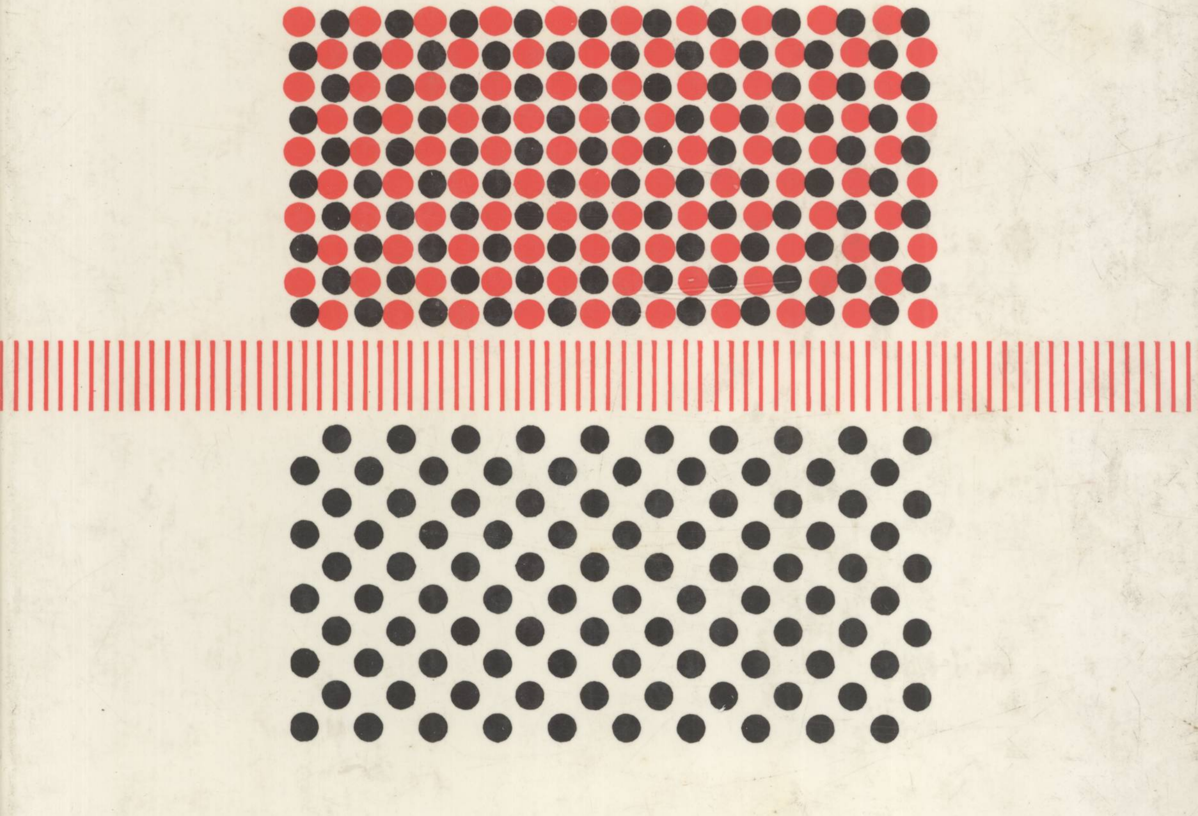
EFFECTIVE INDUSTRIAL MEMBRANE PROCESSES: BENEFITS AND OPPORTUNITIES

Edited by

M.K. TURNER



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PREFACE

The aim of the Technical Advisory Committee, in planning the content of this meeting, was to illustrate the range of separation processes in which the use of membranes was practical and effective at an industrial scale. As Professor Strathmann reveals, the market for process equipment built around membranes is now worth about $\$5x10^9$ annually, and it seemed important to review this technology, and to point the direction of future technical advances.

All but the most critical reader should find some items of interest. The Committee would admit to not fulfilling all of thier aims, although those delegates who attended the meeting in Edinburgh judged it a success. In the event it provided representative examples of processes from the food and beverage industry, from water treatment, and from the chemical industry, of which the removal of alcohol from fermented beverages, shipboard desalination and solvent recovery are three.

The major uses of charged membranes and sterile processes are not covered, nor is the largest market, $\$1.2x10^9$ annually, for artificial kidney dialysis. However, it is interesting to see artificial kidney now finding an alternative use as a reactor for the production of monoclonal antibodies. We are also reminded by Professor Michel of the importance and efficiency of natural membranes in the kidney under conditions where fouling is crucial to their performance and enhances their selectivity.

In contrast, fouling and poor selectivity are two problems which limit the application of synthetic membranes. Several papers consider the methods of pretreating liquid streams to reduce fouling, or of cleaning the membranes to reverse it. The electron microscope recently revealed that the fouling layer from these liquids penetrates deeper into the membrane than was once assumed. Selectivity in these liquid processes remains crude and unpredictable, raising the comment from Dr Carpenter that confidence in the viability of membrane processes only arises out of extensive testing at a pilot scale. Perhaps this explains why so much new discussion concerns the use of membranes for the rather crude separations needed to retain the waste released from traditional processes.

Gas separations are an exception. The selectivity of the membranes can now produce gases of sufficient purity at competitive costs, although the membrane step must still integrate effectively with the rest of the process.

The conference was interesting. For that, I would like to thank the Advisory Committee and its Overseas Members whose meetings I had the pleasure of chairing. I would also like to thank Tracey Peters and Carl Welch of the BHR Group who administered the Conference and organised its publication. I hope this book makes a useful addition to the literature.

PROFESSOR M.K. TURNER
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ECONOMIC ASSESSMENT OF MEMBRANE PROCESSES

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1. Introduction

In recent years membranes and membrane processes have become industrial products of substantial technical and commercial importance. The worldwide sales of synthetic membranes in 1990 were in excess of US \$ 2.0 x 10^9. Taking into consideration that in most industrial applications membranes account for about 40% of the total investment costs for a complete membrane plant, the total annual sales of the membrane based industry is close to US \$ 5 x 10^9 [1]. Membranes and membrane processes have found a very broad range of applicaions. They are used today to produce potable water from seawater, to treat industrial effluents, to recover hydrogen from off-gases or to fractionate, concentrate, and purify molecular solutions in the chemical and pharmaceutical industry. Membranes are also key elements in artificial kidneys and controlled drug delivery systems. The growing significance of membranes and membrane processes as efficient tools for laboratory and industrial scale mass separations is based on the several properties, characteristic of all membrane separation processes, which make them superior to many conventional mass separation methods. The mass separation by means of membranes is a physical procedure carried out at ambient temperature, thus the constituents to be separated are not exposed to thermal stress or chemical alteration. This is of particular importance for biochemical or microbiological application where often mixtures of sensitive biological materials have to be separated. Furthermore membrane processes are energy efficient and rather simple to operate in a continuous mode. Up- or downscaling is easy and process costs depend only marginally on the plant size.

In spite of impressive sales and a growth rate of the industry of about 12 to 15% per year the use of membranes in industrial scale separation processes is not without technical and economic problems. Technical problems are related to insufficient membrane selectivities, poor transmembrane fluxes, general process operating problems and lack of application know-how. Economic problems originate from the multitude of different membrane products and processes with very different price structures in a wide range of applications which are distributed on a very heterogeneous market consisting of a multitude of often very small market segments for

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individual products. This has led to relatively large production volumes for some products, such as hemodialysers, disposable items used only once for a few hours and sold in relatively large and uniform market segments. Other membranes, such as certain ceramic structures, used in special applications in the food, chemical or pharmaceutical industry are expected to last for several years in operation and can only be sold in relatively small quantities to small market segments. Consequently production volumes for these items are low and prices high. The rapid development of new membrane products and processes opening up new applications makes it difficult to predict the growth rate of the market with reasonable accuracy. The demand for efficient separation processes in the chemical, food and drug industry as well as in biotechnology and for solving challenging environmental problems, however, has not only led to a rather optimistic view but also to a considerable amount of speculation concerning the future development of the membrane based industry.

In this paper the different membrane products and processes are evaluated in terms of their state of development and their technical and economic relevance. Their potentials and limitations are pointed out. The present market for membranes and related products is analysed in terms of areas of application, technical requirements, economic limitations and regional distribution. The structure of today´s membrane industry is examined in terms of its product lines, operating strategies and regional distribution. Main parameters affecting the present and future utilization of membranes and membrane processes, such as membrane performance and costs, process reliability, longterm experience etc. are described. Different strategies used by various companies for handling their membrane related business are illustrated and evaluated.

The critical needs in terms of basic and applied research, capital investments, and personal education for a further growth of the membrane industry are discussed. Various research topics are identified as being crucial for the future development of membranes and membrane processes. They are analysed for their technical relevance, commercial impact, prospects for successful realization and the financial effort this will require.

2. Fundamentals of Membranes and Membrane Processes

To understand better the significance, both technical and economic, that membrane processes have in solving mass separation problems, some basic aspects concerning membranes and their function shall be briefly reviewed at this point.

2.1 Definition of a Membrane, its Function and Structure

In a most general sense, a membrane is an interphase separating two homogenous phases and affecting the transport of different chemical components in a very specific way. A multitude of different structures is summarized under the term "membrane". Often a membrane can be described easier by the way it functions than by its structure. Three different modes of transport can be distinguished in synthetic membranes, as indicated in Figure 1. Finally a component may also be transported against its chemical potential gradient through the membrane if coupled to a carrier and an energy delivering reaction. However, this mode of mass transport, referred to as active transport, has no up-to-date technical or commercial relevance.

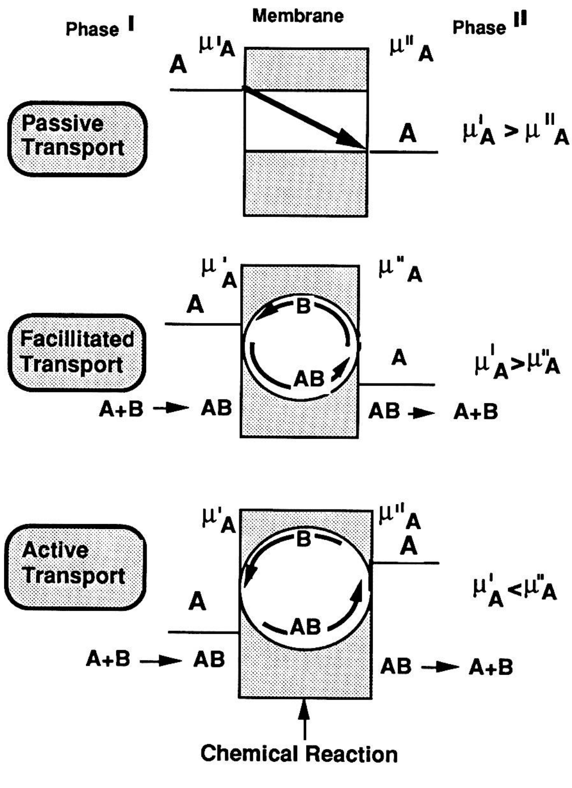

Fig. 1: Schematic drawing illustrating the various modes of mass transportation in synthetic membranes

2.2 Properties and Applications of Technically Relevant Membranes

Process design and chemical engineering aspects are important for the overall performance of a membrane separation process. The key element, however, is the membrane. Various structures are used as membranes. Some are very simple, such as microporous structures, others are more complex containing functional groups and selective carriers. A summary of technically relevant membranes, their structure and area of application is given in Table I.

The most simple form of a synthetic membrane are porous plates or foils. They are produced by pressing and sintering a polymeric, ceramic or a metal powder. These membranes have relatively large pores, a wide pore size distribution and a low porosity. The symmetric or asymmetric phase inversion membranes are more complex in their production as well as in their structure. They are produced by precipitation of a polymer solution. These membranes are used today in micro- and ultrafiltration as well as in gas separation and pervaporation. Composite membranes are more and more employed in the last three processes mentioned above. The selective layer and the support structure of these membranes consist of different materials. Membranes with functional groups, like the simple ion exchange membranes, are used in electrolysis and electrodialysis. Liquid membranes that are used in coupled transport with selective complexing agents and chelates are gaining increasing importance.

2.3 Technically Relevant Membrane Separation Processes and their Applications

Membrane processes are just as heterogeneous as the membranes. Significant differences occur in the membranes used, the driving forces for the mass transport, the applications and also in their technical and economical significance. Technically relevant membrane processes and their most important characteristics are given in Table II. In some of the processes the membranes as well as the processes have reached such a level that completely new developments can not be expected. Examples of this are the micro- and ultrafiltration, reverse osmosis, dialysis or electrodialysis. In these processes only improvements and optimization of existing systems and their adaptation to special applications are to be expected. Other processes are in the very beginning of their industrial application and offer the possibility of totally new developments of membranes and modules.

TABLE I Properties and applications of technically relevant synthetic membranes

Membranes	Basic Materials	Manufacturing Procedures	Structures	Applications
Ceramic membranes	Clay, silicate, aluminiumoxide, graphite, metal powder	Pressing and Sintering of fine powders	Pores from 0.1 to 10 micron diameter	Filtering of suspensions, gas separations, separation of isotopes
Stretched membranes	Polytetrafluoro-ethylene, polyethylene, polypropylene	Stretching of partially crystalline foil perpendicular to the orientation of crystallyts	Pores of 0.1 to 1 micron diameter	Filtration of aggressive media, cleaning of air, sterile filtration, medical technology
Etched polymer films	Polycarbonate	Radiation of a foil and subsequent acid etching	Pores of 0.5-10 micron diameter	Analytical and medical chemistry, sterile filtration
Homogeneous membranes	Silicone rubber, hydrophobic liquids	Extruding of homogeneous foils, formation of liquid films	Homogeneous phase, support possible	Gas separations, carrier-mediated transport
Symmetrical microporous membranes	Cellulose derivatives, polyamide, polypropylene	Phase inversion reaction	Pores of 50 to 5000 nonometers diameter	Sterile filtration, dialysis, membrane distillation
Integral asymmetric membranes	Cellulose derivatives, polyamide, polysulfone, etc.	Phase inversion reaction	Homogeneous polymer or pores of 1 to 10 nanometers diameter	Ultrafiltration, hyperfiltration, gas separations, pervaporation
Composite asymmetric membranes	Cellulose derivatives, polyamide, polysulfone, polydimethylsiloxane	Application of a film to a microporous membrane	Homogeneous polymer or pores from 1 to 5 nanometers diameter	Ultrafiltration, hyperfiltration, gas separations, pervaporation
Ion exchange membranes	Polyethylene, polysulfone polyvinylchloride etc.	Foils from ion exchange resins or sulfonation of homogeneous polymers	Matrix with positive or negative charges	Electrodialysis, electrolysis

TABLE II Technically relevant membrane processes

Membrane separation process	Driving force for mass transport	Type of membrane employed	Separation mechanism of the membrane	Application
Micro-filtration	Hydrostatic pressure difference 50-100 kPa	Symmetrical porous membrane with a pore radius of 0.1 to 20 μm	Sieving effect	Separation of suspended materials
Ultra-filtration	Hydrostatic pressure difference 100-1000 kPa	Symmetrical porous membrane with a pore radius of 1 to 20 nm	Sieving effect	Concentration, fractionation and cleaning of macromolecular solutions
Reverse osmosis	Hydrostatic pressure difference 1000-10000 kPa	Asymmetric membrane from different homogeneous polymers	Solubility and diffusion in the homogeneous polymer matrix	Concentration of components with low molecular weight
Dialysis	Concentration difference	Symmetrical porous membrane	Diffusion in a convection-free layer	Separation of components with low molecular weight from macromolecular solutions
Electro-dialysis	Difference in electrical potential	Ion exchange membrane	Different charges of the components in solution	Desalting and de-acidifying of solutions containing neutral components
Gas separation	Hydrostatic pressure difference 1000-15000 kPa	Asymmetrical membrane from a homogeneous polymer	Solution and diffusion in the homogeneous polymer matrix	Separation of gases and vapors
Pervaporation	Partial pressure difference 0 to 100 kPa	Asymmetrical solubility membrane from a homogeneous polymer	Solution and diffusion in the homogeneous polymer matrix	Separation of solvents and azeotropic mixtures

TABLE III Membrane modules, their properties and applications

Type of module	Membrane area per volume (m^2/m^3)	Price	Control of concentration polarization	Application
Pleated Filter Cartridge	800-1000	low	very poor	Dead end filtration
Tube	20-30	very high	very good	Cross-flow filtration of solutions with high solids content
Plate-and-frame	400-600	high	fair	Filtration, pervaporat-ion, gas separation and reverse osmosis
Spiral-wound	800-1000	low	poor	Ultrafiltra-tion,reverse osmosis, pervaporation gas separation
Capillary tube	600-1200	low	good	Ultrafiltrat-ion,perva-poration liquid membranes
Hollow fiber		very low	very bad	Reverse osmosis, gas separation