DESIGN OF INDUSTRIAL CHEMICAL REACTORS FROM LABORATORY DATA

JOSEF HORÁK
JOSEF PAŠEK

Associate Professor, University of Chemical Technology, Prague

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PREFACE

In recent years, Chemical Reaction Engineering has developed to a science that uses complicated theoretical apparatus and sophisticated mathematical models to describe the behaviour of reacting systems. It is not simple to find a realistic approach to application of the theory in practical technological research, especially for engineers who were not educated in this field. The aim of this book is to facilitate the way to application. The book is destined not only for Chemical Engineering students but also for engineers in design, industrial research and production.

The text is based on long-term experience with teaching Chemical Reaction Engineering, both for undergraduate students and for engineers from chemical plants, in courses organised by the Department of Organic Technology of the Prague Institute of Chemical Technology. The selection of chapters and problems included was influenced by the close cooperation of the Department with chemical plants resulting in development of several new technological processes.

The Authors

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The Authors

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Chapter 1

MACRO- AND MICROKINETIC PROPERTIES

The approach which has been and often still is used for the design of industrial chemical plant is an empirical one based on the intuition and experience of the chemical process engineer. The engineer studies the reaction in a laboratory reactor and learns to control the reactor until a satisfactory result is obtained. Through experiments he seeks a suitable régime to operate the bench scale reactor, constructs an intermediate pilot plant reactor, etc., and finally designs the full scale reactor.

This empirical way may, of course, lead to the desired goal, but the prospects and the scope of this approach are considerably limited. It may be successful for simple processes, but for more complex ones, either fails completely or its costs and laboriousness are prohibitive. Because the development of technical chemistry tends towards ever more sophisticated processes and puts ever increasing requirements on the economy of the operation, reliability and control, an empirical approach can no longer be trusted. New, more exact methods of technological development must be sought enabling more complex processes to be mastered with minimum cost. For example, the medieval artillery man learned to hit the target by the intuitive use of his experience. The burning of the gun powder and the motion of the cannon ball are described by very complicated differential equations but he availed himself of the ability of his brain to process analogies into a generally valid experience. In an intuitive way he disentangled the problem of putting an object on a trajectory passing through a given point.

An analogous problem, although a great deal more difficult, is putting a space research laboratory into an orbit around the moon or reaching some other planet. It is quite obvious that an empirical way consisting of gathering experience of how to propel a missile to reach a desired object would either fail or be prohibitively time-consuming and expensive. This problem necessarily calls for new, exact methods utilizing a system of carefully planned experiments for evaluation.

1.1 Sources of information for technical solution to a problem

The job of the chemical process engineer is to design the plant and determine the way it should be operated. The plant will be referred to sometimes as the objective. In order that the chemical engineer may be able to design the objective he must know its behaviour. This is not an ultimate but a necessary stage in solving the problem for which information must be obtained and processed.

There are several ways of gathering information. For technical reasons concerning the development of a new process and its associated economies it is convenient to divide these methods into five classes:

(a) *The results of direct experiments on the objective*

By experimenting with the objective the engineer can obtain direct information about its behaviour. Clearly, the method is applicable only if the plant has been put into operation and is available for experiments. The method finds its use in the process optimization of industrial equipment.

(b) *The results of indirect experiments of the designer*

The design engineer performs his experiments on either a laboratory or a pilot plant set up to obtain experimental data about the process. Such data can be used in turn for the design of the full scale plant, provided that the engineer knows how to use them.

(c) *The results of other authors*

Such information comes from the literature, research reports, discussions with fellow workers, patent literature and so on. This is similar information to that in (b) except that the engineer himself does not have to perform the experiments, which may appear as an advantage. However, for the same reason it is more difficult to assess the reliability of the information obtained.

(d) *Information about related processes*

To illustrate this, if the aim of the research is the design of a unit for the nitration of isopropylbenzene, then useful information may well be obtained from the evaluation of work performed on the nitration of benzene and toluene.

(e) *Generalized experimental results-theory*

The laws of theoretical science represent a generalization of experimental results and experience of whole generations. This fact is frequently overlooked, and an engineer who cannot or does not make full use of theoretical

background deprives himself of the rich experimental implications of that theory.

At the same time it should be realized that the validity of theories and "laws" may be limited. Each theory or law is valid, strictly speaking, only within the region within which it has been verified experimentally. Extrapolation outside these limits is always uncertain. In applications it should be ascertained whether the limits within which the theory holds with sufficient accuracy are not exceeded. The validity of a theory or a law is always somewhat open to question.

Transfer of data or information

If the chemical engineer cannot obtain from the published literature the information he needs about the process he must investigate data measured on an experimental set-up either of his own or of other researchers. The process of using data obtained for one apparatus to predict the behaviour of another apparatus will be referred to as the transfer of data.

In connection with data transfer we sometimes use the term "scale-up". This term emphasizes that laboratory apparatus or pilot plant is as a rule much smaller than the full scale equipment and implies also the aim to use small scale experiments for design of the process plant.

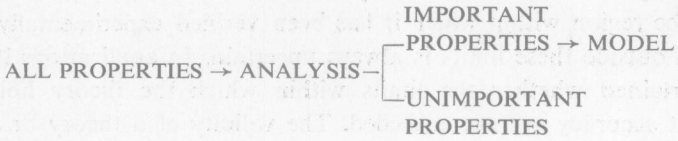
Data transfer, however, is not limited to the transfer from the laboratory equipment to the large scale apparatus of the same type. The data can be obtained in an apparatus which differs entirely in its function. For example, viscosity of the reaction mixture can be determined in a viscometer. The result then may be used for reactor design.

1.2 Mathematical models

The design of a reactor and its operating régime, optimization and control require knowledge of the behaviour of the process or, more specifically, of the quantitative aspects of its behaviour. The process is usually described in the form of equations and relationships containing its properties. The set of computational relationships describing the behaviour of the process is termed a mathematical model.

A mathematical model, of course, need not reflect all aspects of the behaviour but it must describe all those that are essential to the underlying problem. An initial task is therefore an analysis to determine which features of the behaviour must be incorporated into the model. In later stages, too,

the chemical engineer must constantly observe which properties of the behaviour of the process are fundamental and which are not, in order to obtain a model reflecting all the important properties.



Significance of mathematical models

Chemical technology was formerly a science about facts. It compiled data about conditions under which certain substances are produced, facts such as: phenol can be sulphonated by heating with 95 % sulphuric acid for 5 hours at 50 °C.

Present chemical technology is not a science about facts but rather about dependences and relationships. The scope of the questions to be answered is thus much broader.

Under the modern approach the sulphonation of phenol data just mentioned must be extended by answering the following questions:

What happens if the reaction time is prolonged?
What happens if sulphuric acid of a different concentration is used?
What economies may the previous changes effect?

Modern technology then is often the study of functional dependences such as those describing the effect of temperature, concentration, loading of the reactor by the feed mixture, etc., on the course of the process and the related economic implications. The description of these functions is the mathematical model. The aim of technological research and analysis should tend towards a quantitative evaluation of the process using a mathematical model.

Use of mathematical models is thus a logical consequence of the development of technical chemistry. The application of mathematical models now of course goes hand in hand with the efficient utilization of analog and digital computers. In the field of reactor techniques the advent of computers has meant more than a revolution. In fact, in view of the complexity of the processes involved, chemical reactor science could not have developed at all without computers.

Computers, of course, can be put to full use only if programmed by experts who are able to formulate the problem in a manner digestible by the computer. A suitable form is in fact the mathematical model.

1.3 Methods leading to a mathematical model

From the viewpoint of methodology there are two extreme ways of obtaining a mathematical model:

1. *The black box method.* This method makes no effort to learn anything about the phenomena existing within the process. The process is regarded as the provider of a relationship between the input and the output, as a generator of the output response. The model is obtained by determining experimentally over the whole range of conditions the relation between the input and the response. The result is then expressed by a suitable mathematical expression [2].

Example: The aim is to obtain a mathematical model describing the behaviour of a batch reactor. The quantities that can be varied, namely, duration of a charge and the temperature of heat transfer medium are regarded as inputs. A series of experiments is carried out varying the inputs and observing the degree of conversion of the reactant, which is regarded as the output. The results may be recorded as a set of points in a three-dimensional, temperature-time-degree of conversion space. Fitting a surface to these points by means of a suitable statistical method leads to the mathematical model.

The advantage offered by the black box method is that it obviates the study of the phenomena within the reactor; It is sufficient to observe the input/output relationship. On the other hand, the very fact that we know nothing about the fundamentals of the process means that the model is not applicable to other equipment. This model is thus incapable of answering the question: "what happens if the size of the reactor is enlarged?" The black box model thus describes the behaviour of a single reactor.

2. Methods based on the concept of mechanism. The notion mechanism is taken here more broadly; it does not imply merely the mechanism of chemical reaction but also mechanisms of physical phenomena and their interactions. Using this method we attempt to determine what happens within the reactor, subdividing the process into simpler phenomena the mechanisms of which can be more readily understood. It is particularly useful to break down the process into phenomena for which theoretical laws have been established, such as diffusion, heat transfer, chemical reaction and so on. The mathematical model of the process then synthesizes models of individual phenomena [1, 3, 4].

Example: Applying this method to the reactor in the previous example we can break down the process into chemical reactions and heat transport. A study of the reaction kinetics would yield a model of the chemical reaction;

measurement of the heat transfer coefficient would yield a model of heat transfer, etc. All partial models would then be combined by means of balances into a model of the whole reactor.

The model contains physically meaningful quantities such as reaction rate constants, exchange surface areas, etc. Thus, provided that the model has been correctly formulated, it is capable of answering the question of what happens if some of these quantities are changed, e.g. if we use a reactor of different size, or a different area of cooling surface.

Mathematical models based on the concept of mechanism permit data transfer through the prediction of the behaviour even those objects which were not subjected to direct experiment. This appears to be the major advantage. Another advantage is that these models fully utilize the information embodied in theory which is entirely ignored by the black box model.

Mathematical models sometimes facilitate the drawing of analogies between the behaviour of systems that are seemingly widely different. Comparison of the mathematical expressions used to set up mathematical models sometimes shows that various pieces of equipment may be described by relations which are from a mathematical point of view identical and hence that all of the equipment will behave similarly. An example is the analogy between the behaviour of the batch reactor and the continuous tubular reactor. Mathematical models thus provide an abstract treatment for specific equipment.

Models based on the concept of mechanism may sometimes demand a greater amount of information than the black box model; it is necessary to find out which phenomena are involved and to describe their behaviour. This ultimately necessitates additional indirect measurements which might be avoidable in the case of the black box model (e.g. the study of reaction kinetics, diffusion of species, etc.).

The choice of a mathematical model for a particular "object" may depend on the following circumstances:

The "object" is available and can be experimented with: the aim of the research is merely a mathematical model of the particular "object" with no need for data transfer to another system; there is no requirement to identify the phenomena within the "object".

Situations favouring the model based on the concept of mechanism:

Direct measurements on the particular "object" are not feasible, the aim being to transfer the data to other systems; the phenomena within the "object" are identifiable and describable. Note that the meaning of the term "object" is not limited in any way; it may be the equipment as a whole, a part of the equipment, one of the phenomena involved, a molecule, a catalyst pellet or simply anything for which a mathematical model is sought. The decision which of the two models to use should therefore be

examined on several levels because even for the latter model there is always a limit of sophistication beyond which it is no longer advantageous to proceed. For example, the properties of a molecule are mostly described from direct data, i.e. by the black box method. The two types of model are often combined.

Stochastic and deterministic models

These terms distinguish the models from the methodological standpoint. Using a deterministic model it is assumed that the model reflects all effects acting on the system. A stochastic model, however takes account of random unknown effects. In the former case the model describes the state of the system, in the latter the probability of a certain state. Stochastic models are thus based on the theory of random processes.

The boundary between the two types of model is not sharp: they often overlap.

Example: The reaction rate constant of the rate equation used for the description of a chemical reactor was determined by statistical processing of experimental data. If we used the mean value of the reaction rate constant we would apply a deterministic model. If we analysed consistently throughout our calculation the effect of the scatter of the values of the reaction rate constant on the yield, the model would acquire some stochastic features.

1.4 Definition of a system

The problems regarding the transfer of data are common to all disciplines and valid at all stages of the solution. It is therefore useful to examine these problems in a broader context with the view of pointing out the general laws which must be observed in data transfer.

Let us define a system. A system is a group of interacting elements. By looking at the process as a system we have assumed the separation of two different categories: elements and interactions. The element is a part of the system characterized by properties representative of this element only. Interaction is a relation between two or more elements. Consequently, interaction is a property common to two or more elements.

The concept of an element may be understood in a broader sense. An element may be a spatially separated section of the reactor, for example water bath, catalyst, reaction mixture, heat exchanger, etc. In other instances it may be more convenient to view different properties of the same part of

some equipment as separate elements, e.g. the heat and mass capacity of the reaction mixture.

If the description of the behaviour of a system calls for subdivision into elements, the subdivision must lead to elements and interactions whose properties have been known or can be determined.

In order that we may obtain a mathematical model of the whole system we must be able to formulate mathematical models of all the elements and interactions.

Consider again the method of gathering data for the design of equipment. The black box model views the system as a single element and the procedure of subdivision to elements is not therefore utilized. Methods based on the concept of mechanism involve subdivision because we try to isolate the individual phenomena, the elements, and determine their interaction. Here, too, the only concepts of mechanism useable are those that lead to elements and interactions that we can describe.

On changing to more and more profound concepts of mechanism the system is being subdivided into ever greater numbers of elements and interactions until a limit is reached beyond which we are no longer capable of describing the properties of the elements and interactions. Here we have to resort to the black box method.

Example: Consider a reaction taking place in a solvent. The aim is to obtain the reaction rate equation which would represent a mathematical model describing the behaviour of the reaction. Theoretically, this can be accomplished in several ways:

(a) By determining directly the reaction rate for given compositions and temperature of the reaction mixture. The black box method is applied to the whole mixture.

(b) By determining the mechanism of the chemical reaction, the activity coefficients of the reacting species and evaluating the reaction rate equation from kinetic measurements carried out under standardized conditions. In this case, the black box method is applied to the properties of the molecules implicitly contained in the activity coefficients, reaction rate constants, equilibrium constants, etc.

(c) Theoretically it might be possible to study the properties of the molecules and from these, without direct study of the reaction kinetics, evaluate the reaction rate constants. The black box method is now applied to molecules.

(d) By studying the properties of the atoms and calculating molecular properties from them. The black box method is thus applied to atoms, and further.