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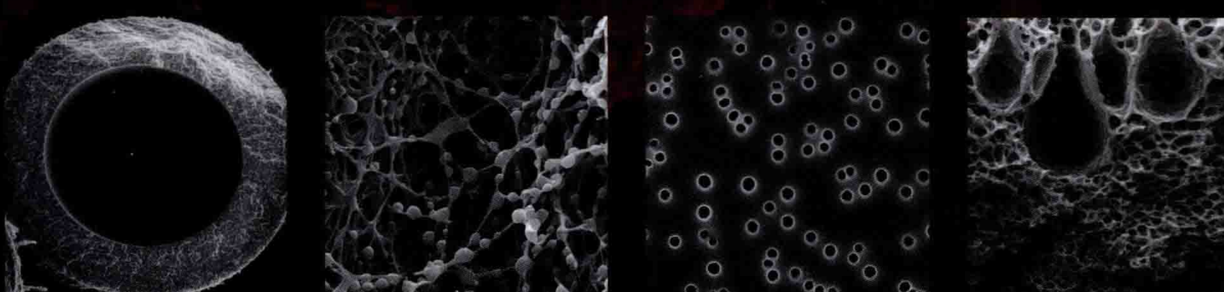
COMPREHENSIVE MEMBRANE SCIENCE AND ENGINEERING



Edited by
Enrico Drioli • Lidietta Giorno

VOLUME
4 Membrane Contactors and Integrated Membrane Operations

COMPREHENSIVE MEMBRANE SCIENCE AND ENGINEERING

Editors

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Volume 4

MEMBRANE CONTACTORS AND INTEGRATED MEMBRANE OPERATIONS

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COMPREHENSIVE MEMBRANE SCIENCE AND ENGINEERING

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Introduction

The last century has been characterized by a huge resource-intensive industrial development, particularly in some Asian countries, spurred by the growth in the global population level, by a significant elongation of life expectation, and by an overall increase in the standards characterizing the quality of life. These positive aspects of our recent history have been combined however with the emergence of related problems such as water stress, the environmental pollution, and the increase of CO_2 emissions into the atmosphere. These negative aspects of the transformations which have been characterizing our recent progress have been very much related to the momentum at which transformations themselves occurred and to the lack of innovations and introduction of new strategies capable of both controlling and minimizing the relatively obvious negative aspects of industrial development worldwide. A clear example is represented by the wastewater treatment strategy. As illustrated in **Figure 1**, from 1556 until today, the same concept is basically present in various wastewater-treatment systems.

The need to achieve a knowledge-intensive industrial development is nowadays well recognized. This will permit the transition from an industrial system based on quantity to one based on quality. Human capital is increasingly becoming the driving force behind this socio-economical transformation. The challenge of sustainable growth relies on the use of advanced technologies. Membrane technologies are in many fields already recognized as amongst the best-available technologies (BATs) able to contribute to this process (**Figure 2**).

Process engineering is one of the disciplines most involved in the technological innovations necessary to face the new problems characterizing the world today and in the future as well. Recently, the logic of process intensification has been suggested as the best process engineering answer to the situation. It consists of innovative equipment, design, and process development methods that are expected to bring substantial improvements in chemical and any other manufacturing and processing, such as decreasing production costs, equipment size, energy consumption, and waste generation, and improving remote control, information fluxes, and process flexibility (**Figure 3**).

How to implement this strategy is, however, not obvious. An interesting and important case is the continuous growth of modern membrane engineering whose basic aspects satisfy the requirements of process intensification. Membrane operations, with their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, compatibility between different membrane operations in integrated systems, low energetic requirement, good stability under operating conditions and environmental compatibility, easy control and scale-up, and large operational flexibility, represent an interesting answer for the rationalization of chemical and any other industrial productions. Many membrane operations are practically based on the same hardware (materials), only differing in their software (methods). The traditional membrane separation operations (reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF), electrodialysis, pervaporation, etc.), already largely used in many different applications, are today conducted with new membrane systems such as catalytic membrane reactors and membrane contactors. At present, redesigning important industrial production cycles by combining various membrane operations suitable for separation and conversion units, thus realizing highly integrated membrane processes, is an attractive opportunity because of the synergic effects that can be attained.

In various fields, membrane operations are already dominant technologies. Interesting examples are in seawater desalination (**Figure 4**); in wastewater treatment and reuse (**Figure 5**); and in artificial organs (**Figure 6**).

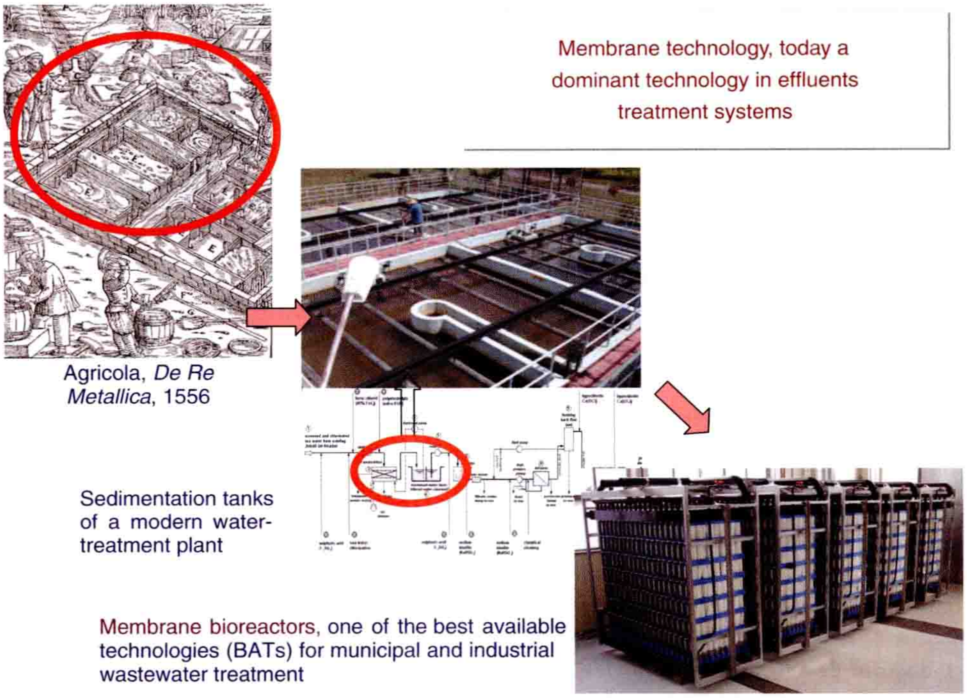

Figure 1 Wastewater-treatment technological approach in the past and today.

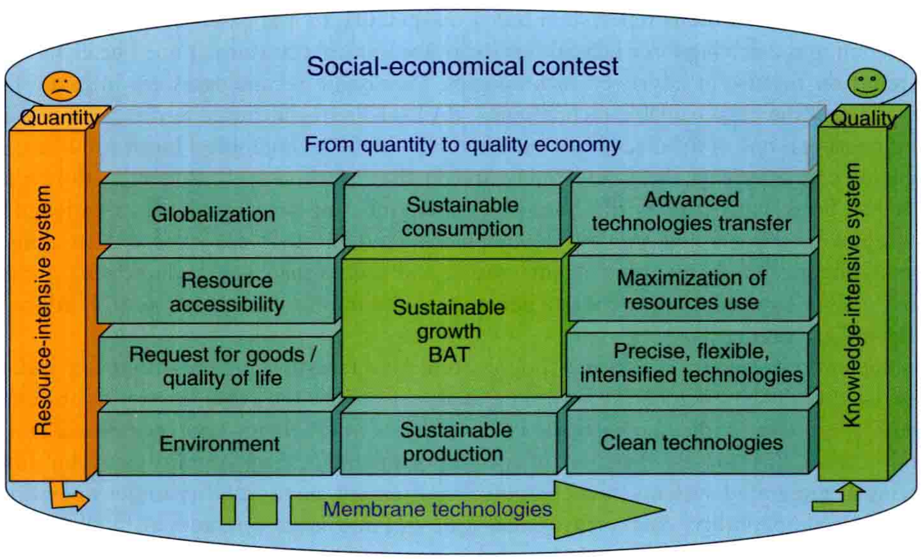

Figure 2 Current social-economical and technological contest driving the transition towards a knowledge-intensive system to guarantee sustainable growth.

It is interesting to consider that a large part of the membrane operations realized today at the industrial level has been in existence in the biological system and in nature ever since life came into being. A major part of biological systems is, in fact, well represented by membranes which operate molecular separations, chemical transformation, molecular recognition, energy, mass and information transfer, etc. (**Figure** 7).

Some of these functions have been transferred at the industrial level with success. We are, however, far away from being able to reproduce the complexity and efficiency of the biological membranes, to integrate the

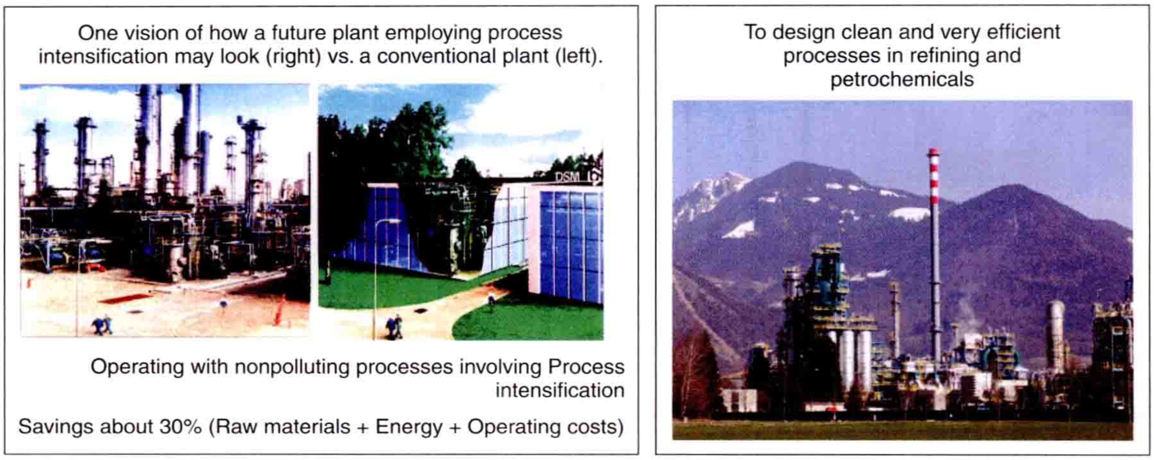

Figure 3 Process intensification strategy. Reproduced from Jean-Claude Charpentier, Modern Chemical Engineering in the Framework of Globalization, Sustainability, and Technical Innovation, Ind. Eng. Chem. Res., Vol. 46, No. 11, 2007.

Figure 4 Membrane desalination plant. RO membrane units from El Paso Desalintion Plant, Texas: the site of the word's largest inland desalination plant (104 000 m^3 d^{-1}). Production costs for water are less than less than 0.36 \$ m^{-3}. From http://www.epwu.org/167080115.

various functionalities, the capability to repair damage, and to maintain for a very long time their specific activities, avoiding fouling problems, degradation of the various functions, and keeping the system alive. Therefore, future generations of membrane scientists and engineers will have to address their attention to understanding and reproducing the astonishing natural systems, which are at the basis of the life with which we are familiar.

In *Comprehensive Membrane Science and Engineering*, we have tried to present and discuss the most relevant results of membrane science and engineering reached during the last years.

Authors from all around the world, senior scientists, and PhD students have contributed to the four volumes covering fundamental aspects of membrane preparations and characterization, their applications in various unit

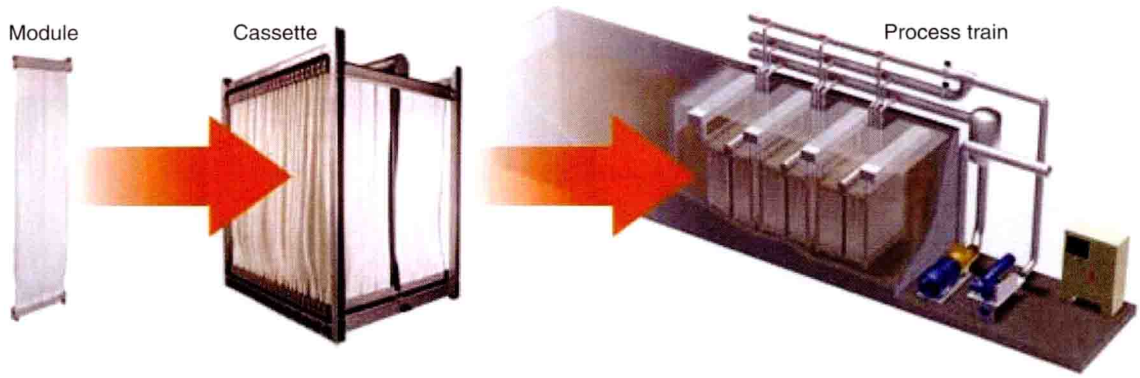

Figure 5 Submerged membrane module for wastewater treatment. From ZeeWeed® Submerged Membrane System, from http://www.gewater.com.

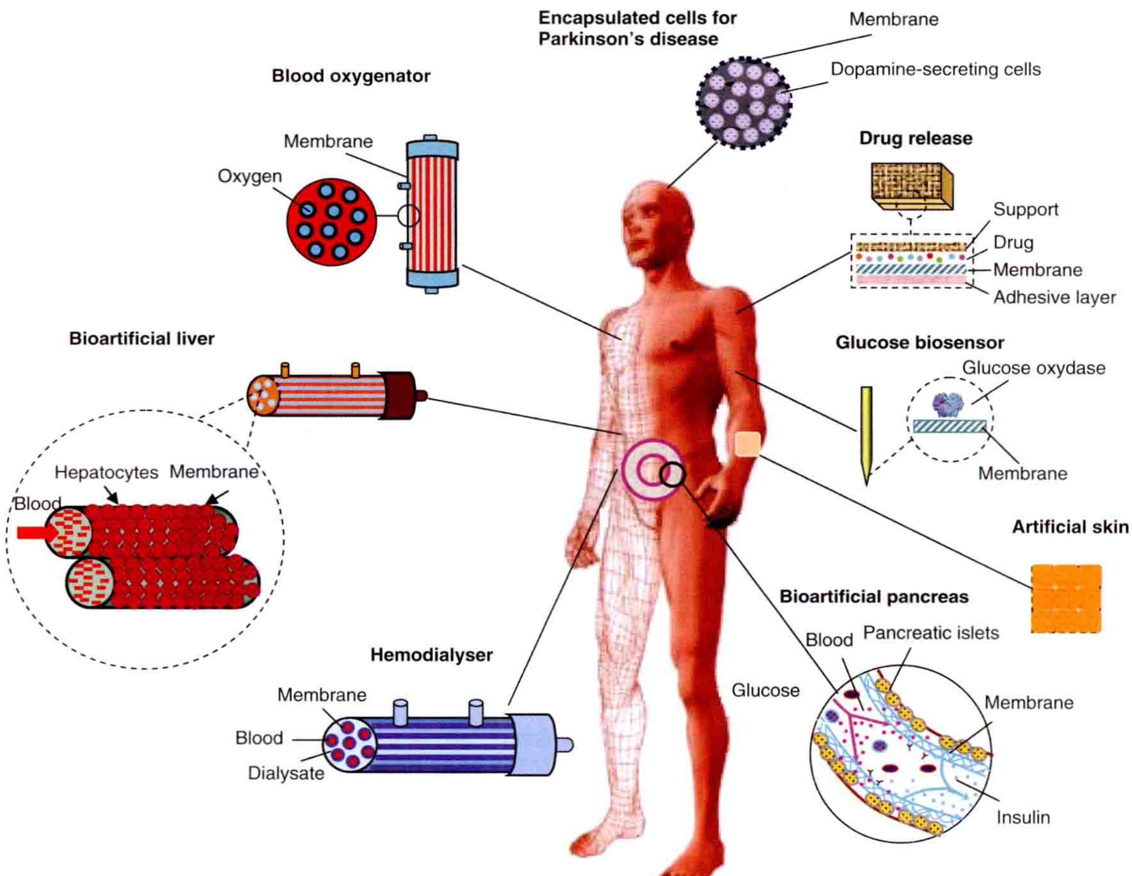

Figure 6 Membranes and membrane devices in biomedical applications. Modified from L. De Bartolo e E. Drioli. "Membranes in artificial organs" In Biomedical and Health Research vol. 16: New Biomedical Materials – Basic and Applied Studies Haris, P.I. and Chapman, D. (Eds.) IOS Press: Amsterdam/Berlin/Tokjo/Washington, (1998) pp. 167–181.

operations, from molecular separation to chemical transformations in membrane reactors, to the optimization of mass and energy transfer in membrane contactors. Their application in strategic fields, including energy, environment, biomedical, biotechnology, agro-food, and chemical manufacturing, has been highlighted.

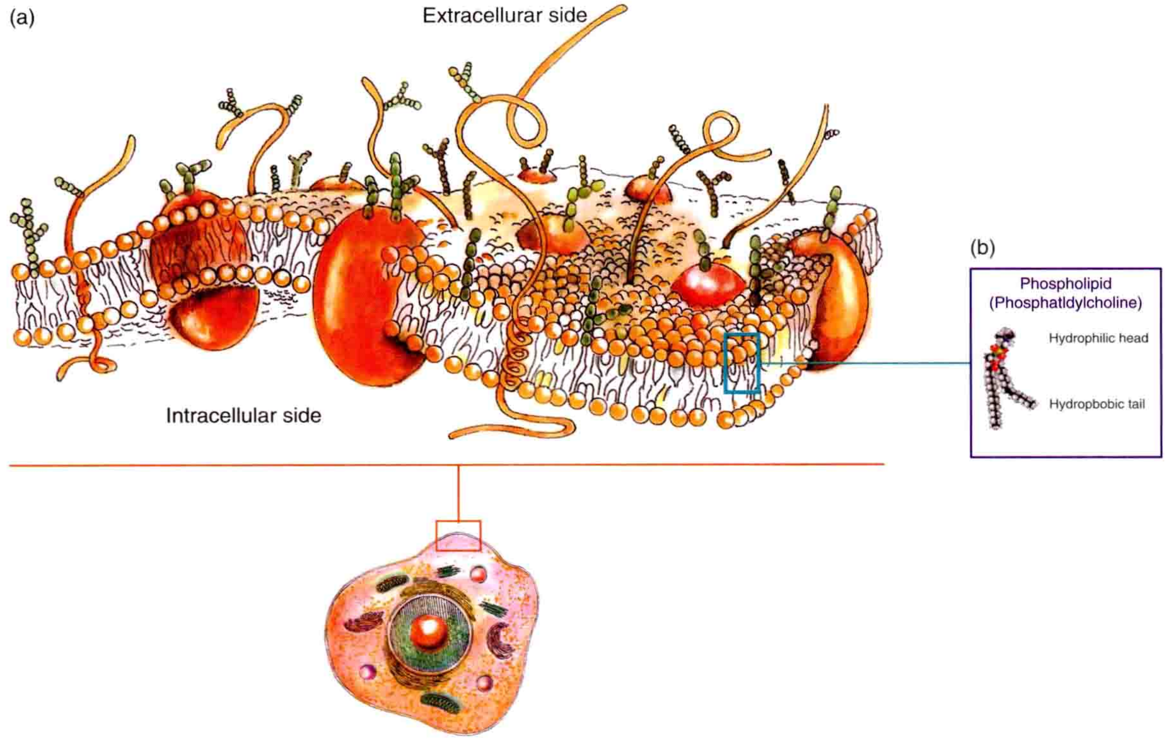

Figure 7 Biological membrane functions. From http://www.mcgraw-hill.it/.

Today, the possibility of redesigning a significant number of membrane operations, introduced via industrial production, is becoming more and more attractive and realistic.

Strong efforts are however necessary for spreading the available knowledge in membrane engineering to the public and for educating the younger generations more and more in the fundamentals and applications of these creative, dynamic, and important disciplines.

With this text we have tried to contribute to these efforts.

In Volume 1, fundamental aspects of the transport phenomena, which characterize permeability and selectivity in molecular separations based on polymeric, inorganic, and mixed-matrix membranes are discussed together with the basic principles for their preparation in various possible configurations (flat sheets, tubular fiber, microcapsules, etc.). The basic methodology generally utilized for their characterization is also discussed.

In Volume 2, the most relevant membrane operations such as the pressure-driven systems in liquid phase (MF, UF, NF, and RO) and in gas phase (gas separation and vapor permeation) together with other separation processes, such as dialysis, pervaporation, and electrochemical membrane systems, are analyzed and discussed in their basic principles and applications.

In Volume 3, the recent interest in the combination of molecular separations with chemical transformations largely present in biological systems is presented. It is important to recall that the industrial development of these membrane reactors and catalytic membrane systems is not yet at the level of the more well-known pressure-driven processes. However, the expectation of a significant fast growth of membrane reactors and membrane bioreactors is very significant. Interesting success, in fact, can already be indicated by the recognition of the submerged membrane reactors such as BAT in municipal wastewater treatment and reuse. The potentialities of this system in the area of bioengineering and biomedical applications are also very attractive, where bioartificial organs, such as bioartificial liver and pancreas, are in some case already at clinical trial level.

Volume 4 is addressed to the description of relatively new membrane operations, where membranes are not required to be selective. Their role is the optimization of the best mass and energy transfer between different phases, acting as membrane contactors. Membrane distillation, membrane crystallizers, membrane emulsifiers,

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Volume 4 Membrane Contactors and Integrated Membrane Operations

Basic Principles of Membrane Contactors

Integrated Membrane Operations in Various Industrial Sectors: Case Studies

4.01 Membrane Distillation and Osmotic Distillation

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4.01.1 Definition and Basic Principles

Membrane distillation (MD) is an emerging nonisothermal separation technique that uses microporous hydrophobic membrane in contact with an aqueous heated solution on the one hand (feed or retentate) and a condensing phase (permeate or distillate) on the other [1]. This technique belongs to the class of membrane contactors in which a nonwetting membrane does not act as a conventional barrier or filter, but promotes mass and energy exchange between two opposite interfaces according to principles of phase equilibrium.

In MD, the hydrophobic nature of the membrane prevents the mass transfer in liquid phase and creates a vapor–liquid interface at the entrance of each pore. Here, volatile compounds (most commonly water) evaporate, diffuse and/or convect across the membrane, and are condensed and/or removed on the opposite side of the system.

The specific method used to activate the vapor pressure gradient across the membrane characterizes four main different MD configurations. In the most common arrangement – known as direct contact membrane distillation (DCMD) – the permeate side of the membrane consists of a condensing fluid (often pure water) that is directly in contact with the membrane. Alternatively, the vaporized solvent can be recovered on a condensing surface separated from the membrane by an air gap (AGMD), vacuum (VMD), or removed by a sweep gas (SGMD). All these variants are schematized in **Figure 1**.

The selection of a specific configuration depends upon feed and permeate compositions and characteristics, as well as upon requested productivity. In general, DCMD (cheaper and easier to operate) is the best choice for applications in aqueous

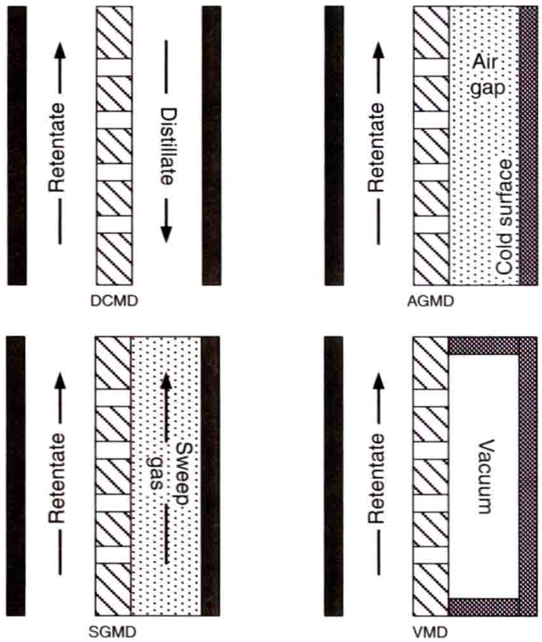

Figure 1 Scheme of the four most common membrane distillation (MD) configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), vacuum membrane distillation (VMD).

environments, SGMD and VMD are used to remove volatile organic components from aqueous solutions, and AGMD (the most versatile) can be employed to concentrate various nonvolatile solutes whenever high fluxes are not required. Compared to reverse osmosis (RO), MD does not suffer limitations of concentration polarization and can therefore be employed when high permeate recovery factors or high retentate concentrations are requested. Moreover, RO fluxes are drastically reduced at high concentration due to the increase in osmotic pressure, while MD fluxes slightly decrease as consequence of both reduction of the solution activity and increase of the solution viscosity.

With respect to traditional separation units and methods of the chemical industry, MD offers several important advantages. The nature of the driving force, coupled with the hydro-repellent character of the membrane, allow – at least theoretically – the complete rejection of nonvolatile solutes such as macromolecules, colloidal species, and ions. Lower temperature gradients (20–40 °C) with respect to those generally used in conventional distillation columns are generally sufficient to establish a transmembrane flux in the order of 1–20 $kg\,m^{-2}\,h^{-1}$, with consequent reduction of energy costs and mechanical requirements of the materials. Typical feed temperatures vary in the range of 40–60 °C and permit the efficient recycle of low-grade or waste heat streams, as well as the use of alternative energy sources (solar, wind, or geothermal) [2]. In addition, the possibility to use plastic equipments reduces or avoids erosion problems. On the other hand, MD suffers from some drawbacks. MD fluxes of permeate are usually lower than in RO, and a higher energy consumption is necessary to drive this thermal membrane operation. Moreover, only a restricted class of polymeric materials present a sufficient chemical resistance and operational stability and, despite the decreasing trend of membrane costs, commercial modules are still quite expensive.

4.01.2 Membrane Materials

When producing microporous membranes for MD operations, the selection of the material is mainly driven by the necessity to achieve a high chemical and thermal stability, high hydrophobicity, and porosity. Typology and main characteristics of the polymers frequently used as starting material for microporous hydrophobic membranes are given in **Table 1**.

More recently, inorganic (stainless steel) membranes typically used in microfiltration, modified by depositing on their surface a very thin film of silicone compounds, have been tested for MD operations [3]. Microporous polymeric membranes are prepared by various techniques: sintering, stretching, and phase inversion.

Sintering is a simple technique: a powder of polymeric particles is pressed into a film or plate and sintered to just below the melting point [4]. The process yields a microporous structure having a porosity in the range of 10–40% and rather irregular pore sizes, ranging from 0.2 to 20 μm (**Figure 2(a)**).

Microporous membranes can also be prepared by stretching a homogeneous polymer film made from a partially crystalline material [5]. Films are obtained by extrusion of a polymeric powder at temperature close to the melting point, coupled with a rapid drawdown. Crystallites in the polymers are aligned in the direction of drawing. After annealing and cooling, mechanical stress is applied perpendicularly to the direction of drawing. This manufacturing process gives a relatively uniform porous structure with pore-size distribution in the range of 0.2–20 μm and porosity of about 90% (**Figure 2(b)**).