# Process Modeling and Control in Chemical Engineering

edited by

**Kaddour Najim**

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# Preface

The advent of high speed computers has made possible the simulation and on-line control of complex systèms such as chemical processes. At the same time, a considerable amount of effort has been made in process modeling, simulation and the development of digital controllers which can adapt themselves to the nonlinear and time-varying dynamics of chemical plants.

In view of rapid changes in requirements, it has become necessary to place at the reader's disposal a book dealing with basic and up-to-date concepts on and techniques for the modeling and simulation of chemical process, with the estimation of parameters and control, as well as with aspects of the implementation of these different techniques.

Chemical engineering covers a very wide spectrum of subjects which make it difficult to cover its whole subject matter in a single book.

The ideas in this book are intended as a solid background for modeling, simulation and control in chemical engineering. Ample references are given at the end of each chapter to allow the reader to pursue his interests further.

Fifteen colleagues have collaborated on this work. Thirteen of them are members of the teaching faculty of the E.N.S.I.G.C., which is directed by Professor H. Angelino. This book contributes to the celebration of the fortieth anniversary of this Chemical Engineering School and demonstrates its vitality.

The chapters contain material aimed at three different levels: the first level is for undergraduate students in chemical engineering and automatic control on modelling and control techniques; the second level is very academic and is aimed at post-graduate and researchers; the third level is for practicing engineers in industry.

The eight chapters which compose this book have been developed in a systematic manner. Their foundations have been carefully built. Each chapter is independent of the others, in such a way that the reader who is interested only in chemical reactors, for example, can find the notions concerning the modeling and simulation of chemical reactors in Chapter 1, which is dedicated to them.

The difference between the eight chapters constitutes one of the positive qualities of the book.

Since chemical reactions, separation techniques, energy management and automatic control are of primary importance in chemical engineering, they are treated in considerable detail.

Different kinds of chemical reactors (tubular and mixed continuous, and batch, fixed and fluidized bed reactors) are presented in this chapter, which gives a rational approach to their treatment. First, homogeneous reaction systems with ideal flow are considered, then liquid-fluid reactors are examined and the last part is devoted to catalytic reactors.

Bioreactor simulation and modeling concepts are detailed in Chapter 2. The modeling of bioreactors is similar to that of chemical reactors, the only difference being due to the kinetic rate equations of the biochemical or biological reactions. The specific kinetics of enzymatic reactions and the growth of microorganisms are presented and the modeling of a tubular continuous immobilized enzyme reactor and that of a continuous culture with recycling of cells are examined.

The third chapter is concerned with distillation columns. A general model describing the functioning of a distillation column is presented, and is applied to several specific cases by simplifying assumptions which take into consideration the operating conditions for each case. A costing procedure for plate and packed continuous columns and methods for synthesizing multicomponent distillation sequences are presented.

The classification and operation of liquid-liquid extraction columns, which involve hydrodynamics and mass transfer aspects, are presented in Chapter 4. The link between flooding conditions and the optimal operation range is clearly pointed out.

In the first part of Chapter 5, absorption analysis is presented, concerning the determination of degree of freedom and the minimum liquid rate in both isothermal or non-isothermal cases. A general model for absorbers has been developed and applied to packed and plate columns for several cases: isothermal or non-isothermal operation, absorption of one or many components. In the last part of the chapter, an analysis of stripping columns is given, using the same general model.

Chapter 6 deals with the modeling and simulation of heat exchangers. The principal modes of heat transfer with or without phase changes are presented and steady-state and unsteady-state models are detailed. In the last part of this chapter, liquid and gaseous heat resistances are included in the overall heat transfer coefficients for the modeling of condensers and reboilers.

A brief description of the different types of cycles used either for energy upgrading or refrigeration and their schematic representation in various diagrams is given in Chapter 7. An analysis of vapour compression cycles, absorption cycles and heat transformer cycles is presented, with regard chiefly to degree of freedom and modeling. This enables the prediction, according to working conditions, of performances such as COP, temperature lift and exergetic efficiency.

Finally, Chapter 8 deals with parameter estimation, minimum variance and generalized predictive control. The adaptive control strategies are designed by adjusting the model (controller) parameters on the basis of the measured process variables in order to achieve the desired performances. Several case studies are presented. The associated experimental results suggest that these control techniques may be powerful in comparison with conventional control methods.

The material has been arranged in a logical order and great care has been taken to make it possible for the reader to access the book at any point required by the needs and interests of the moment.

We have deliberately avoided presenting a general formulation of the modeling concepts of the separation processes based on theoretical stages and have preferred to give all the elements useful for each separation technique in separate chapters.

Long and tedious mathematical developments have been voluntarily kept out to facilitate understanding of the material presented in this book.

I would like to thank Professor John Keen of the E.N.S.I.G.C., Toulouse, for his help in the preparation of this book, which is a modest contribution to bridging the gap between theory and application in the field of chemical engineering.

Kaddour Najim

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# CHAPTER I

# CHEMICAL REACTORS

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## I. INTRODUCTION

Chemical reactor calculations are based on the elementary conservation laws of matter and energy. Information is needed on flow phenomena, rates at which the reactions proceed, heats of transformation and, sometimes, description of chemical equilibria. Furthermore, the performance of a chemical reactor is ultimately judged on the basis of economic factors, with consideration of such criteria as safety, pollution, raw material availability and social factors.

The purpose of this chapter is to give a rational approach to the treatment of chemical reactors. First, homogeneous reaction systems with ideal flow will be considered. Then liquid-fluid reactors will be examined and the last part will be devoted to catalytic reactors.

## II. QUANTITATIVE ASPECTS OF CHEMICAL REACTIONS

Reactions may occur as soon as the reaction mixture is submitted to appropriate conditions of temperature and pressure with reactants well mixed in a molecular scale. Some of them require the use of a catalyst which takes part on elementary staps. The catalyst may be under the same state as the reactants (homogeneous catalysis) or in a different state, usually the solid state (heterogeneous catalysis).

### II.1. Classification of gross reaction types and reaction rates

From a gross kinetic point of view, chemical reactions are mainly considered under overall formulations which do not refer to elementary processes. Two classes are usually distinguished : single and multiple reactions.

The single reactions comprise :

- uni-directional reactions :

$$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_P P + \upsilon_Q Q$$

- reversible reactions :

$$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_P P + \upsilon_Q Q$$

- autocatalytic reactions :

$$\upsilon_A A \rightarrow \upsilon_P P$$

where the presence of the product P is necessary to provoke the conversion of the reactant A.

The multiple reactions comprise a wide variety of possible kinds of reaction, among which three basic types can be given :

- parallel reactions :

$$\upsilon_{A1} A \rightarrow \upsilon_{P1} P \quad (1)$$

and $\upsilon_{A2} A \rightarrow \upsilon_{Q2} Q$ (2)

- consecutive reactions :

$$\upsilon_{A1} A \rightarrow \upsilon_{P1} P \quad (1)$$

$$\upsilon_{P2} P \rightarrow \upsilon_{Q2} Q \quad (2)$$

- complex reactions which are combinations of parallel and consecutive reactions :

$$\upsilon_{A1} A \rightarrow \upsilon_{P1} P \quad (1)$$

$$\upsilon_{P2} P \rightarrow \upsilon_{Q2} Q \quad (2)$$

$$\upsilon_{A3} A \rightarrow \upsilon_{X3} X \quad (3)$$

$$\upsilon_{P4} P \rightarrow \upsilon_{Y4} Y \quad (4)$$

The reaction formulation can be written under the form of a reaction balance. Thus for the reaction i this form gives :

$$\sum_{j} \upsilon_{ij} A_j = 0$$

where $A_j$ is the component j which corresponds to either a product or a reactant, $\upsilon_{ij}$ is the stoechiometry coefficient of the component $A_j$ for the reaction i. In this description $\upsilon_{ij}$ is positive for a product and $\upsilon_{ij}$ is negative for a reactant.

Single reactions are described by a single reaction balance. Multiple reactions are described by a system of reaction balances, the number of which is that of all the reactions involved.

In a single reaction i, the production rate of a given component $A_j$ is defined by :

$$r_{ij} = \frac{1}{V} \frac{dN_j}{dt} \qquad (1)$$

where V is the volume of the reaction mixture and $N_j$ the mole number of the component Aj.

From the reaction stoechiometry, it can readily be established that $r_{ij}/\upsilon_{ij}$ is the same

for all of the components. This rate is called the kinetic rate of the reaction i :

$$r_i = \frac{r_{ij}}{\upsilon_{ij}} \qquad (2)$$

It can be noted that $r_i$ is positive.

In the case of multiple reactions, the overall production rate of the component $A_j$ is given by :

$$R_j = \underset{i}{\omega}\, u_{ij}\, r_i \qquad (3)$$

The summation corresponds to all the reactions involved.

Chemical reaction rates are expressed as functions of the concentrations or partial pressures. In the case where two reactants A and B are involved, the kinetic rate is most often expressed by :

$$r = k\, C_A^m\, C_B^n \qquad (4)$$

where m and n are respectively the order of the reaction with respect to A, and the order with respect to B. The total order of the reaction is m+n.

For reversible reactions, one has :

$$r = k_1\, C_A^m C_B^n - k_2\, C_P^p C_Q^q \qquad (5)$$

and for autocatalytic reactions, this becomes :

$$r = k\, C_A^m\, C_P^p \qquad (6)$$

However, for complex mechanism reactions formed by a combination of a number of elementary kinetic processes it is sometimes impossible to approximate the chemical reaction rate by one of the three equations above. The following types of rate equations can give better results :

$$r = \frac{k\, C_A\, C_B}{1 + K_1 C_A + K_2 C_B} \qquad (7)$$

$$r = \frac{k\, C_A\, C_B}{(1 + K_1 C_A + K_2 C_B)^2} \qquad (8)$$

In the chemical reaction rate equations, the influence of temperature is taken into account in the reaction rate constant k which is expressed by :

$$k = k_0 \exp(-E/RT) \qquad (9)$$

It can be noted that the chemical reaction rate has been referred to the unit volume of the reaction mixture. However, for heterogeneous systems it can be more convenient to base it on another property : the volume of the liquid or the solids contained in the reactor, the mass of solids or their internal or external surface area, the interfacial area between two phases, etc. Conversions from one form to the other are easily derived.

Note that data relative to the kinetic rate of a reaction reflect the chemical kinetics of the system under conditions where conversion is not influenced by physical transport of reactants toward the reaction site or of products away from it. In cases where fluids are poorly mixed or with rapid reactions in heterogeneous systems, the physical transport phenomena may reduce the conversion rate. It is therefore to take necessary the transport resistances into account.

## II.2. Relative degree of conversion, selectivity and yield

The relative degree of conversion of a reactant A is a measure of the extent of the reaction. It is defined as the fraction of the amount of the reactant, fed in prior to and during the reaction, which has been converted :

$$\zeta_A = \frac{N_{A0} - N_A}{N_{A0}} \qquad (10)$$

From a single reaction and from the stoechiometry requirements, it can easily be shown that :

$$\frac{N_{A0}\,\zeta_A}{\upsilon_A} = \frac{N_{B0}\,\zeta_B}{\upsilon_B} \qquad (11)$$

When products other than those desired are formed from the reactants A and B, it is convenient to use the concepts of selectivity and yield. The selectivity $\sigma_P$ of a desired product P with respect to a key reactant A is the ratio between the amount of P obtained and the amount of A converted. These amounts must take into account stoechiometry of the reaction :

$$\sigma_P = \frac{N_P - N_{P0}}{N_{A0} - N_A} \; \frac{\upsilon_A}{\upsilon_P} \qquad (12)$$

The yield of the product P with respect to the key component A is the ratio of the amount of P obtained to the amount of A fed in, corrected for the stoechiometry considerations :

$$\eta_P = \frac{N_P - N_{P0}}{N_{A0}} \quad \frac{\upsilon_A}{\upsilon_P} \qquad (13)$$

By combining equations (10) and (13), we obtain :

$$\eta_P = \sigma_P \, \zeta_A \qquad (14)$$

## III. CLASSIFICATION OF CHEMICAL REACTORS

The range of forms of chemical reactors is so wide that it is practically impossible to establish a complete, systematic classification. Moreover, there is no correlation between the type of reaction to be processed and the type of the equipment in which the reaction is carried out. However, an initial classification can be based on the number of phases to be contacted. When only one phase is needed, the system is said to be homogeneous. when more phases are required, the system is a heterogeneous one. Nevertheless, a heterogeneous catalytic reactor may often be considered as a homogeneous one for modeling considerations. Then, the way in which the reaction is processed can be introduced to define general classes of reactors : batch, semi-batch or continuous flow reactors.

Homogeneous reaction systems are mainly, on the one hand, tank (or autoclave) reactors in which the reaction mixture is stirred and which run in one of the three ways mentioned above, and, on the other hand, tubular reactors which are operated only with a continuous flow.

Heterogeneous reaction systems are more varied since either one or more phases may be processed continuously. Two limit cases regarding the flow pattern are referred to : the stirred tank reactor and the (tubular) plug flow reactor. In fact, the flow of a given phase may be more or less mixed, so this ranks the system between the two ideal cases above. Futhermore the contact between the different phases is a predominant factor. Thus, in continuous gas-solid reactions in a rotary kiln, the two phases are poorly mixed in the direction of flow. In a fluidized bed, the solid phase is well mixed while the flow of gas is heterogeneous and can itself be divided into two sub-phases : one dispersed and the other continuous. Only a fraction of the gas flow comes into direct contact with the solids and the resulting pattern is intermediate between that in a stirred tank reactor and a plug flow reactor.

## IV. IDEAL HOMOGENEOUS REACTION SYSTEMS

First, the material balance will be derived for isothermal reactions in tank and tubular reactors. Combination of model reactors will then be applied to a cascade of continuous tank reactors and to the recycle tubular reactor. Finally, when heat effects have to be considered the energy balance will be written and some treatments will be shown.

The tank reactors will be assumed to be well mixed with uniform composition which is equal to the outlet composition when it is continuously operated. The tubular reactor will be considered with a plug flow of the reaction mixture.

### IV.1. The batch reactor (BR) under isothermal conditions

In this type of reactor (figure 1) a given amount of material is introduced first, but no material is fed or withdrawn as the reaction proceeds. The total mass of the reaction mixture remains constant ,while the composition is a time function. For a component $A_j$, the material balance is :

$$\frac{dN_j}{dt} = V R_j \qquad (15)$$

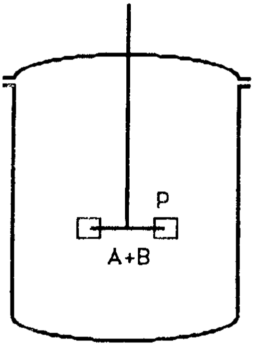

Figure 1: Stirred batch reactor