLES OF CONSTRUCTION

A mathematical model is defined as a simplified representation of the process in the reactor which retains the most essential properties of the real object and reflects them in a mathematical form. In this sense one can talk of the homomorphism of the object (reactor or its parts) into its model. Depending on the problem set, the mathematical model takes into account different numbers of the object's features and hence can be either broad or narrow. A broad model reflects the object's properties more completely and more accurately than does a narrow model. In a certain field these models are homomorphic, i.e., they can yield very close or identical results. There is also a homomorphism between a stronger model reflecting the features of the separate parts and of the entire object itself simultaneously, and a model reflecting the features of the object as a whole. In this instance two or several factors (groups of factors) of the stronger model bear a simple correspondence to a smaller number of factors (groups of factors) of the reactor model as a whole.

The mathematical model of a catalytic reactor must, on the one hand, be sufficiently simple to simulate, clearly and distinctly, every qualitative aspect of the phenomenon in question (only in this instance does it appear possible to retain the "physical control" of the model used) and, on the other, simulate accurately enough the quantitative regularities of the process operation. These requirements contradict each other, for without a thorough study of the system's properties it is unclear which factors are essential.

How then, is a model of the catalytic process in a reactor to be built? Which way should be chosen, so as to avoid, according to the well known mathematician Bellman, the traps of oversimplification and the swamp of overcomplication? The only rational approach seems to be a hierarchical one, prompted by the nature of the chemical reactor itself.

The reactor and the reaction unit are complex objects. They have a multi-stage structure, and their mathematical models are built consecutively on the basis of the preliminary construction

of the models of their component parts. The piece-by-piece investigation of a complicated process makes it possible to proceed to a higher level model including, as a component part, a lower level narrow model. This transition, however, can only be correct if (a) we know all the relevant variation domain of dependent and independent variables entering the broad lower level model (including the boundary and initial conditions), (b) the narrow model has been analysed throughout this domain and (c) the narrow model is shown to describe the process satisfactorily on a lower level.

The above way of constructing a reactor level model presupposes that for a model of a given level to be constructed all the essential chemical and physical regularities that determine the properties of this level have been thoroughly investigated and corroborated by experiment. In this case the regularities acquire the predicting power of physical laws and are invariant in space and autonomous in time. Hence we have the principles of invariance of the model components to the geometrical dimensions of the system and of the autonomy of these components in time. The principle can be formulated as follows. The regularities of the processes occurring in the components of the given model level, and also those of interactions between these components, are expressed in a form independent of the size of the level in question and of time. Note that it is the invariance and autonomy of the regularities in the processes on the lower level with respect to those on the higher level rather than the invariance and autonomy of the quantitative dependences that have been dealt with in this definition. Hence a change in the size of the higher level may deform the quantitative picture on the lower level while the regularities of the processes must remain unchanged.

For a correct transition from the lower to the higher level it is not only the regularities, but also the parameters contained in the mathematical description of the higher level components and in the boundary conditions that should remain invariant with respect to size and autonomous in time. It is precisely the independence of the regularities and the values of the parameters of level size and of time which is indicative of their objectiveness and enables one to predict the operation of the process in apparatus of almost any type and size.

The construction of a mathematical model on the above principle opens up possibilities for an independent experimental investigation of the unknown parameters of this model under the conditions when, first, the process is observed to be highly sensitive to these parameters (which provides for high accuracy) and, second, any influence of most factors on the process can be neglected. The consecutive building of a mathematical model from a lower to a higher level on the basis of the invariance and autonomy of the model components implies rather than excepts the mathematical procedure of consolidating and "compressing" the information in some part of a level, representing it in a compact form convenient for its further analysis. In this simplified form the mathematical model may lose its physical visuality, there may appear some traces of empiricism and the coefficients may become "effective". However, it should retain the principal attribute - the essential quantitative information on the analysis carried out in this level component. In a number of instances a mathematical model fails to remain invariant to the size of the model component that has been studied and frequently it is not autonomous in time. Such a model makes it possible to realize only a one-way transition from a lower to a higher level. "Compressing" the information and representing it as a mathematical description with effective coefficients can be illustrated by a model of the observed rate, W_v, of chemical transformation on a particle of catalyst under the conditions of considerable intra-diffusional resistance. The function W_v determines the chemical reaction rate, depending on the composition and temperature of the gas phase on the surface of a catalyst particle of a definite size. A change in this size entails a change in the value of the coefficients and sometimes even in the form of the W_v function.

Hence the division of a complex process in a reactor into components should be preceded by careful research into the essence of the chemical and physical processes, which results in the investigator having to deal further not so much with mathematical expressions as with size- and time-independent physical representations. From this standpoint it is precisely the construction of the model of an aggregate and a reactor rather than its postulation or an intuitive choice that is the point in question. Consecutive, step-by-step construction of a

model enables one to carry out a correct transition from a lower to a higher level, to reveal and take into account relationships between various components of the given level and to formulate correctly the boundary and initial conditions. True, the investigator's great experience and his scientific intuition often help him choose a model that describes experimental data sufficiently well, but in this instance it is no easy task to define a domain of its possible application without resorting to special prolonged and varied experimental research. What has been said above becomes expecially clear if one takes into account that, first, the accuracy of an experiment is a necessary,but not a sufficient, condition in substantiating a model, and, second, an accuracy of experimental results relative to those calculated from the model under the given conditions cannot be the only reason for applying the same model under some other conditions.

The mathematical model of a reactor or any of its components may be either deterministic or probabilistic. The model of a catalytic reactor will be probabilistic if some of its properties possess some sharply expressed random characteristics. There may be, however, a deterministic model of a probabilistic real system when the spatial and the temporal scales of microprocesses are so much smaller than those of the macrosystem that it proves possible to average the random values within a certain representative sample and to make use of the averaged characteristics.

The behaviour of an object is determined by a set of values of the parameters entering into its mathematical model. Therefore,in analysing the model, dimensionless complexes of parameters and variables are of great importance. The absolute values of these complexes make it possible to compare factors of different physical natures quantitatively and often to determine their effect on the process even before investigating its mathematical description.

It is useful to distinguish the dimensionless complexes (a) which are formed from time-independent parameters, i.e., criteria; (b) which include time, i.e., numbers of homochronism; (c) which are formed from the ratios of two parameters or variables of the same dimensionality, i.e.,normalized variables; and (d) which, besides dependent and independent variables, consist of parameters entering into the model,i.e.,dimensionless variables.

The same system of differential equations, and also the boundary and initial conditions, can be reduced to various dimensionless forms. It is rational to choose a dimensionless representation of a mathematical model that would include dimensionless complexes with a definite and clearly evident physical sense. The structure of each complex reflects distinctly and simultaneously several internal relationships in the model. It is difficult to give general recommendations as to how to reduce a mathematical model to such a dimensionless form, as in each particular instance there are specific features. However, in the author's opinion, one should always start by carefully analysing the physical sense of the model parameters, by determining the qualitative effect of these parameters and independent variables on the system's behaviour, and by establishing, from general considerations, whether situations are possible in which one or another factor will exert a decisive or an insignificant influence on the properties of the object. Even these preliminary considerations often prove sufficient to choose the values of scales, and it is these which determine the structure of dimensionless complexes. For an awkward mathematical model the final choice of the values of scale can often be made only after a careful analysis of the properties of this model with the values of parameters and the initial conditions varied over a wide range. The scales may be either common for several components and even for the whole level, or different for each model component. Sometimes it is the boundary conditions and the scale of the level under consideration that can serve as the starting point in the search for parameters. The normalized spatial variables are obtained when a characteristic spatial size of the level involved is chosen as a value of the scale.

The choice of a particular structure of dimensionless complexes can be also determined by the aim of the research. Hence the significance of the parameters essential for the unsteady-state regime may be negligible for the steady-state regime and hence the structures of the complexes for steady- and unsteady-state processes can be different.

The set of dimensionless complexes entering into a broad model is sometimes transformed into a set of other complexes whose number is smaller for the narrow model. In this instance the physical meaning of the narrow model complexes may happen to be hidden. Establishing a relationship (strict or approximate)

between the complexes of the two models is a necessary condition in the structural analysis of an object permitting one to determine the domain for the possible application of the narrow model. The characteristic indication of the applicability of the narrow model in a given domain is the similarity of solutions by the broad model in comparison with some criteria. This means that for a given set of dimensionless complexes and initial conditions a significant alteration in some criteria causes no appreciable changes in the dependent dimensionless variables. Then these criteria can be removed out of the number of essential factors, and the model in which they were considered can be simplified.

In constructing the mathematical model of an unsteady-state process, separate structural parts of the level can be regarded as elementary dynamic elements. Each of these elements possesses inertial properties that determine the intensity of the time variation of its own state with quantitative changes both in its outer links and inside this element. Inertness is understood to be a characteristic by which one can estimate how gradually the state of the element varies in time and compare the dynamic characteristics of different elements and the duration of transition regimes in them. In elements with greater inertness the transition processes develop more slowly. The inertness of a structural element is largely determined by its capacity, i.e., the reserve of working medium (matter or energy) inside it. A structural element capable of accumulating a greater amount of working medium is more inert. The inertness of a linear structural element is independent of the value and sign of external action. The inertness of the level as a whole is affected by the inertial properties of each of its elements and by the links between these elements. The inertial properties of the same level may differ considerably, depending on the application site of external action. Also inertness is dependent on the "inlet-outlet" channel under investigation.

The inertness of each component part of the model of a level makes a different contribution to the inertness of the level as a whole. It is not necessary for the parts with greater inertness to exert a greater influence on that of the entire level, as the contribution of a component part is also determined by the character of its links with other parts. If some part of the model possesses inertial properties and links with other components such that it does not affect the total inertness of

the whole level through a given channel, then the process in this part of the level is quasi-stationary through this channel. If there is a strong interaction between the parts of a given level, then the ratio of their inertnesses is proportional to their capacities. The quantitative measure of the inertness of an element or a level as a whole can be the characteristic time of the unsteady-state process or, in other words, the time scale M. Its magnitude is estimated as the ratio of the element capacity to the external link intensity. The characteristic time can serve as a scale in choosing the number of homochronism.

The characteristic time of the level is determined by its structural scheme and by the temporal scales of the components. The links between the level parts are mostly distributed and inverse, so the level time scale value is in a complicated dependence on the time scales of each structure element of this level. This dependence should be studied, designing mathematical models, as it eventually makes it possible to take into account the inertness of only those structural elements which exert a decisive effect on the static and dynamic characteristics of the entire reactor.

The value of M under a monotonous regime in an element, a part or a level as a whole can be quantatively determined using the expression

$$M = \frac{\int_0^\infty [U(\infty)-U(t)]dt}{U(\infty)-U(0)} \qquad (1.1)$$

where U(t) is a solution corresponding to the model of an unsteady-state process for a single-step disturbance at a time t=0, U(0) are the initial conditions which are best given as a solution of a steady-state problem and $U(\infty)$ is an asymptotic value of U(t).

The characteristic times of various processes in a reactor may differ greatly from one another. Thus, e.g., the value of the internal mass transfer time scale on one particle of catalyst can be estimated from the expression $M_D = \varepsilon_p R_o^2/D$, where ε_p is porosity, D is the effective diffusion coefficient and R is the particle radius. With the values of $\varepsilon_p = 0.25$, $D = 0.1$ cm^2/s and $R_o = 0.2$ cm, $M_D = 0.1$ s. The time scale M_p of the rate of poisoning of catalyst activity for many industrial processes is