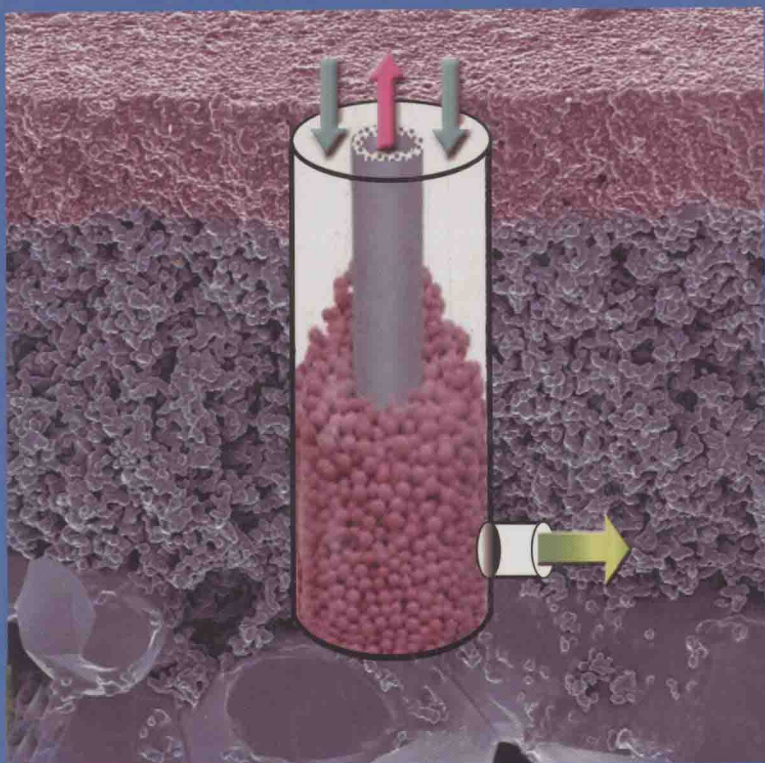


José G. Sanchez Marcano and
Theodore T. Tsotsis

Catalytic Membranes and Membrane Reactors



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 WILEY-VCH

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Dedication

To Betty, Christine, Laura, Benjamin and Anaïs, for their love and ongoing support

JSM/TTT

Preface

The study of catalytic membranes and membrane reactor processes is a multidisciplinary activity, which in recent years has attracted the attention of scientists and engineers in a number of disciplines, including materials science, chemistry and biology, and chemical and biochemical engineering. For a process to qualify as a membrane reactor system, it must not simply combine a membrane separation unit with a chemical reactor; it must integrally couple them in such a fashion that a synergy is created between the two units, potentially resulting in enhanced performance in terms of separation, selectivity and yield. Often the membrane separation module and reactor are physically combined into the same unit. Such combination promises to result in a process, which is more compact and less capital intensive, and with potential substantial savings in processing costs. During the last twenty years this technical concept has attracted substantial worldwide research and process development efforts. This is the first book, we are aware of, that is completely dedicated to the topic of membrane reactors. It aims and hopes to introduce the topic and serve as reference for a wide audience of scientists and engineers.

The book is divided into six chapters, each covering a different aspect of the topic. Chapter 1 provides an introduction of key concepts. For the readers who are completely unfamiliar with membrane processes, some relevant basic concepts and definitions are introduced, followed by a concise review of some of the basic aspects and definitions of membrane reactors. Chapter 2 is dedicated to catalytic and electrochemical membrane reactors. Though notable exceptions exist, most of the catalytic membrane reactor processes are high temperature applications. Membrane reactors have been applied to many common classes of catalytic reactions including dehydrogenation, hydrogenation, and partial and total oxidation reactions; all are reviewed in Chapter 2. There are several configurations of catalytic membrane reactors which utilize catalytically active or inactive membranes of various shapes and types; they may operate, for example, under a transmembrane pressure gradient or through the use of a sweep gas under co-current or counter-current operation; the membrane participates in the removal/addition of various species. The discussion on electrochemical membrane reactors in Chapter 2 is limited to those systems which produce a valuable chemical with or without the co-generation of electricity. Fuel cells are deliberately excluded as there are already several books and detailed reports on the topic.

Chapter 3 is devoted to the topic of pervaporation membrane reactors. These are unique systems in that they use a liquid feed and a vacuum on the permeate side; they also mostly utilize polymeric membranes. Chapter 4 presents a survey of membrane bioreactor processes; these couple a biological reactor with a membrane process. Reactions studied in such systems include the broad class of fermentation-type or enzymatic processes, widely used in the biotechnology industry for the production of amino acids, antibiotics, and other fine chemicals. Similar membrane bioreactor systems are also fin-

ding application in the biological treatment of contaminated air and water streams. Chapter 5 presents modelling studies of the different membrane reactor configurations and processes described previously in chapters 2 to 4. Membrane reactors often show unique and different behavior from their conventional counterparts; efficient modeling is key in understanding the behavior of these systems and important in scale-up and optimization activities. Finally, Chapter 6 discusses a number of issues which determine the technical feasibility and economic viability of such reactors. Membrane bioreactors have already found commercial application. This is, still, not true for high temperature catalytic membrane reactors, though they have been studied equally as intensively and long. Some of the key barriers still hindering their commercial application are discussed in the same chapter.

A number of people have contributed to this book and are acknowledged here. They include Ms. Christine Roure-Sanchez and Ms. Karen Woo for their typing work, Mr. Didier Cot for his kind help with the cover figure, and Mr. Seong Lim for his assistance with various aspects of the book. Theo Tsotsis and Jose Sanchez Marcano gratefully acknowledge the ongoing support of the U.S. National Science Foundation, the Centre National de la Recherche Scientifique, the U.S. Department of Energy and the European Commission for their research efforts in the area.

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1 Introduction

Membrane-based reactive separation (otherwise also known as membrane reactor) processes, which constitute the subject matter of this book, are a special class of the broader field of membrane-based separation processes. In this introduction we will first provide a general and recent overview on membranes and membrane-based separation processes. The goal is to familiarize those of our readers, who are novice in the membrane field, with some of the basic concepts and definitions. A more complete description on this topic, including various aspects of membrane synthesis can be obtained from a number of comprehensive books and reviews that have already been published in this area [1.1, 1.2, 1.3, 1.4]. We will then follow in this introduction with an outline of some of the generic aspects of the field of membrane-based reactive separations, which our reader will, hopefully, find useful while navigating through the rest of this book.

1.1 Principles of Membrane Separation Processes

Membrane-based separation processes are today finding widespread, and ever increasing use in the petrochemical, food and pharmaceutical industries, in biotechnology, and in a variety of environmental applications, including the treatment of contaminated air and water streams. The most direct advantages of membrane separation processes, over their more conventional counterparts (adsorption, absorption, distillation, etc.), are reported to be energy savings, and a reduction in the initial capital investment required.

A membrane is a permeable or semi-permeable phase, often in the form of a thin film, made from a variety of materials ranging from inorganic solids to different types of polymers. The main role of the membrane film, as shown schematically in Figure 1.1, is to control the exchange of materials between two adjacent fluid phases. For this role, the membrane must be able to act as a barrier, which separates different species either by sieving or by controlling their relative rate of transport through itself. The membrane action, as shown in Figure 1.1, results in a fluid stream (defined as the retentate), which is depleted from some of its original components, and another fluid stream (defined as the permeate), which is concentrated in these components. Transport processes across the membrane are the result of a driving force, which is typically associated with a gradient of concentration, pressure, temperature, electric potential, etc. The ability of a membrane to effect separation of mixtures is determined by two parameters, its permeability and selectivity. The permeability is defined as the flux (molar or volumetric flow per unit membrane area) through the membrane scaled with respect to the membrane thickness and driving force; for the case where transport is due, for example, to a partial pressure gradient the units of permeability are $\text{mol (or m}^3\text{)}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$. Often the true membrane thickness is not known and permeance, which is defined as the flux through the membrane scaled with respect to driving force (with units $\text{mol (or m}^3\text{)}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$), is, instead, utilized. The second important parameter is the membrane selectivity, which characterizes the

ability of the membrane to separate two given molecular species, and which is, typically, defined as the ratio of the individual permeabilities for the two species.

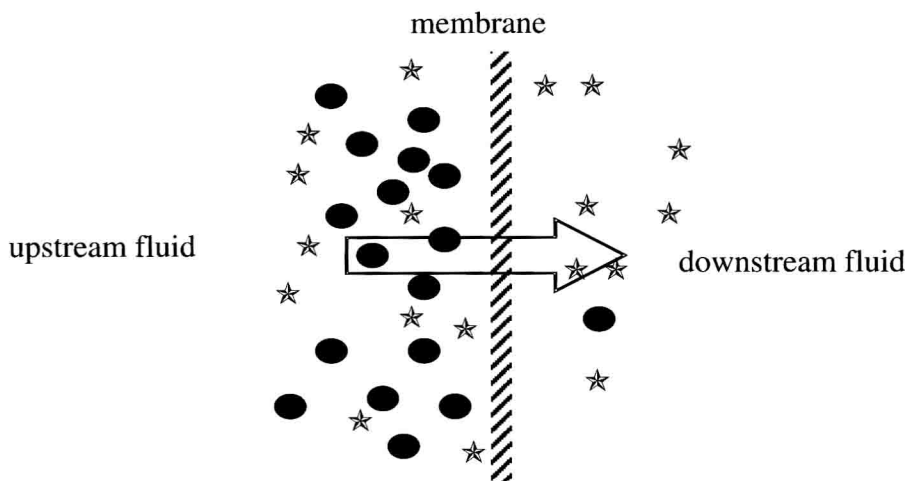


Figure 1.1. Schematic drawing of the basic membrane separation principle.

Membranes are classified by whether the thin permselective layer is porous or dense, and by the type of material (organic, polymeric, inorganic, metal, etc.) this membrane film is made from. The choice of a porous vs. a dense film, and of the type of material used for manufacturing depends on the desired separation process, operating temperature and driving force used for the separation; the choice of material depends on the desired permeance and selectivity, and on thermal and mechanical stability requirements. For membrane reactor applications, where the reaction is coupled with the separation process, the thin film has also to be stable under the reaction conditions.

Porous membranes are made of polymers (they include those used for dense membranes and, in addition, many others including polysulphones, polyacrylonitrile, polypropylene, etc.), ceramics (alumina, silica, titania, zirconia, zeolites, etc.), and microporous carbons. Dense organic and polymeric membranes are commonly used for molecular scale separations involving gas and vapor mixtures. There is a great variety of synthetic polymers, including silicones, perfluoropolymers, polyimides, polyamides, etc., which have, so far, found application in the membrane field. In the membrane reactor area, in addition to polymeric membranes, use is made of metal and solid oxide dense membranes. Metallic membranes are made of precious metals, like platinum, palladium, or silver, and of different alloys containing at least one of these metals. These membranes are specifically used for hydrogen (Pd, Pt, and their alloys) or oxygen (Ag) separations. Dense solid oxide membranes are used for oxygen and hydrogen separation, and are made by different types of ionic conducting materials, such as modified zirconias and perovskites. The use and

application of these dense membranes in catalytic membrane reactors will be further described in the following chapters of this book.

Membranes are also classified by whether they have a symmetric (homogeneous) or an asymmetric structure. Homogeneous or symmetric membranes are prepared when the membrane material has the necessary mechanical stability to be self-supporting. In many instances, however, the thin, permselective layer does not have enough mechanical strength to be self-supporting. In such cases the membrane layer is deposited on a porous support, which could conceivably be made from a different material resulting in asymmetric membranes; the support gives the necessary mechanical stability to the membrane without being an obstacle to the mass transport. Figure 1.2 shows two different electron micrographs, one representing a symmetric, self-standing polymer membrane, and the other representing an asymmetric, composite membrane consisting of a thin permselective, polymeric layer on a macroporous ceramic support. Composite, asymmetric membranes, can be prepared by a variety of techniques, including the incorporation into the separative layer, itself, of nanoparticles made from a different material [1.5]. Other techniques include the deposition of a polymer or metallic thin layer [1.6, 1.7, 1.8] on a ceramic porous support (Figure 1.2a), and also the infiltration or synthesis of a different material into the porous structure of a support [1.9, 1.10].

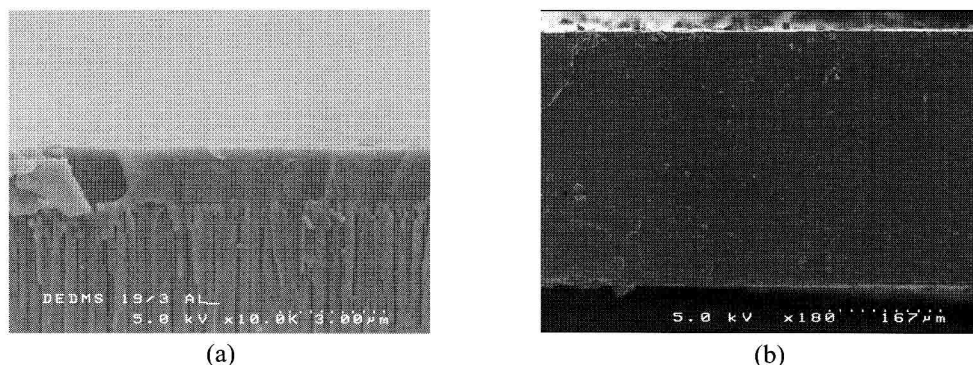


Figure 1.2. Electron micrograph (a) of a composite (polydiethoxydimethylsilane deposited by plasma on a porous alumina support [1.11]) membrane, and (b) a self-standing elastomeric membrane.

Membranes are manufactured in a diverse range of geometries; they include flat, tubular, and multi-tubular, hollow-fiber, and spiral-wound membranes. The type of geometry the membrane is manufactured into depends on the material the membrane is made from. Ceramic membranes, generally, come in tubular, multi-tubular and flat geometries, whereas spiral-wound and hollow-fiber membranes seem, for the most part (with a few notable examples), to be made from polymers.

For porous membranes the molecular size of the species to be separated plays also an important role in determining the pore size of the membrane to be utilized, and the related membrane process. According to the IUPAC classification, porous membranes with aver-

age pore diameters larger than 50 nm are classified as macroporous, and those with average pore diameters in the intermediate range between 2 and 50 nm as mesoporous; microporous membranes have average pore diameters which are smaller than 2 nm. Current membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), gas and vapor separation (GS), and pervaporation (PV). Figure 1.3 indicates the type and molecular size of species typically separated by these different processes.

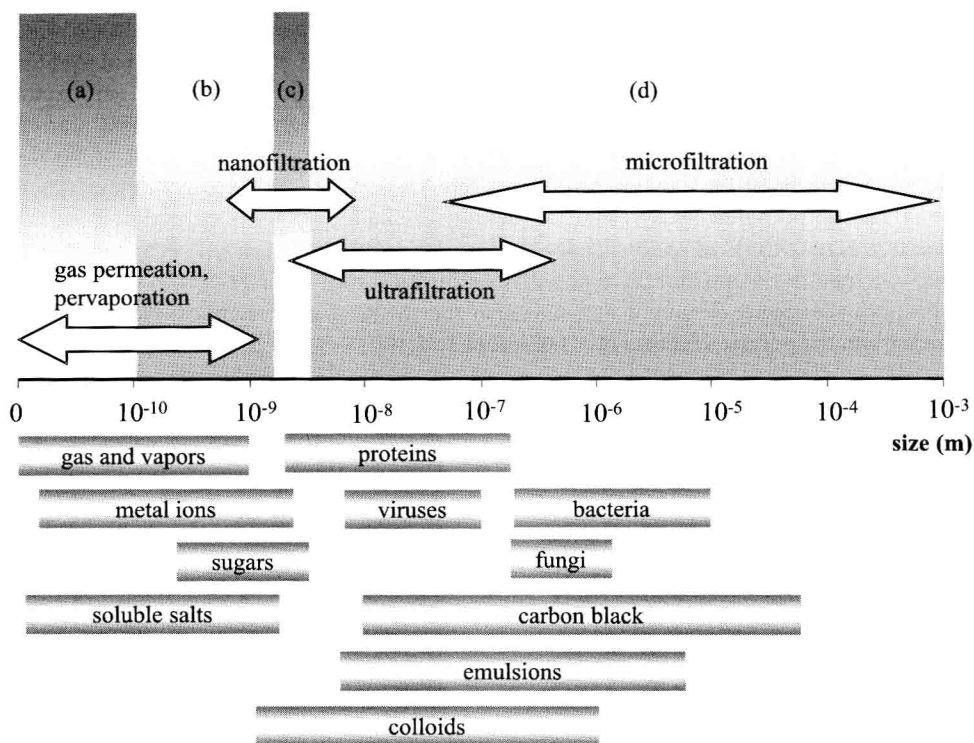


Figure 1.3. Various membrane processes and the different types of membranes and molecular species involved (a) dense and ultramicroporous, (b) microporous, (c) mesoporous, (d) macroporous.

The mass transfer mechanisms through membranes vary, depending on many factors like the membrane structure, the specific interactions between the membrane and the fluid, and the overall operating conditions. Mass transfer through dense polymeric membranes has been, typically, described in the engineering literature by a solution diffusion mechanism [1.1, 1.12, 1.13]. According to this mechanism, the molecular species must first adsorb on the surface and dissolve in the bulk of the polymer, where transport occurs by diffusion through the free volume in the polymer structure. Similar mechanisms taking into account a surface reaction (oxidation or hydride formation) and diffusion (hydride or ionic) in the membrane bulk have been utilized to describe diffusion through metallic or

solid oxide membranes. Understanding transport through such membranes requires measuring both, the sorption and transport characteristics of these materials. The mathematical techniques for the analysis of the experimental data, taking into consideration the effect of the membrane's geometry, have been developed by Crank some years ago [1.14].

For porous membranes the mass transport mechanisms that prevail depend mainly on the membrane's mean pore size [1.1, 1.3], and the size and type of the diffusing molecules. For mesoporous and macroporous membranes molecular and Knudsen diffusion, and convective flow are the prevailing means of transport [1.15, 1.16]. The description of transport in such membranes has either utilized a Fickian description of diffusion [1.16] or more elaborate Dusty Gas Model (DGM) approaches [1.17]. For microporous membranes the interaction between the diffusing molecules and the membrane pore surface is of great importance to determine the transport characteristics. The description of transport through such membranes has either utilized the Stefan-Maxwell formulation [1.18, 1.19, 1.20] or more involved molecular dynamics simulation techniques [1.21].

For membrane processes involving liquids the mass transport mechanisms can be more involved. This is because the nature of liquid mixtures currently separated by membranes is also significantly more complex; they include emulsions, suspensions of solid particles, proteins, and microorganisms, and multi-component solutions of polymers, salts, acids or bases. The interactions between the species present in such liquid mixtures and the membrane materials could include not only adsorption phenomena but also electric, electrostatic, polarization, and Donnan effects. When an aqueous solution/suspension phase is treated by a MF or UF process it is generally accepted, for example, that convection and particle sieving phenomena are coupled with one or more of the phenomena noted previously. In nanofiltration processes, which typically utilize microporous membranes, the interactions with the membrane surfaces are more prevalent, and the importance of electrostatic and other effects is more significant. The conventional models utilized until now to describe liquid phase filtration are based on irreversible thermodynamics; good reviews about such models have been reported in the technical literature [1.1, 1.3, 1.4].

1.2 The Coupling of the Membrane Separation Process with a Catalytic Reaction

Membrane-based reactive separation processes, which seek to combine two distinct functions, i.e. reaction and separation, have been around as a concept since the early stages of the membrane field, itself, but have only attracted substantial technical interest during the last decade or so [1.22]. There is ongoing significant industrial interest in these processes, because they promise to be compact and less capital intensive, and because of their promise for potential substantial savings in the processing costs [1.23].

Membrane-based reactive separation processes (also known as membrane reactor processes) are attracting attention in catalytic reactor applications. In these reactor systems the membrane separation process is coupled with a catalytic reaction. When the separation and reaction processes are combined into a single unit the membrane, besides providing

the separation function, also often results in enhanced selectivity and/or yield. Membrane-based reactive separations were first utilized with reactions, for which the continuous extraction of products would enhance the yield by shifting the equilibrium. Reactions of this type that have been investigated, so far, include dehydrogenation and esterification. Reactive separations also appear to be attractive for application in other types of reactions, including hydrogenation, and partial and total oxidation. In many reactor studies involving these reactions the use of membranes has been shown to increase the yield and selectivity. Published accounts on the application of membrane-based reactive separations in catalytic processes report the use of catalytically active and inactive membranes of various types, shapes, and configurations [1.24, 1.25, 1.26]. Reactor yield and reaction selectivity are found to be strongly dependent on the membrane characteristics, in addition to the more conventional process parameters.

Biotechnology is another area in which membrane-based reactive separations are attracting great interest. There, membrane processes are coupled with industrially important biological reactions. These include the broad class of fermentation-type processes, widely used in the biotechnology industry for the production of amino acids, antibiotics, and other fine chemicals. Membrane-based reactive separation processes are of interest here for the continuous elimination of metabolites, which is necessary to maintain high reactor productivity. Membranes are also increasingly utilized as hosts for the immobilization of bacteria, enzymes, or animal cells in the production of many high value-added chemicals. Similar reactive separation processes are also finding application in the biological treatment of contaminated air and water streams. Many of these emerging applications will be reviewed and evaluated in Chapter 4 of this book.

Reactor modelling has proven valuable for understanding the behavior of these systems. It will continue to serve in the future as an important tool for predicting and optimizing the behavior, and for improving the efficiency of these processes. Membrane reactor modelling will be discussed in Chapter 5. In this chapter, we will review key aspects of process modelling, design, and optimization that have been applied to the different membrane reactor types, that have been utilized in reactive separation studies.

In the early stages of the membrane-based reactive separations field, the coupling of the two functions happened by simply connecting in series two physically distinct units, the reactor and membrane separator (see Figure 1.4a). The membrane reactor concept, shown in Figure 1.4b, which combines two different processing units (i.e., a reactor and a membrane separator) into a single unit, was the result of natural process design evolution from the concept of Figure 1.4a. There are obvious advantages resulting from the design configuration of Figure 1.4b relating to its compact design, and the capital and operating savings realized by the elimination of intermediate processing steps. Other advantages relate to the synergy that is being realized between separation and reaction. This synergy is immediately obvious for reactions limited by thermodynamic equilibrium considerations, as is frequently the case with catalytic hydrocarbon dehydrogenation or esterification reactions. There, the continuous separation of one or more of the products (e.g., hydrogen or water) is reflected by an increase in yield and/or selectivity. Despite the obvious advantages of the reactor concept of Figure 1.4b over the design in Figure 1.4a, the more con-

ventional membrane-based reactive separation concept of Figure 1.4a, because of its simplicity, is often the design of choice in biotechnological applications. In the membrane reactor concept in Figure 1.4b the presence of the membrane (tubular, hollow-fiber, or plate) helps to define two different chambers. These are the retentate chamber, where the reactants are fed and the reaction often takes place, and the permeate chamber. The latter is either swept by an inert gas or evacuated in order to maintain a differential pressure or concentration gradient for mass transfer between the two compartments.

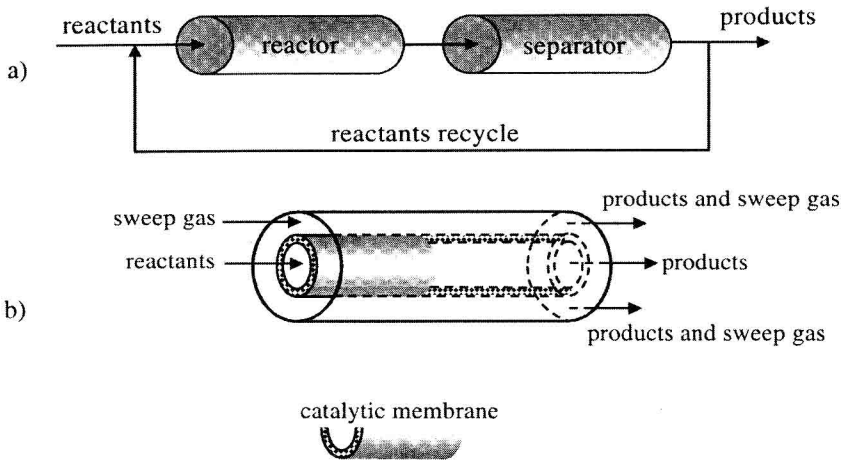


Figure 1.4. A conventional membrane reactor system (a) and an integrated membrane reactor system (b).

Publications discussing the membrane reactor concept first started appearing in the late 1960's [1.27, 1.28]. Most of the real progress in this area, however, has happened in the last twenty years [1.22]. This parallels progress in the overall field of membrane processes. There, as noted above, the development of new membrane materials during the last twenty years has opened the world of membrane technology to a broader range of applications beyond the classical ones, which, typically, involve low temperature microfiltration or ultrafiltration of liquids using polymeric membranes. The development of membranes made with a variety of inorganic materials has provided the opportunity to apply the catalytic membrane reactor concept for a much broader set of operating conditions. Inorganic membranes offer advantages in this regard over organic membranes, because they are stable at relatively high temperatures (> 373 K), and have good chemical and mechanical resistance [1.23]. The progress realized, over the last ten years, in the synthesis of stable microporous or dense inorganic materials for the preparation of membranes, has been the key factor motivating, for example, the application of membrane-based reactive separations in the catalysis field. Inorganic membranes are also more frequently being utilized in biotechnology for the production of fine chemicals via the use of both enzyme and whole-cell bioreactors [1.29], and for large-scale environmental clean-up type appli-