1

Basic Problems of Chemical Reaction Engineering and Potential of Membrane Reactors

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1.1

Challenges in Chemical Reaction Engineering

Currently there are more then 30 000 specialty chemicals produced industrially from approximately 300 intermediate chemicals (Moulijn, Makkee, and Diepen, 2001). The vast majority of these intermediates are produced from a very limited number of approximately 20 simple base chemicals for example, ethylene, propylene, butane, ammonia, methanol, sulfuric acid and chlorine. To perform efficiently the large spectrum of chemical reactions of interest an arsenal of specific reactor types and dedicated operating regimes has been developed and is applied in various industries. The design of efficient and reliable reaction processes is the core subject of Chemical Reaction Engineering, a discipline which can be considered nowadays as rather mature. The progress achieved and important concepts developed are summarized in several excellent monographs (e.g., Froment and Bischoff, 1979; Schmidt, 1997; Levenspiel, 1999; Missen, Mims, and Saville, 1999; Fogler, 1999).

The main starting point of an analysis of reacting systems is typically an evaluation and quantification of the rates of the reactions of interest. Hereby, based on the specific physical an chemical properties of the reactants and products a wider range of temperature and pressure conditions has to be considered during the early development phases. The spectrum of reactor types available and operating principles applicable is very broad.

Reactions and reactors are often classified according to the phases present (Levenspiel, 1999). There are reactions that can be carried out in a single phase. However, in a reaction system often more phases are present requiring more sophisticated configurations and operation modes.

Another useful classification is based on the character of the process and distinguishes between continuous and discontinuous (batch) operations. Between these exist semi-batch processes which are often applied to carry out highly exothermal reactions exploiting adjusted dosing concepts (Levenspiel, 1999; Fogler, 1999).

To accelerate the desired reactions and/or to influence the selectivity in reaction networks with respect to the target products, frequently specific catalysts are

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applied. These catalysts might be present in the same phase as the reactants (homogeneous catalysis). To fix these often expensive materials in continuously operated reactors, catalysts are often deposited (immobilized) on the surface of solid porous supports (heterogeneous catalysis).

Despite the large efforts devoted to further develop the field of Chemical Reaction Engineering, the performance of how chemical reactions are carried out indutrially still suffers from several severe limitations. Very important and not sufficiently solved problems are:

Problem 1: The rates of chemical reactions leading to desired products are often too low to establish economically attractive processes.

Problem 2: The conversion of many reactions of interest is thermodynamically limited, that is, the reactions proceed also in the opposite direction and convert products back (reversible reactions).

Problem 3: The energy efficiency of endothermal and exothermal reactions performed industrially is often not satisfactory.

Problem 4: In reaction networks the selectivities and yields with respect to a certain target product are limited.

In recent decades several promising new approaches and innovative reactor concepts have been developed to tackle the mentioned problems.

Enhancing the rates of desired reactions (Problem 1) is the main field of catalysis. Significant progress has been achieved in recent years, both in homogeneous catalysis (e.g., Bhaduri and Mukesh, 2000) and heterogeneous catalysis (e.g., Ertl *et al.*, 2008).

To overcome equilibrium limitations (Problem 2) new reactor concepts have been suggested and developed. One of the most successful concepts in this area is reactive distillation which is based on separating certain reactants from each other directly in the reactor (column) by distillation. Thus, undesired backward reactions can be suppressed (Sundmacher and Kienle, 2003). The subject of integrating also other separation processes into chemical reactors is discussed, for example, in a review (Krishna, 2002) and a more recently published book (Sundmacher, Kienle, and Seidel-Morgenstern, 2005).

There has long been interest in applying reactor principles which allow for an efficient use of energy (Problem 3) when developing new reaction processes. Recently developed elegant autothermal reactor concepts exploit dedicated heat transfer processes and the dynamics of periodically operated reactors (Eigenberger, Kolios, and Nieken, 2007; Silveston, 1998). Examples of new reactor types include the reversed flow reactor (Matros and Busimovic, 1996) and the loop reactor (Sheintuch and Nekhamkina, 2005).

One of the most difficult problems in chemical reaction engineering is to navigate in a reaction network efficiently in order to optimize the production of the desired target component (Problem 4). In this field again catalysis is a main tool. In recent years many new and highly selective catalysts have been developed, allowing an increase in the selectivity and yield with which many base chemicals, intermediates and fine chemicals can be produced (Ertl *et al.*, 2008). Complementarily there are permanent activities devoted to identifying the most suitable reactor types and applying the most beneficial operating conditions in order to achieve high selectivities and yields. In this important field new reactor types can be expected for the future.

One promising option considered when tackling Problem 4 and the subject of this book is to apply optimized dosing strategies using specific membrane reactors. Before introducing the basic principle of these reactors, the broader field of membrane reactors is briefly introduced in the next section.

1.2
Concepts of Membrane Reactors

The application of membranes which divide two specific parts of a reactor possesses the potential to improve in various ways the performance of chemical reactors compared to conventional reactor concepts. For this reason membrane reactors have long been the focus of intensive research. The state of the art regarding this rather broad field has been described in several reviews (Zaspalis and Burggraaf, 1991; Saracco *et al.*, 1999; Dittmeyer, Höllein, and Daub, 2001; Dixon, 2003; Seidel-Morgenstern, 2005). Comprehensive summaries were recently given by (Sanchez Marcano and Tsotsis, 2002; Dittmeyer and Caro, 2008). Modern developments were reported on a regular basis during the "*International Congresses on Catalysis in Membrane Reactors*" (ICCMR, 1994–2009).

Due to the availability of the mentioned extensive overviews and conference proceedings it is not the goal of this chapter to review the field again. To introduce the main principles suggested and partly already applied, just a short overview is given below.

Figure 1.1 illustrates schematically six membrane reactor concepts (I–VI) related to different problems which should be tackled using membranes within the reactor. For illustration, and because it is frequently the competing principle, at the top of the figure the classic tubular reactor is shown. This reactor possesses closed walls. Thus, the reactants are typically introduced together at the reactor inlet (co-feed mode). Often tubular reactors are filled with solid catalyst particles in order to increase the rates and selectivities. This classic fixed-bed or packed-bed reactor (PBR) is intensively studied and used widely (Eigenberger, 1997). It serves as a reference in several sections of this book.

Concept I: Retainment of homogeneous catalysts

The first membrane reactor concept shown in Figure 1.1 exploits the membrane to retain in the reactor soluble (homogeneous) catalysts. Thus, it allows for continuous operation without the need to separate and recycle the typically valuable catalysts. An introduction into the concept is given, for example, by (Cheyran and Mehaaia, 1986; Sanchez Marcano and Tsotsis, 2002). Successful application for various synthesis reactions are described, for example, by (Kragl and Dreisbach, 2002).

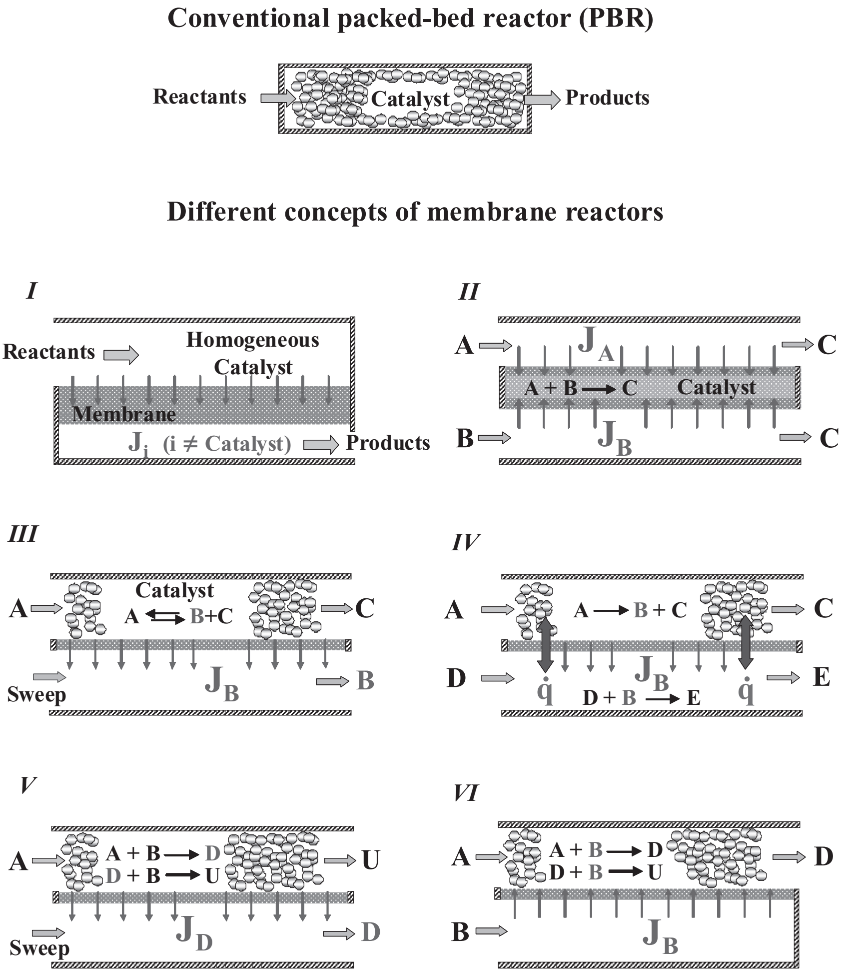

Figure 1.1 Illustration of the conventional packed bed reactor (PBR) and six membrane reactor concepts (I–VI). Concept I: catalyst retainment. Concept II: membrane as "contactor". Concept III: membrane as "extractor" (shift of equilibria). Concept IV: coupling of reactions. Concept V: membrane as "extractor" (removal of intermediates). Concept VI: "distributor" (reactant dosing).

Concept II: Contactor

Another interesting and promising membrane reactor principle is based on applying the membrane as an active "Contactor". The reactants are fed into the reactor from different sides and react within the membrane (Miachon *et al.*, 2003; Dittmeyer and Caro, 2008). There are significant efforts in order to exploit this principle for heterogeneously catalyzed gas/liquid reactions (three-phase membrane reactors) (Dittmeyer and Reif, 2003; Vospernik *et al.*, 2003).

Concept III: Extractor

A widely studied and rather well understood type of membrane reactors is the so-called "Extractor" which removes selectively from the reaction zone certain products via a membrane. As already recognized early (Pfefferie, 1966), this concept possesses the potential to enhance the conversion if the reactions are reversible. To remove the permeated products and to increase the driving force for the transport, additional sweep gases or solvents are needed to apply the "Extractor" principle. Several systematic studies were carried out (e.g., Itoh *et al.*, 1988; Ziaka *et al.*, 1993; Kikuchi, 1997; Schramm and Seidel-Morgenstern, 1999; Schäfer *et al.*, 2003). An evaluation of the potential considering also the additional sweep gas is given e.g. by (Seidel-Morgenstern, 2005).

Concept IV: Energetic coupling

Membranes can be also used to separate two reactor segments in which different reactions take place (Gryaznov, Smirnov, and Mischenko, 1974). The courses of these reactions are influenced when there is a selective transport of certain components which participate in both reactions (e.g., component B in the Figure 1.1). Reactive sweep gases might further improve the performance of the "Extractor" concept described above. If the two reactions are endothermal and exothermal an attractive thermal coupling can be realized (e.g., Gobina, Hou, and Hughes, 1995). In this case an additional heat flux over the membrane takes place which offers interesting degrees of freedom to optimize the reactor from an energetic point of view (Eigenberger, Kolios, and Nieken, 2007).

Concept V: Selectivity enhancement through withdrawal of a product

This concept resembles concept III. However, the component of interest that should be removed ("Extraction") via the membrane is an intermediate component generated in a network of reactions. This removal leads to the reduction or complete avoidance of undesired consecutive reactions and, thus, to enhanced selectivities with respect to this target component (Kölsch *et al.*, 2002; Dittmeyer and Caro, 2008). Unfortunately, the application of this elegant principle requires very selective membranes which are often not available for industrially relevant problems.

Concept VI: Selectivity enhancement through optimized reactant dosing (distributor)

The main focus of this book is to contribute to achieve higher selectivities and yields and thus tackling Problem 4 mentioned above. Hereby, an interesting and attractive approach is based on using membranes to dose (distribute) certain reactants into the reactor. Compared to conventional PBR operation different local concentrations and residence time characteristics can be established and exploited to enhance selectivities. Although the general idea has long been known and significant efforts have been undertaken to exploit the potential of the concept (e.g., Mallada, Menendez, and Santamaria, 2000; Al-Juaied, Lafarga, and Varma, 2001; references in Section 1.8), no industrial applications of such a "Distributor" type of membrane reactor have been reported. In implementing the concept, several degrees of freedom can be exploited. Some important questions considered in more or less detail in this book are:

- Which component should be dosed via the membrane and which should be introduced at the reactor inlet?
- Which kind of membrane and which separation mechanism should be exploited?
- To what extent does multi-stage dosing improve the performance compared to the application of a simple uniform dosing profile?
- Is a particulate catalyst (as used in the packed-bed membrane reactor, PBMR) more suitable than a thin catalytic layer on the membrane surface (as used in a catalytic membrane reactor, CMR)?
- What is the dynamic behavior of such a configuration?

Before discussing in more detail some reaction engineering aspects related to the selectivity problem, a short overview is given concerning the field of membrane materials and types.

1.3
Available Membranes

During the past decades a broad spectrum of different membrane types was developed. Extensive overviews are available (e.g., Bhave, 1991; Ohlrogge and Ebert, 2006; Peinemann and Pereira Nunes, 2007).

The two most suitable classification categories are related to: (a) the membrane materials and (b) the membrane permeabilities and selectivities.

Concerning the materials a distinction can be made between organic and inorganic membranes. Organic polymeric membranes can be synthesized with very specific properties using well developed concepts of macromolecular chemistry. Hereby, a large flexibility exists and a broad spectrum of materials can be made with properties adjusted to the specific separation problem. A drawback of organic membranes is their limited thermal stability. At higher temperatures only inorganic membranes can be applied. Also in this area there is a broad spectrum of membranes available based, for example, on ceramics, perovskites, metals, metal alloys and composites of these materials (e.g., Julbe, Farrusseng, and Guizard, 2001; Verweij, 2003).

Another classification distinguishes between dense and porous membranes. Whereas dense membranes offer typically high selectivities for certain components, they suffer from limited permeabilities. Overviews are given, for example, by (Dittmeyer, Höllein, and Daub, 2001) for metal membranes and by (Bouwmeester, 2003) for ion- and electron-conducting materials. The transport behavior is opposite when porous membranes are applied, allowing for higher fluxes but providing limited selectivities. Porous membranes are typically classified according to their pore size, defining the various types af membrane separation processes as, for example, microfiltration, ultrafiltration and nanofiltration (Li, 2008).

Besides pore size the chemistry of the membrane surface also plays an important role. Traditionally membranes are used to carry out transport and separation processes. In such applications they are chemically inert. Membranes might also possess certain surface properties which catalyze chemical reactions. Such catalytically active membranes are of particular interest for the "Contactor" type of membrane reactors. However, they might be applicable also in some of the other membrane reactor concepts depicted in Figure 1.1.

The quantitative description and prediction of component specific transport rates through dense and porous membranes has been studied intensively. Introductions into the transport theories available are given, for example, by (Mason and Malinauskas, 1983; Sahimi, 1995; Wesselingh and Krishna, 2000; Bird, Stewart, and Lightfoot, 2002). Specific problems of quantifying accurately transport rates are often related to the composite structure of the membranes of interest (Thomas *et al.*, 2001). The accurate prediction of permeabilities and separation factors is still a difficult task and the subject of further intensive research.

In general, the identification, provision and quantitative description of materials suitable to tackle a specific separation problem is still not a routine task.

There is a particular aspect related to membrane reactors which is addressed in Section 1.7. A successful operation requires a sufficient kinetic compatibility of the rates of the transport through the membranes and the rates of the reactions of interest.

Evaluating the general potential of membrane technology Burggraaf and Cot predicted already in 1996 that membrane reactors possess a significant and growing potential in particular for high-temperature reactions using inorganic membranes (Figure 1.2; Burggraaf and Cot, 1996).

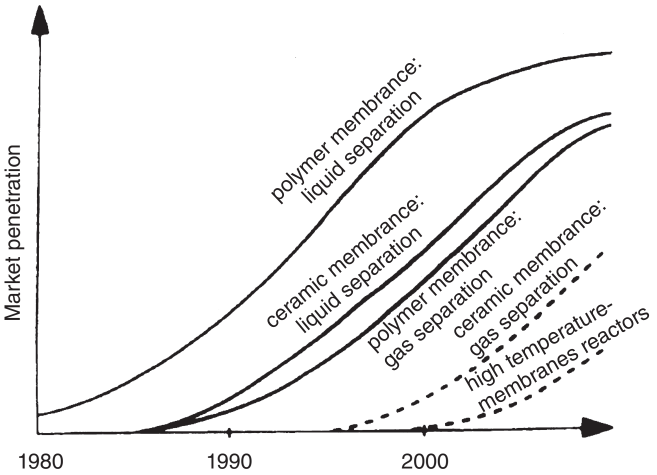

Figure 1.2 Quantitative scheme of expected market penetration as a function of time for different groups of membrane applications (reprinted from [Burggraaf and Cot, 1996], with permission).

1.4
Illustration of the Selectivity Problem

Impressive and frustrating examples characterizing the dilemma and importance of the selectivity problem introduced in Section 1.1 as Problem 4 were given for the industrially important class of partial oxidation reactions by (Haber, 1997; Hodnett, 2000). The latter author presented a large number of selectivity versus conversion plots for various hydrocarbon oxidations. An example is shown in Figure 1.3 for the partial oxidation of *n*-butane to maleic anhydride catalyzed by a vanadium phosphorus oxide (VPO) catalyst. In this plot the results of various studies reported in the literature are superimposed. Hereby, different reactor types and catalysts were applied. There is obviously a clear border which current technology cannot pass. For other reactions of this type which are applied in a large scale the "dream corner" (100% selectivity, 100% conversion) is even more remote. The problem described for oxidation reactions exists in a similar manner for the important class of selective hydrogenation reactions.

As mentioned above, selectivity improvements are the objective of intensive research in catalysis. Examples of successful new catalysts were summarized by (Ertl *et al.*, 2008). However, there are still many "dream reactions" for which satisfactory catalysts are not yet available. The alternative way to improve selectivities is to develop better reactors using currently available catalysts. In this case it is particularly important to understand the relation between local concentrations and temperatures and the selectivity–conversion behavior. To follow this second route is the focus of this book.

The next section summarizes a few basics of chemical reaction engineering which are important for understanding how membrane reactors of the distributor type can contribute to achieve improvements in selectivities and yields.

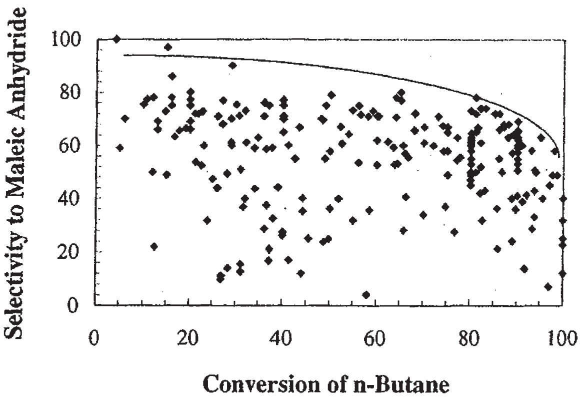

Figure 1.3 Multiple selectivity–conversion plot for *n*-butane selective oxidation to maleic anhydride over a range of catalysts and in a variety of reaction conditions (reprinted from Hodnett, 2000, with permission).

1.5
Reaction Rate, Conversion, Selectivity and Yield

In order to evaluate the potential of membrane reactors in general and "Distributors" in particular, the classic approaches of chemical reaction engineering are available. Basic aspects of analyzing and optimizing various types of chemical reactors have been discussed extensively in standard textbooks of the field (e.g., Levenspiel, 1999; Fogler, 1999). Below is given a selected summary introducing important quantities and performance criteria.

1.5.1
Reaction Rates

The reaction rates are the key information required to quantify chemical reactions and to describe the performance of chemical reactors.

The rate of a single reaction in which N components are involved is defined as:

$$r_{\text{Scale}} = \frac{1}{\text{Scale}} \frac{1}{\nu_i} \frac{dn_i}{dt}\bigg|_{\text{Reaction}} \qquad i = 1, N \tag{1.1}$$

The use of the stoichiometric coefficient ν_i guarantees that the reaction rate does not depend on the component i considered. There are several possibilities regarding the selection of an appropriate scale. For reactions taking place in a homogeneous phase, frequently the reaction volume V_{R} is used leading to a reaction rate which has the dimension [mol/m^3 s]. In heterogeneous catalysis often the mass or surface area of the catalyst, M_{Cat} or A_{Cat}, are more useful scaling quantities leading to reaction rates in [mol/kg s] or [mol/m^2 s]. Obviously, it is necessary to use r_{Scale} and the chosen scaling quantity consistently. If different scales are of relevance, for example, "a" and "b", it must hold:

$$\text{Scale}_{\text{a}} \text{r}_{\text{Scale}_{\text{a}}} = \text{Scale}_{\text{b}} \text{r}_{\text{Scale}_{\text{b}}} \tag{1.2}$$

To illustrate the relevance of the reaction rate, in this chapter the reactor volume is selected for scaling. For the sake of brevity no scale index is used. Please note that other chapters of this book also use mass-related reaction rates.

If the reactor volume V_{R} is assumed to be constant, the reaction rate r can be expressed as:

$$r = \frac{1}{\nu_i} \frac{d\tilde{c}_i}{dt} \qquad i = 1, N \tag{1.3}$$

where $\tilde{c}_i$ is the molar concentration of component i defined as:

$$\tilde{c}_i = \frac{n_i}{V_R} \qquad i = 1, N \tag{1.4}$$

or for open systems with the (also constant) volumetric flow rate $\dot{V}$ as:

$$\tilde{c}_i = \frac{\dot{n}_i}{\dot{V}} \quad i = 1, N \tag{1.5}$$

Reaction rates depend on temperature and the molar concentrations (Levenspiel, 1999), that is:

$$r = r(T, \tilde{c}_1, \tilde{c}_2, \ldots, \tilde{c}_N) \tag{1.6}$$

If only one reaction occurs, knowledge regarding the concentration change of a single key component is sufficient to describe all other concentration changes.

1.5.2
Conversion

If a reactant A is chosen as the key component, its conversion can be defined as:

$$X_{\mathrm{A}} = \frac{n_{\mathrm{A}}^0 - n_{\mathrm{A}}}{n_{\mathrm{A}}^0} \tag{1.7}$$

or for constant volumes:

$$X_{\mathrm{A}} = \frac{\tilde{c}_{\mathrm{A}}^0 - \tilde{c}_{\mathrm{A}}}{\tilde{c}_{\mathrm{A}}^0} \tag{1.8}$$

The mole numbers n_{A}^0 or concentrations $\tilde{c}_{\mathrm{A}}^0$ stand here for the initial or inlet states. The conversion can be considered as a dimensionless concentration. Using this quantity Equation 1.6 can be reformulated:

$$r = r\left(T, \tilde{c}_{\mathrm{A}}^0, X_{\mathrm{A}}\right) \tag{1.9}$$

The temperature dependence of the reaction rate, $r(T)$, can be accurately described using the well known Arrhenius equation (Levenspiel, 1999).

Regarding the conversion (i.e., concentration) dependence, r can be split into a constant contribution r^0 (related to the initial or inlet state) and a conversion-dependent function $f(X_{\mathrm{A}})$ describing the rate law valid for the specific reaction considered:

$$r = r^0\left(\tilde{c}_{\mathrm{A}}^0\right) f\left(X_{\mathrm{A}}\right) \tag{1.10}$$

1.5.3
Mass Balance of a Plug Flow Tubular Reactor

One of the simplest models used to describe the performance of tubular reactors is the well known isothermal one-dimensional plug flow tubular reactor (PFTR) model. The mass balance of this model is for: (a) steady-state conditions, (b) a network of M simultaneously proceeding reactions and (c) a constant volumetric flow rate $\dot{V}$ (Froment and Bischoff, 1979; Levenspiel, 1999):

$$\frac{d\tilde{c}_i}{dz} = \frac{A_{\mathrm{R}}}{\dot{V}} \sum_{j=1}^{M} \nu_{ij} r_j \quad i = 1, N \tag{1.11}$$

The ν_{ij} in Equation 1.11 are the elements of the stoichiometric matrix, A_R stands for the cross-sectional area of the tube and z is the axial coordinate.

With the residence time τ in a reactor section of length z:

$$\tau = \frac{A_R}{\dot{V}} z \tag{1.12}$$

the mass balance of the PFTR can be expressed also in the following manner:

$$\frac{d\tilde{c}_i}{d\tau} = \sum_{j=1}^{M} \nu_{ij} r_j \quad i = 1, N \tag{1.13}$$

The systems of ordinary differential equations (1.11) or (1.13) can be integrated numerically with the initial conditions $\tilde{c}_i^0 = \tilde{c}_i(z = 0 \; or \; \tau = 0)$ and the specific rate laws.

If only one reaction needs to be considered ($M = 1$) and the conversion of component A is chosen to be the state variable of interest, the mass balance of the PFTR can be also expressed as follows:

$$\frac{dX_A}{d\tau} = \frac{(-\nu_A) r^0 f(X_A)}{\tilde{c}_A^0} \tag{1.14}$$

Integration from 0 to the residence time corresponding to the reactor length L_R, that is, $\tau(L_R)$ and from 0 to $X_A(\tau)$ leads to the following dimensionless mass balance of the PFTR:

$$\mathrm{Da} = \int_0^{X_A(\tau)} \frac{dX_A}{f(X_A)} \tag{1.15}$$

In this equation Da is the Damköhler number (Levenspiel, 1999):

$$\mathrm{Da} = \frac{(-\nu_A) r^0}{\tilde{c}_A^0} \tau \tag{1.16}$$

which represents the ratio of the characteristic times for convection and reaction.

The dimensionless mass balance equation (1.15) can be solved analytically for various simple rate laws $f(X_A)$ providing instructive $X_A(\mathrm{Da})$ profiles.

If for example the rate of a reaction A → Products can be described by a simple first-order kinetic expression:

$$r = k\tilde{c}_A \tag{1.17}$$

the dimensionless balance provides with $r^0 = k\tilde{c}_A^0$ and $f(X_A) = 1 - X_A$:

$$X_A = 1 - e^{-\mathrm{Da}} \tag{1.18}$$

In contrast, for a second-order reaction with the rate expression:

$$r = k\tilde{c}_A^2 \tag{1.19}$$

holds:

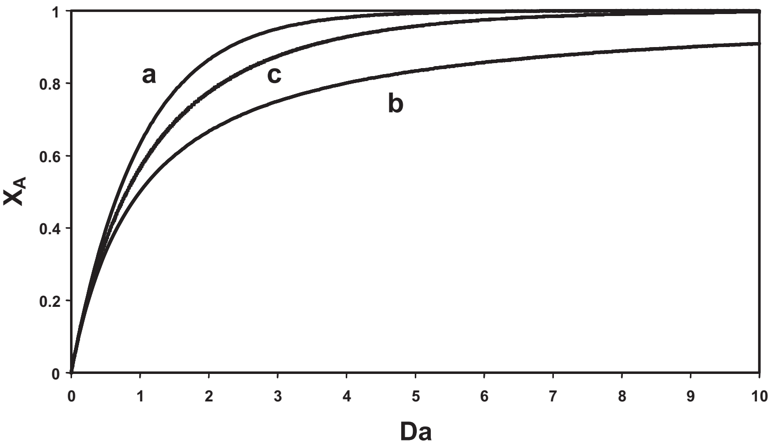

Figure 1.4 Dependence of conversion on Damköhler number for: (a) a first-order reaction (1.18), (b) a second-order reaction (1.20) and (c) a second-order reaction with two reactants and a non-stoichiometric feed composition (Equations 1.21 and 1.22, here for $\lambda = 0.5$).

$$X_A = \frac{\text{Da}}{1+\text{Da}} \tag{1.20}$$

In the case of a bimolecular reaction of the type $\nu_A A + \nu_B B \rightarrow$ Products the composition of the feed mixture is an important free parameter. This can be conveniently expressed using a stoichiometric feed ratio λ defined as follows:

$$\lambda = \frac{\nu_B \tilde{c}_A^0}{\nu_A \tilde{c}_B^0} \tag{1.21}$$

When component B is introduced in excess, that is, when $0 < \lambda < 1$, the solution of the mass balance provides:

$$X_A = \frac{e^{\text{Da}(1-\lambda)} - 1}{e^{\text{Da}(1-\lambda)} - \lambda} \tag{1.22}$$

The three different functions described by Equations 1.18, 1.20 and 1.22 are illustrated in Figure 1.4. The curves shown reveal the following two well known and important facts: (a) higher reaction orders require larger Da numbers (i.e., larger residence times) in order to reach the same conversion and (b) an excess of a reactant increases conversion of the other reactant.

1.5.4
Selectivity and Yield

In general, several reactions proceed simultaneously in a reactor. Thus, the selectivity and yield with respect to a certain desired target component D achievable in networks of parallel and series reactions are essential quantities.

The integral selectivity with respect to the desired component D, S_D, is related to the corresponding consumption of the reactant A. Considering the molar fluxes of the components at the inlet and outlet of a continuously operated reactor, S_D is defined as follows:

$$S_D = \frac{\dot{n}_D}{(\dot{n}_A^0 - \dot{n}_A)} \frac{(-\nu_A)}{\nu_D} \tag{1.23}$$

Of even more practical relevance is the yield of component D, Y_D, which is:

$$Y_D = \frac{\dot{n}_D}{\dot{n}_A^0} \frac{(-\nu_A)}{\nu_D} \tag{1.24}$$

Obviously, for the yield holds:

$$Y_D = S_D X_A \tag{1.25}$$

Let us consider a desired "reaction D" leading to the target product D:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D} \tag{1.26}$$

and an undesired consecutive "reaction U" leading to an undesired product U:

$$\mathrm{D} + \mathrm{B} \rightarrow \mathrm{U} \tag{1.27}$$

The rates of these two reactions could be, for example, described by the following power law kinetics:

$$r_D = k_D \quad \tilde{c}_A^{\alpha} \quad \tilde{c}_B^{\beta_1} \tag{1.28}$$

$$r_U = k_U \quad \tilde{c}_D^{\delta} \quad \tilde{c}_B^{\beta_2} \tag{1.29}$$

The selectivity and the yield with respect to D depend strongly on the values of the two reaction rate constants k_D und k_U and on the reaction orders α, β_1, β_2, δ. Illustrative results assuming that all reaction orders are unity were obtained solving numerically the mass balance equations of the PFTR model (1.13) for three different ratios k_D/k_U. The courses of the $S_D(X_A)$ and $Y_D(X_A)$ curves shown in Figure 1.5 reveal the strong impact of the reaction rates. Obviously, it is very desirable to operate in the upper right ("dream") corners of these plots where all performance criteria (conversion, selectivity and yield) are unity. Obviously, this corner is closer when k_D/k_U is large.

1.6
Distributed Dosing in Packed-Bed and Membrane Reactors

In networks of parallel-series reactions optimal local reactant concentrations are essential for a high selectivity towards a certain target product. It is well known that it is advantageous to avoid back-mixing when undesired consecutive reactions can occur (e.g., Levenspiel, 1999; Fogler, 1999). This is one of the main reasons why partial hydrogenations or oxidations are performed preferentially in tubular

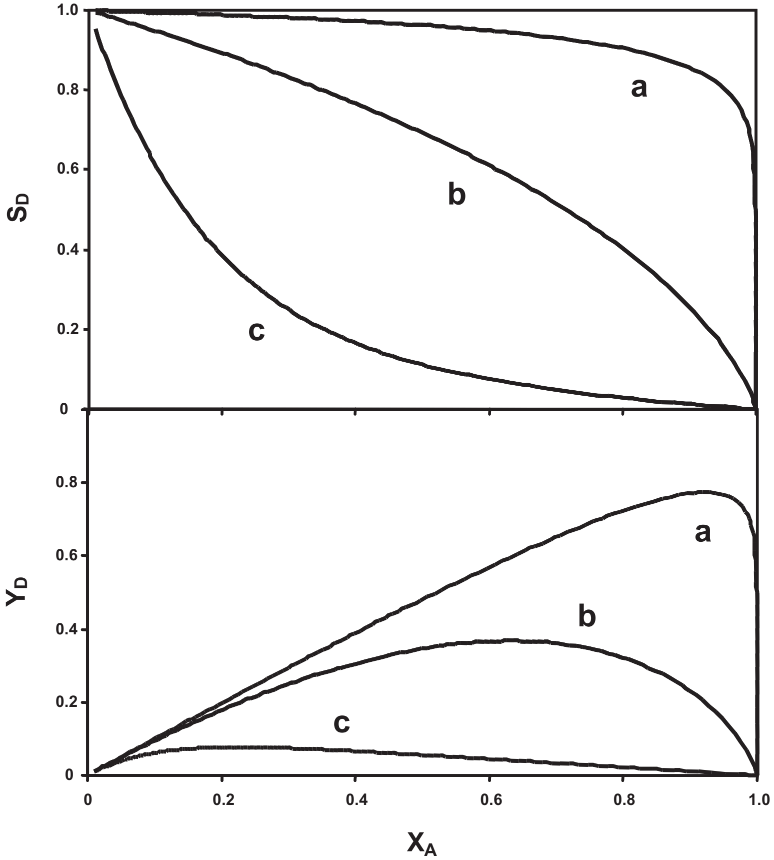

Figure 1.5 Selectivity S_D and yield Y_D as a function of conversion X_A for the two consecutive reactions $A + B \rightarrow D$ and $D + B \rightarrow U$ calculated with the PFTR model (1.11), fixing the residence time and varying the feed composition in a wide range. The reaction rates were described with Equations 1.28 and 1.29 assuming that all reaction orders are unity. Three different ratios of the rate constants of the desired and the undesired reaction were considered: (a) $k_D/k_U = 10$, (b) $k_D/k_U = 1$, (c) $k_D/k_U = 0.1$.

reactors. All reactants enter typically such tubular reactors together at the reactor inlet (co-feed mode, Mode 1 in Figure 1.6). In order to influence the reaction rates along the reactor length, essentially the temperature remains as the parameter that could be influenced. However, the realization of a defined temperature modulation in a tubular reactor is not trivial (Edgar and Himmelblau, 1989). An alternative and attractive possibility, also capable to influence the course of complex reactions in tubular reactors, is to abandon the co-feed mode and to install more complex dosing regimes. It is relatively simple to add one or several of the reactants to tubular reactors in a locally distributed manner. This approach obviously offers a large variety of options differing mainly in the positions at which the components

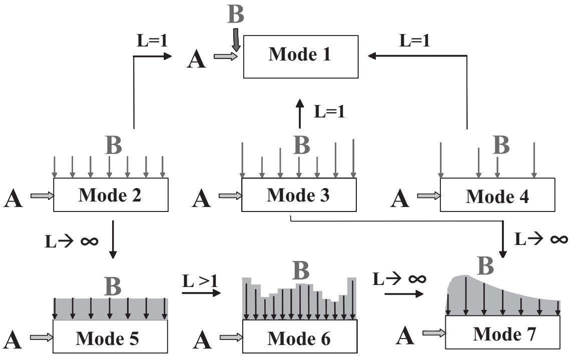

Figure 1.6 Illustration of possible dosing concepts for tubular reactors: conventional reactor (co-feed, Mode 1), possibilities of discrete dosing (Modes 2, 3, 4), possibilities of continuous dosing (Modes 5, 6, 7). *L* is the number of segments or stages.

are dosed. Figure 1.6 illustrates several possible scenarios differing from the conventional feeding strategy (Mode 1).

In the top row are depicted three scenarios of discrete dosing (Modes 2, 3, 4) differing in the positions and amounts of introducing a reactant B along the reactor length. If the number of discrete dosing points L is reduced to one the conventional reactor principle results. In the lower row of Figure 1.6 are illustrated schematically three concepts of dosing continuously over the reactor wall. These concepts are obviously connected with the membrane reactor Concept VI shown in Figure 1.1. Uniform dosing over one reactor segment (Mode 5), stage-wise segmented dosing (Mode 6) and the implementation of a fully continuous dosing profile (Mode 7) are possible options. The larger the number of segments L the more the concepts converge into the continuous dosing profile case (Mode 7).

1.6.1
Adjusting Local Concentrations to Enhance Selectivities

The different dosing concepts illustrated in Figure 1.6 provide different outlet compositions and, thus, performance criteria. To quantify and compare them it is instructive to introduce differential local selectivity with respect to a specific desired product D, $S_{\mathrm{D}}^{\mathrm{diff}}$, which depends on the local concentrations. Assuming that a valuable reactant A is converted the local selectivity $S_{\mathrm{D}}^{\mathrm{diff}}$ can be expressed as a function of the corresponding reaction rates of all M reactions occurring in the reaction network as follows:

$$S_{\mathrm{D}}^{\mathrm{diff}} = \frac{\sum_{j=1}^{M} \nu_{\mathrm{D},j} \cdot r_j}{\sum_{j=1}^{M} (-\nu_{\mathrm{A},j}) \cdot r_j} \tag{1.30}$$

To evaluate typical trends it is again instructive to consider the simple reaction scheme of two consecutive reactions introduced above (1.26 and 1.27) and the power law rate expressions given by Equations 1.28 and 1.29. In such a case for the differential selectivity with respect to D follows:

$$S_{\mathrm{D}}^{\mathrm{diff}} = \frac{r_{\mathrm{D}} - r_{\mathrm{U}}}{r_{\mathrm{D}}} = 1 - \frac{k_{\mathrm{U}}(T)\tilde{c}_{\mathrm{D}}^{\delta}}{k_{\mathrm{D}}(T)\tilde{c}_{\mathrm{A}}^{\alpha}}\tilde{c}_{\mathrm{B}}^{\beta_2-\beta_1} \tag{1.31}$$

Equation 1.31 clearly reveals that for this reaction scheme and the kinetics assumed an improved differential selectivity $S_{\mathrm{D}}^{\mathrm{diff}}$ can be achieved when:

- The reactions take please at a temperature which minimizes $k_{\mathrm{U}}/k_{\mathrm{D}}$,
- The concentration D is kept low (favoring a removal of D, for example, with a membrane reactor of the extractor type shown in Figure 1.1 as Concept V),
- The concentration of A is kept high (i.e., conversion should be restricted and back-mixing avoided; the former fact leading to concepts with a recycle of A, the latter fact favoring tubular reactors compared to stirred tanks),
- For $\beta_2 < \beta_1$ a high concentration of B is advantageous, which favors a concentrated feeding of this reactant at the reactor inlet,
- For $\beta_2 > \beta_1$ a low concentration of B is advantageous, which can be realized by a distributed feeding of this reactant.

Since these trends are specific for the reaction scheme and the rate equations considered no generalization is possible. However, a detailed inspection of the specific differential selectivities allows drawing similar conclusions for other cases.

Of special relevance for the example of partial oxidation reactions of hydrocarbons and for the chapters of this book is the following fact. Typically desired oxidation reactions leading to the intermediate products of interest possess lower reaction orders with respect to oxygen compared to the undesired total oxidation reactions leading to carbon dioxide and water (Mezaki and Inoue, 1991). Considering Equation 1.31 and the final conclusion listed above leads to the hypothesis that a low oxygen concentration achievable by implementing a spatial distribution can be beneficial for the selectivity with respect to a target component. Such a regime can be realized by the distributor type of membrane reactor shown in Figure 1.1 as Concept VI.

1.6.2
Optimization of Dosing Profiles

Knowing the structure of the reaction network of interest and the concrete concentration dependences of the reaction rates allows determining specific dosing profiles which are optimal for a certain reactor configuration. Only for a limited number of cases characterized by a small number of rate expressions and simple reactor models can analytical results be generated (Hamel *et al.*, 2003; Thomas, Pushpavanam, and Seidel-Morgenstern, 2004).

Using a modified PFTR model the different dosing modes illustrated in Figure 1.6 were analyzed. Mode 1 required just the direct application of Equation 1.11 with the boundary condition describing the co-feed mode of components A and B. Modes 2, 3 and 4 can be simulated using Equation 1.11 in a stagewise manner applying for each segment the boundary conditions corresponding to the specific discrete dosing approach and the series connection of the segments. To describe dosing over the reactor walls (Modes 5, 6, 7) the mass balance equation of the PFTR has to be extended by an additional transport term as follows:

$$\frac{d\tilde{c}_i}{dz} = \frac{A_R}{\dot{V}} \sum_{j=1}^{M} \nu_{ij} r_j + \frac{P_R}{\dot{V}} J_i \quad i = 1, N \tag{1.32}$$

In this equation P_R is the perimeter of the tube and the J_i are the molar flux densities of the transport of component i through the reactor wall. Hereby, below-specific uniform dosing profiles (constant J_i) were assumed for each reactor segment.

To illustrate the principle and potential of distributed dosing selected results of a case study are summarized. The following three reactions of a parallel-consecutive reaction scheme were considered, converting the two reactants A and B into a desired product D and an undesired product U:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D} \tag{1.33}$$

$$\mathrm{A} + 2\mathrm{B} \rightarrow \mathrm{U} \tag{1.34}$$

$$\mathrm{D} + \mathrm{B} \rightarrow \mathrm{U} \tag{1.35}$$

The rates of these three reactions were described by the following power law kinetics:

$$r_D = k_D \quad \tilde{c}_A^{\alpha_D} \quad \tilde{c}_B^{\beta_D} \tag{1.36}$$

$$r_{U1} = k_{U1} \quad \tilde{c}_A^{\alpha_{U1}} \quad \tilde{c}_B^{\beta_{U1}} \tag{1.37}$$

$$r_{U2} = k_{U2} \quad \tilde{c}_D^{\alpha_{U2}} \quad \tilde{c}_B^{\beta_{U2}} \tag{1.38}$$

The reactor model given with Equation 1.32 was solved numerically for selected parameters of these rate expressions. With a sequential quadratic programming (SQP) optimization algorithm (Press *et al.*, 1992) the optimal amounts of component B that should be dosed were determined with the selected objective of maximizing the molar fraction of component D at the reactor outlet. The discrete dosing Mode 3 assuming equidistant feeding positions and the continuous dosing Mode 6 were compared assuming segments of identical length. In a series of optimizations in both cases the numbers of segments L were fixed to the following three values: 1, 3 or 10. Hereby the results of Mode 3 for $L = 1$ correspond to the conventional co-feed fixed-bed reactor (Mode 1). The specific degrees of freedom specified were the L molar flows of component B dosed, $\dot{n}_D^{\mathrm{dosed}}$, at the inlet of each segment (Mode 3) or over the segment wall (Mode 6, calculated from the optimal J_D and the wall area).

Below for the purpose of illustration, selected results are presented in Figures 1.7 and 1.8. The calculations were done assuming that the reaction orders are $\alpha_D = \alpha_{U1} = \alpha_{U2} = \beta_D = 1$ and $\beta_{U1} = \beta_{U2} = 2$. This implies that in the undesired reactions (1.37) and (1.38) the order with respect to D is higher then in the desired reaction (1.36). The rate constants k_j were assumed to be identical. A stream of 1 mol/s of pure A was introduced at the inlet of the first segment of a reactor possessing an overall volume $V_R = 0.01\,\mathrm{m}^3$. The figures show over the reduced reactor length the dosed amounts, the total flow rates, the local molar fractions of the dosed component B and those of the other three components, including the optimized molar fraction of D, x_D ($x_i = \dot{n}_i/\dot{n}_{\mathrm{tot}}$).

The results obtained for this specific case provide the following conclusions:

- For both modes decreasing dosing profiles are found to be optimal, that is, the largest amounts are dosed in the segments close to the reactor inlet and lower amounts are dosed into the following segments. Some B is also dosed into the last segment.
- There is for both modes an increasing amount of D found at the reactor outlet for increasing segment numbers L.
- The diluted dosing of B leads in comparison to the conventional co-feed mode (discrete dosing, $L = 1$, Mode 1) to larger molar amounts of D.
- The continuous dosing (Mode 6, e.g., applied in a membrane reactor) outperforms for the same segment numbers the discrete dosing (Mode 3) as indicated by larger x_D at the reactor outlet.
- For $L = 1$ there is a significant performance increase of Mode 6 compared to the conventional co-feed operation.
- Already for $L = 3$ the potential of Mode 6 seems to be reached. Further segmentation does not lead to significant further enhancement in x_D.

The results of more systematic theoretical studies explaining in more detail the significance of the reaction orders regarding the selection of the component that should be dosed and regarding the shapes of suitable dosing profiles are available (Lu *et al.*, 1997a, 1997b, 1997c; Hamel *et al.*, 2003; Thomas, Pushpavanam, and Seidel-Morgenstern, 2004).

Examples for the application of the above theoretical considerations in concrete case studies are given in the next chapters of this book. As per (Kuerten *et al.*, 2004), limits of the above-used simplified one-dimensional isothermal membrane reactor model are also discussed.

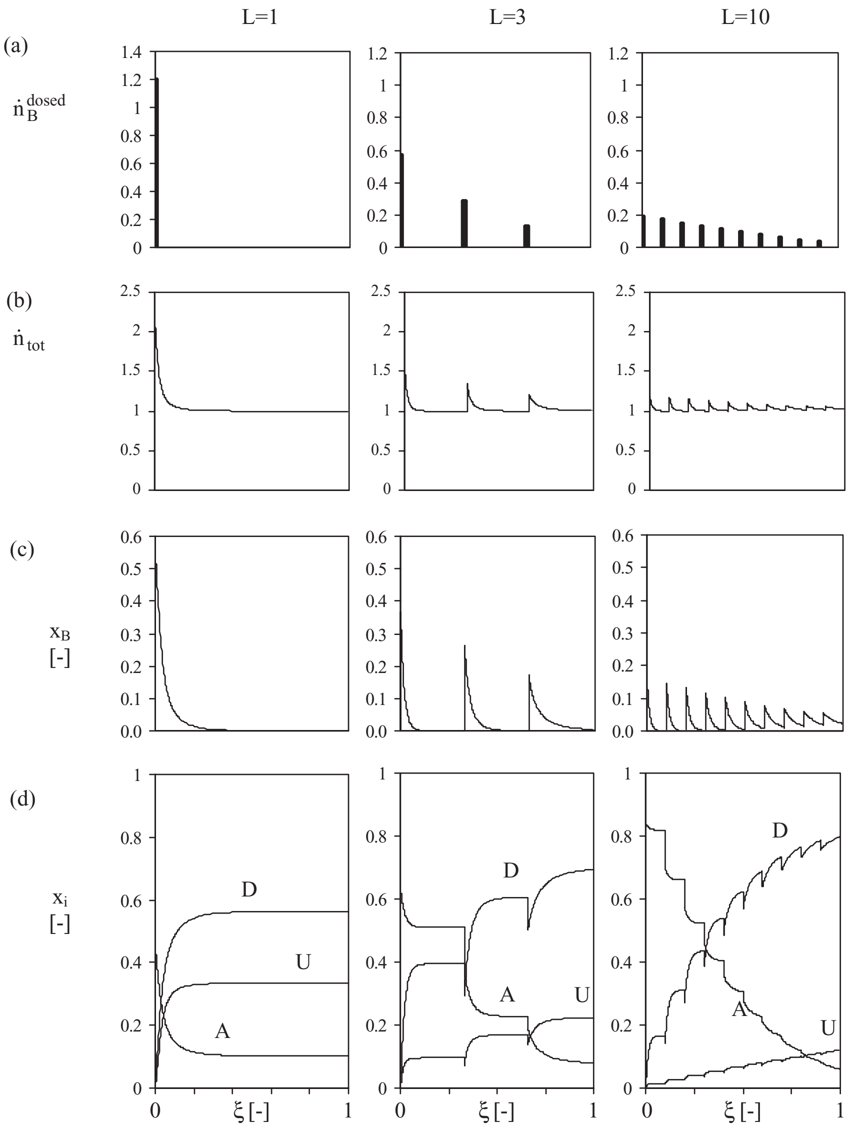

Figure 1.7 Optimized dosed amounts of B, local total molar fluxes and local molar fractions over the reduced reactor length for the discrete dosing Mode 3 and different segment numbers. Kinetic parameters: $\alpha_D = \alpha_{U1} = \alpha_{U2} = \beta_D = 1$, $\beta_{U1} = \beta_{U2} = 2$, $k_D = k_{U2} = k_{U1} = 10^4\,\text{mol}/(\text{s}\cdot\text{m}^3)$.

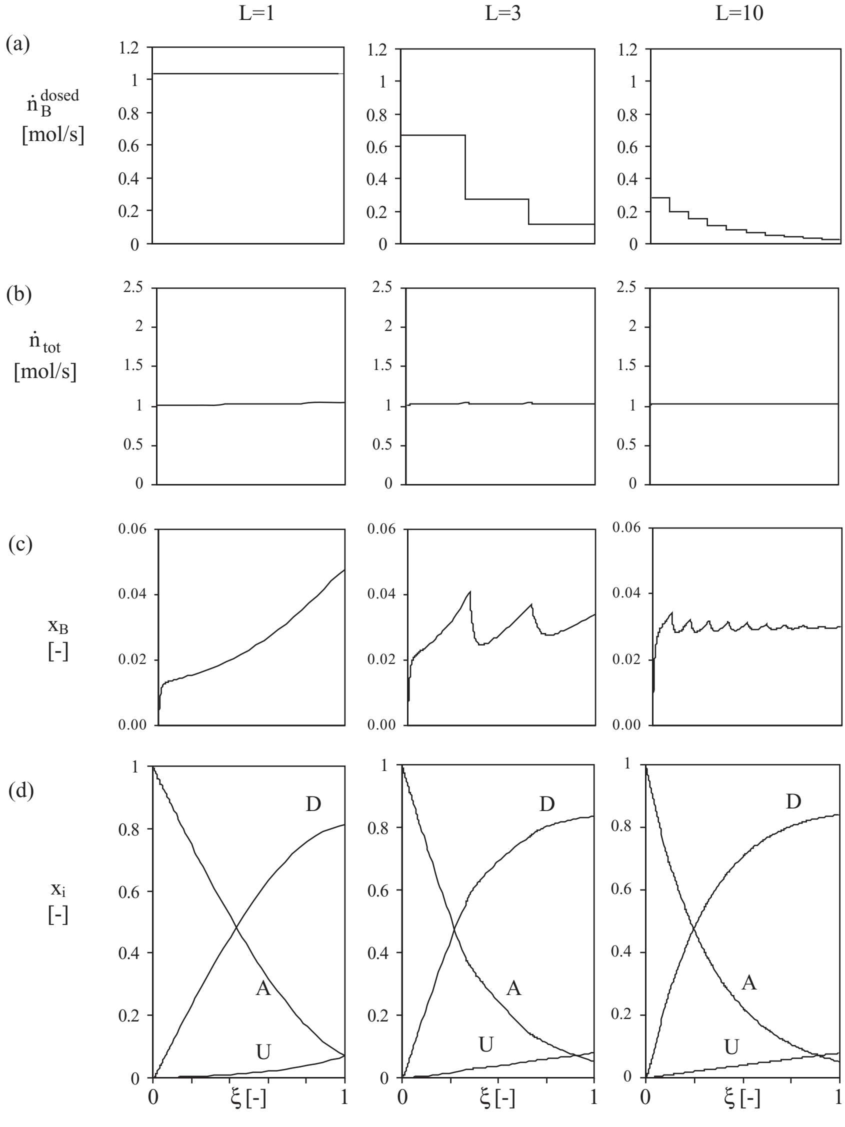

Figure 1.8 Optimized dosed amounts of B, local total molar fluxes and local molar fractions over the reduced reactor length for the continuous dosing Mode 6 and different segment numbers. Kinetic parameters: $\alpha_D = \alpha_{U1} = \alpha_{U2} = \beta_D = 1$, $\beta_{U1} = \beta_{U2} = 2$, $k_D = k_{U2} = k_{U1} = 10^4\,\text{mol}/(\text{s}\cdot\text{m}^3)$.

1.7
Kinetic Compatibility in Membrane Reactors

In order to achieve significant effects of membranes introduced into a reactor compared to conventional reactor operation, there should be certain compatibility between the fluxes that pass the membrane and the amounts consumed or produced during the chemical reactions. The specific amounts related to the simultaneous occurrence of *M* chemical reactions can be expressed based on Equation 1.1 as follows:

$$\left.\frac{dn_i}{dt}\right|_{\text{Reaction}} = \text{Scale}\sum_{j=1}^{M} \nu_{ij} r_{\text{Scale},j} \quad i = 1, N \tag{1.39}$$

As mentioned before different scales might be appropriate to quantify the reaction rates. Regarding the transport through membranes usually the membrane area A_{M} is the appropriate scaling parameter. The molar flux of a component *i* through a membrane can be expressed as:

$$\dot{n}_i|_{\text{Membrane}} = A_M \ J_i \quad i = 1, N \tag{1.40}$$

In the above J_i designates, as in Equation 1.32, the molar flux density of component *i*.

Provided there is information available regarding the amounts transformed by the reactions and the amounts that could be transported through the membranes (based on Equations 1.39 and 1.40, respectively), several important questions could be answered in early development stages as, for example,: “how much membrane area must be provided per scale of the reaction zone?” and “is a more detailed investigation of coupling reaction and mass transfer through a specific membrane justified?”.

Following this approach recently a useful estimation was given by (van de Graaf *et al.*, 1999). Regarding the productivity of reactions, achievable space time yields (STY) of currently operated catalytic reactors were considered. Concerning this quantity currently the following “window of reality” holds:

$$\text{STY} = \frac{\dot{n}_{\text{Prod}}}{V_R} \approx 1 - 10 \quad \frac{\text{mol}}{\text{m}^3\text{s}} \tag{1.41}$$

The achievable fluxes through membranes, *J*, were designated by (van de Graaf *et al.*, 1999) as area time yields (ATY, in mol/m^{2}s). Figure 1.9 provides an estimation of the current state regarding the possibility of matching the two processes. For the wide range of considered membranes, the required ratios of membrane areas to reactor volumes ($A_{\text{M}}/V_{\text{R}}$) are between 10 and 100 m^{-1}. These values allow estimating that the diameter of applicable cylindrical tubular reactors should be in a range between 0.04 and 0.4 m. This appears to be a reasonable range for industrial applications indicating that a matching of the two processes under consideration is achievable with currently available membranes.

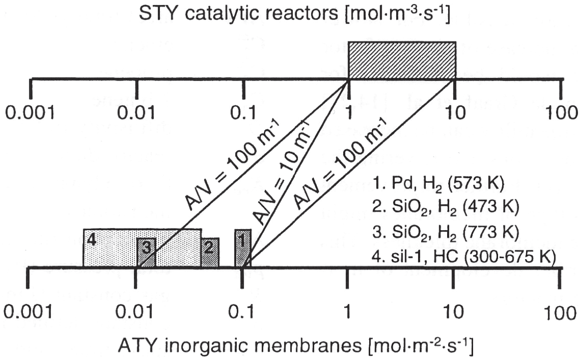

Figure 1.9 Comparison of the space time yield (STY) of catalytic reactors with the area time yield (ATY) of several inorganic membranes (reprinted from [van de Graaf *et al.*, 1999], with permission).

1.8
Current Status of Membrane Reactors of the Distributor Type

There are several profound theoretical and experimental studies at the laboratory scale available which focus on the application of various configurations of membrane reactors as a reactant distributor in order to improve selectivity–conversion performances.

In particular several industrially relevant partial oxidations were investigated. Examples include the oxidative coupling of methane (Coronas, Menedez, and Santamaria, 1994), the oxidative dehydrogenation of propane (Alonso *et al.*, 1999), butane (Tellez, Menedez, and Santamaria, 1997) and methanol (Diakov and Varma, 2003, 2004), the epoxidation of ethylene (Al-Juaied, Lafarga, and Varma, 2001) and the oxidation of butane to maleic anhydride (Mallada, Menedez, and Santamaria, 2000). Specific aspects of membrane reactors related to carrying out the oxidative dehydrogenation of ethane to ethylene, which are described and studied in detail in this book, were investigated by (Coronas, Menedez, and Santamaria, 1995; Tonkovich *et al.*, 1996).

There appears to be potential in using membrane reactors of the distributor type also for other types of reaction networks. Another promising field can be for example selective hydrogenations. The hydrogenation of acrolein to allyl alcohol was studied by (Hamel *et al.*, 2005).

All the studies mentioned were done exclusively at the laboratory or pilot scale. They focused on high-temperature reactions and applied different types of ceramic membranes. Currently there are no industrial applications applying a membrane reactor of the distributor type on a larger scale.

To further promote the promising concept systematic studies are required quantifying both the reaction and transport processes and describing in more detail the processes occurring in such membrane reactors. Hereby, various options applicable with respect to the types of membranes and the reactor principles should be considered and compared. This book contains various contributions to the mentioned problems.

The following chapter summarizes theoretical concepts required to model membrane reactors.

Notation used in this Chapter

A_{Cat}	m^2	catalyst surface area
A_M	m^2	membrane surface area
A_R	m^2	cross section area of a tubular reactor
Y_i	%	yield with respect to component i
J_i	$mol \cdot s^{-1} \cdot m^{-2}$	molar flux density of component i
k_j	$mol \cdot s^{-1} \cdot m^{-3}$	reaction rate constant
L		number of reactor segments
L_R	m	length of a tubular reactor or reactor segment
M	–	number of reactions
M_{Cat}	kg	catalyst mass
$\dot{n}$	mol/s	molar flux
P_R	m	perimeter of a tubular reactor
r	$mol \cdot s^{-1} \cdot m^{-3}$	rate of reaction
S_i	%	integral selectivity with respect to component i
S_i^{diff}	%	differential selectivity with respect to component i
T	K	temperature
V_R	m^3	reactor volume
$\dot{V}$	mol/s	volumetric flowrate
X_i	%	conversion of reactant i
x_i	–	molar fraction of component i
z	m	axial coordinate of tube

Greek Symbols

α	–	reaction order
β	–	reaction order
δ	–	reaction order
λ	–	stoichiometric feed ratio
ν	–	stoichiometric coefficient
ξ	–	non-dimensional axial reactor length, $\xi = z/L_R$
τ	s	residence time

Superscripts and Subscripts

i	component
j	reaction

tot	total
0	initial or inlet state

Abbreviations

CMR	Catalytic membrane reactor
PBR	Packed bed reactor
PBMR	Packed bed membrane reactor

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