

MASS TRANSFER OPERATIONS: HYBRID MEMBRANE PROCESSES

E. Drioli, E. Curcio, E. Fontananova

National Research Council of Italy, Institute on Membrane Technology (ITALY)

Department of Chemical Engineering and Materials, University of Calabria (ITALY)

Keywords: Membrane technology, hybrid membrane systems, chemical engineering

Contents

1. Introduction
 2. Hybrid Membrane Desalination Systems
 - 2.1. MSF/RO Systems
 - 2.2. NF/MSF Systems
 - 2.3. MF and UF as Pretreatment Processes
 3. Integrated membrane systems in agrofood industry
 4. Hybrid membrane operations for wastewater treatment
 5. Integrated membrane operations in Gas Separation
 6. Integration of molecular separation and chemical/energy conversion
 - 6.1. Catalytic Membrane Reactors
 - 6.2. Fuel Cells
 7. Conclusions
- Glossary
Bibliography and Suggestions for further study
Biographical Sketches

Summary

Among the various technical options offered by Chemical Engineering for a sustainable industrial growth, membrane science and technology provide today some of the most interesting and concrete solutions for design, rationalization, and optimization of innovative production cycles. The attractive prospects are related to the possibility of integrating various membrane units in different industrial cycles, with important overall benefits in terms of product quality, plant compactness, environmental impact, and energetic aspects. In the following are presented some successful and interesting examples of membrane processes integrated into industrial practice or hybridized with conventional schemes

1. Introduction

In the frame of a globalized market, Chemical Engineering faces today the crucial challenge to find sustainable solutions to the increasing demand for raw materials, energy and tailored-made products. Within the more and more stringent constraints of legislative and social rules, answers might be found in the rational integration and implementation of innovative technologies and approaches, able to increase process performance, save energy, reduce costs, minimize environmental impact. In this respect, membrane science and technology contributed to significant innovations in both

processes and products since the 1980s, because they are flexible processing techniques, able to maximize phase contact, to integrate conversion and separation processes with improved efficiency and with significant lower energy requirement compared to conventional techniques.

Membrane technology is today recognized as key factor for a sustainable growth in many industrial segments. Some of the basic properties of membrane operations, such as simplicity in concept and operation, modularity for an easy scale-up, and reduced energy demand, make them potentially attractive for a more rational utilization of raw materials and wastes minimization.

Various membrane operations are available today for a wide spectrum of industrial applications, and most of them can be considered as well accepted unit operations, as in the case of pressure-driven processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO); electro dialysis (ED) is another example of a mature technology.

Membrane operations show potential in molecular separations, clarifications, fractionations, concentrations, etc. in the liquid phase, in the gas phase, or in suspensions, so covering practically all existing aspects of process engineering.

Although membranes already represent the standard in various sectors (desalination, water treatment, gas separation etc.), their utilization as hybrid systems – in combination with other conventional techniques or integrated with different membrane operations – is considered the way forward more widespread and rationale applications.

The synergic interactions that can be achieved make hybrid membrane systems advantageous in many industrial processes, where they can be eventually integrated with other traditional unit operations, so optimizing their global performance.

As suggested by the several and excellent examples pertaining to water treatment processes, hybrid or integrated systems give today the concrete possibility to reduce the environmentally harmful effects, to decrease the energetic requirements, and to recycle and reuse by-products streams so approaching the concept of Zero Liquid Discharge. Additional cases in which hybrid membrane systems have increased their industrial relevance are presented.

2. Hybrid Membrane Desalination Systems

2.1. MSF/RO Systems

The integration of thermal desalination and membrane operations as hybrid desalination systems with power generation is currently considered as viable alternative to dual purpose plants based on traditional and energetically-extensive processes, such as Multistage Flash evaporators (MSF) or Multiple Effect Distillation (MED).

RO plants do not involve changes of phase and, therefore, they require a half to a third of energy with respect to MSF plants. In most cases, MSF and RO are operated in

parallel and independently with the aim to increase the overall water recovery factors (Figure 1). This simple and traditional hybridization concept in which the permeate from RO units is blended to distillate from thermal MSF has been implemented in Saudi Arabia dual-purpose plants (Jeddah, Yanbu-Medina). If MSF is fed by the brine of RO, the water recovery factor can increase up to about 30%.

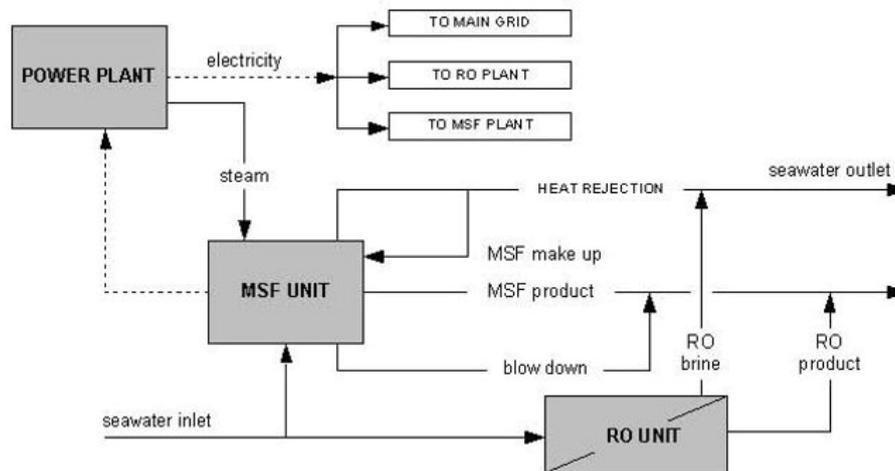


Figure 1. Hybrid MSF/RO plant with thermal and membrane units operating in parallel.

The 100 MGD desalination plant in Fujairah (United Arab Emirates), the largest hybrid installation in the world, combines a 62.5 MGD MSF and 37.5 MGD SWRO units. The cogeneration plant produces 500 MW of electrical energy. The flexibility of hybrid desalination plants well support the needs of this country, where the demand of water is nearly constant throughout the whole year while the power demand drops by about 40% during the winter season. In this case, the RO system helps to improve the load duration curve.

The power plant comprises 4 gas turbines each rated 109 MW and 4 heat recovery steam generators (380 t/h at 68 bar and 537°C) supplying 2 steam turbine generators. The expanded steam serves the MSF units. Seawater desalination process is designed for feed water with 40 000 ppm TDS and temperature in the range of 22-35°C. The thermal line of the plant includes 5 MSF units each of 12.5 MGD capacity, with performance ratio of 8 and top brine temperature in the range of 107-109°C. The RO plant is dimensioned for a recovery factor of 43% in the first pass (18 trains), and for a recovery rate of 90% in the second pass.

2.2. NF/MSF Systems

Application of nanofiltration as seawater pre-treatment results in the reduction of salt concentration and removal of most of the hardness ions (Ca^{2+} , Mg^{2+}) and co-ions (SO_4^{2-} , HCO_3^-) which are responsible for the formation of precipitate (scaling) on the heat transfer surfaces of thermal desalination processes. Pre-treatment of raw seawater by nanofiltration gives the possibility to safely increase the top brine temperature (TBT)

of thermal desalination units above their present TBT limit. An increase of TBT results in the enhancement of water production and performance ratio.

A hybridized NF/MSF pilot plant was operated successfully in Al-Jubail up to a top brine temperature (TBT) of 130°C, which is the design TBT limit of the unit, without injection of scale control additive for a period of 1200 h and the product recovery was increased up to 70% compared to 35% obtained from conventional operated MSF desalination plants (Figure 2).

It is expected that higher TBT can be attainable (up to 160°C), leading to high-efficiency dual-purpose plants at increased production of water and power.

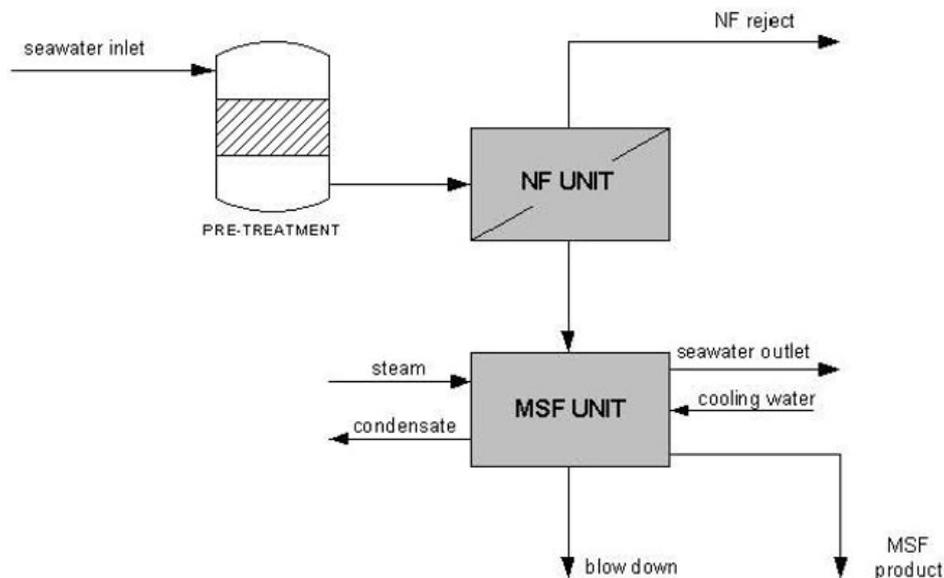


Figure 2. Hybrid NF/MSF desalination system.

2.3. MF and UF as Pretreatment Processes

Feed water for RO desalination plants needs extensive pre-treatment in order to prevent the damages related to membrane fouling. At present, the conventional pre-treatment still remains the preferred approach because of the lower investment cost and relative lack in experience of implementing low-pressure membrane operations. Due to the advancement in microfiltration and ultrafiltration technologies, their implementation for water filtration was drastically expanded since 2000, and several hundred systems have been started up for municipal drinking water systems worldwide. Microfiltration is a low energy-consuming technique extensively used to remove suspended solids and to lower Chemical Oxygen Demand (COD)/Biochemical Oxygen Demand (BOD) and Silt Density Index (SDI) to values below 5. Ultrafiltration, retains suspended solids, bacteria, macromolecules and colloids; despite of the larger pressure gradient with respect to MF, this membrane separation method remains competitive against conventional pretreatments.

The growth of membrane filtration market has been exponential in the 1990s: in 1995 it

was estimated that less than 25 MGD installed capacity was in operation in North America; five years later that number has grown to about 400 MGD. In 2006, the updated technical market research report from BCC Research estimated the global market for microfiltration (MF) membranes used in liquid separations at \$792 million in 2005, rising at an average annual growth rate (AAGR) of 9.4% through the forecast period, to more than \$1.2 billion.

With the introduction of modern ultrafiltration (UF) and microfiltration technologies, it is expected that these membrane filtration processes would provide the optimum pretreatment technology for reverse osmosis (RO) applications. These expectations have been realized in the reclamation of municipal wastewater. Practically, all new wastewater reclamation systems that use RO for salinity reduction apply UF or MF technology as a pretreatment step before RO (Figure 3). Effectiveness of membrane pretreatment in producing better quality RO feed water is proven and well documented. In a wastewater reclamation process with integrated membrane pretreatment, the benefits of significantly lower fouling rates of RO membranes, low cost of chemicals and disposal of pretreatment waste stream, outweighs the higher cost membrane pretreatment equipment.

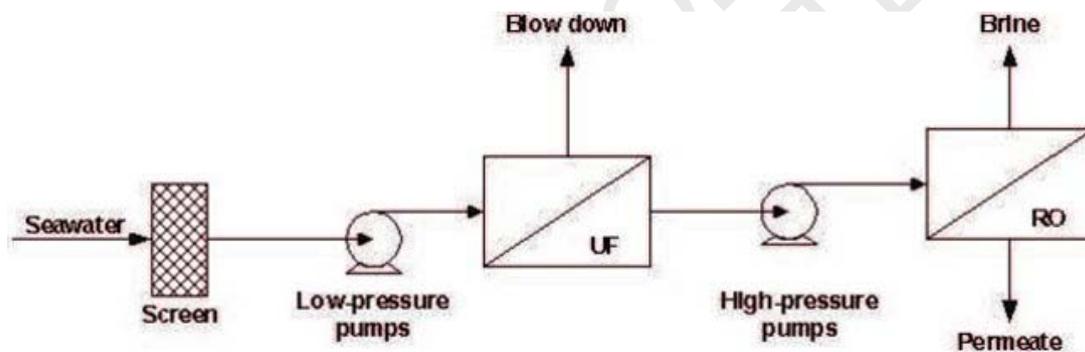


Figure 3. Seawater desalination: UF pretreatment to RO trains

3. Integrated Membrane Systems in Agrofood Industry

In agrofood industry, integrated membrane processes are today proposed for the production of high quality fruit juice concentrate. Flowsheet in Figure 4 offers a practical example of this kind of application. Ultrafiltration is used in order to separate fruit juices into the serum and the pulp (clarification). The clarified juices are pre-concentrated to 20–25°Brix by Reverse Osmosis, and the Reverse Osmosis retentates can be concentrated up to 60-70°Brix by Osmotic Distillation. The UF retentate could be submitted to a pasteurization process and then added to the final OD concentrate. The stability of the antioxidant activity (TAA) during juice processing is of interest since they play an important role in reducing the risk of free radical related oxidative damage associated with a number of diseases. Analysis showed that the content of ascorbic acid, phenolics and total antioxidant, besides anthocyanins and Vitamin C, did not decrease significantly during the processing.

Successful application of integrated membrane operations in fruit juice concentration has been developed by the Australian company (Wingara Wine Group, Melbourne). A

hybrid pilot plant where UF/RO and OD are integrated has been realized. It consists of UF and RO pretreatment stages, an OD unit and a single-stage brine evaporator. This pilot plant concentrates fresh juices up to 65–70 Brix and has a capacity of 50 l/h. Being athermal, OD allows concentrating without product deterioration or loss of flavors.

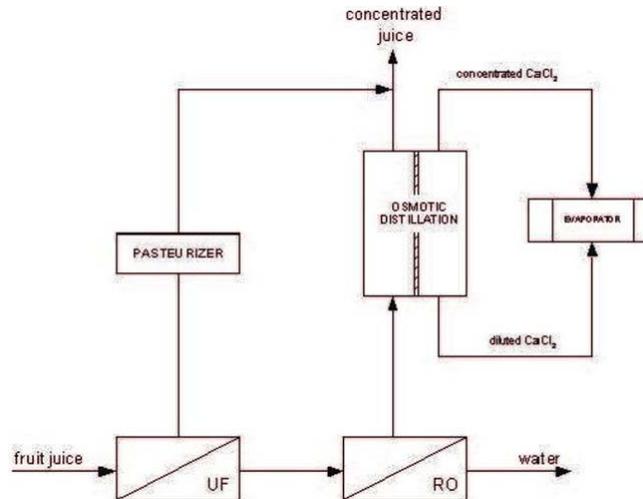


Figure 4. Integrated membrane system for fruit juice concentration.

Gas-Liquid Membrane Contactors (GLMC) are today used to transfer soluble gases, to/from an aqueous stream, in a variety of applications in the food and beverage industries. Liqui-Cel®, Extra-Flow™ Membrane Contactor manufactured by Celgard, Inc. of Charlotte, NC is, at present, the most popular GLMC module available for agrofood industrial applications.

For instance, N₂ introduction is requested to lower CO₂ content into “smooth” beer. Direct injection leads to highly undesirable turbulence that knocks CO₂ out of solution; with the Celgard technology, nitrogen could be introduced at low pressure (30-45 psi), a level that is actually lower than the 60 psi pressure needed to move the beer around.

Since 1993, a bubble-free membrane-based carbonation line has processed about 112 gal/min of beverage by membrane contactors having a total interfacial area of 193 m² (Pepsi bottling plant in West Virginia).

4. Hybrid Membrane Operations for Wastewater Treatment

Demand for membrane materials will exceed \$10 billion in 2010, predicts the McIlvaine Company (www.mcilvainecompany.com) and water and wastewater treatment and water and wastewater treatment is expected to remain the major outlet, accounting for about half of the overall demand.

Necessity of recycling use of municipal wastewater has been recognized to resolve the shortage of water resources.

Among the most promising emerging technology, membrane bioreactors (MBR) offer the most interesting developments for the future of wastewater treatment. Although this

technology has been in commercial use for little over 10 years, it is now beginning to show some of the initial market promise and is attracting the attention of municipal and industrial facilities in search of effective wastewater recycling processes.

The MBR combines the use of membrane filtration and bioreactors. Low-pressure membranes (either MF or UF) are used for solid and high molecular compounds separation from the treated sludge. Sludge concentration in the MBR is controlled by continuous liquid extraction from the bioreactor. An easy control of the process guarantees a high water-quality effluent produced.

Main advantages of MBRs over conventional processes include small footprint, easy retrofit and upgrade of old wastewater treatment plants into MBRs. With the membrane directed immersed into the bioreactor, submerged MBR systems are usually preferred to sidestream configuration (with the membrane situated into a pressurized external loop), especially for municipal wastewater treatment (Figure 5).

MBR are mainly operated according to two configurations: 1) external circulation, 2) submerged membranes. In the first case, the membrane unit is situated externally to the bioreactor and the separation is achieved by a tangential recirculation of the bacterial suspension at high pressure (usually from 1 to 4 bar) and at high speed (from 0.5 to 4 m/s) in the membrane module. As the mixed liquor circulates, the permeate passes through the membrane and the concentrate is returned back to the bioreactor. In the MBR with a submerged membrane unit, the withdrawal of permeate is achieved with a suction pump at low trans-membrane pressure (from 0.05 to 0.5 bar). In the external system, the permeate flux generally varies between 50 and 120 L h⁻¹m⁻², while in the submerged configuration from 15 to 50 L h⁻¹ m⁻².

Many studies have demonstrated that the MBR systems enable a virtually complete retention of parasites and bacteria, and at least 2 to 3 log unit removal of viruses, due to the absorption onto the concentrated biomass.

Several immersed MBR designs are currently proposed by the leading membrane suppliers such as GE-Zenon, X-Flow, USFilter, Mitsubishi and Kubota.

BIOSEP[®] process, developed since 1993 by Anjou Recherche (Veolia Water) using hollow-fiber submerged modules produced by Zenon and Memcor (Australia); thanks to the successful results, Veolia Water commissioned in 1999 the plant of Perthes-en-Gâtinais, which was one of the first full-scale MBR plants to be constructed in Europe for municipal wastewater treatment. In 2004, the largest MBR plant in the world, equipped with Zenon modules, was commissioned in Kaarst (Germany), and designed by VA Tech Wabag Germany to serve a population of 80,000 people.. In March 2005, Zenon announced the contract award for an MBR plant to treat 144,000 m³/d in Washington. These examples are representative of the rapid development of MBR technology, also in terms of size of installations, grown exponentially in few years.

One of the largest membrane bioreactor units in the world was recently built in Porto Marghera (Venice) in order to extract remaining pollutants in tertiary water prior to disposal into the Venetian Lagoon. The ultrafiltration unit, containing submerged PVDF

hollow fibers membranes (ZeeWeed[®] by Zenon), is designed to treat 1600 m³/h of wastewater with a COD/h of 445 kg and the suspended matter of the treated water is <1mg/L.

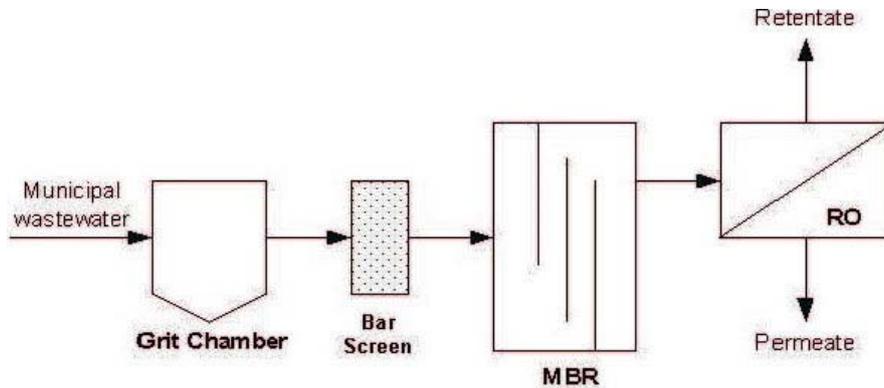


Figure 5. Integrated MBR/RO system for municipal wastewater treatment

Leather industry represents an interesting example of a better rationalization of the productive cycles by using membrane separation processes. In particular, NF has been identified as a technically viable method for recovering tannins from spent tannin liquors and pollution control in vegetable tanning factories.

According to the scheme reported in Figure 6, the exhausted tanning solution is fed to a NF unit for a purification/concentration process, producing retentate solutions that can be reused for the preparation of new tanning baths. The permeate stream can be reused in other steps of the tanning cycle (e.g. the pretannage), as washing water for the membrane modules, or in other operations of the production cycle. The skins treated with the recovered solutions exhibit chemical and physical properties very similar to those measured on control skins. The advantages are particularly significant in terms of reduction of environmental impact (up to 75% of COD reduction of the global effluent), simplification of cleaning-up processes of wastewaters, saving of chemicals and water, easy reuse of sludges and decrease of disposal costs.

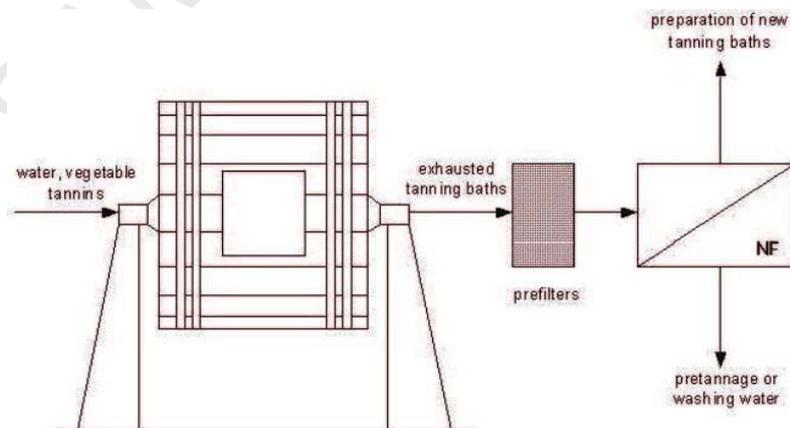


Figure 6. Tannins recovery from exhausted tanning baths.

-
-
-

TO ACCESS ALL THE 23 PAGES OF THIS CHAPTER,
Visit: <http://www.desware.net/DESWARE-SampleAllChapter.aspx>

Bibliography and Suggestions for further study

Al-Sofi M.A.K., Hassan A.M., Mustafa G.M., Dalvi A.G.I., Kither M.N.M. (1998). Nanofiltration as a means of achieving higher TBT of 120°C in MSF. *Desalination* 118, 123–129 [Potentialities of nanofiltration as softening process integrated to MSF]

Bernardo P., Criscuoli A., Clarizia G., Barbieri G., Drioli E., Fleres G., Picciotti M. (2004). Applications of membrane unit operations in ethylene process. *Clean Tech. Environ. Policy* 6, 78–95 [Possible integration of membrane contactors and catalytic membrane reactors in the ethylene process]

Bonchio M., Carraro M., Scorrano G., Fontananova E., Drioli E. (2003). Heterogeneous Photooxidation of Alcohols in Water by Photocatalytic Membranes Incorporating Decatungstate, *Advanced Synthesis & Catalysis*. 345, 1119-1126 [The incorporation of decatungstate in polymeric membranes provides new heterogeneous photocatalysts for the oxidation of organic substrates]

Carraro M., Gardan M., Scorrano G., Drioli E., Fontananova E., Bonchio M. (2006). Solvent-free, heterogeneous photooxygenation of hydrocarbons by Hyflon® membranes embedding a fluorine-tagged decatungstate: the importance of being fluorine. *Chemical Communications* 43, 4533–4535 [The improved performance of decatungstate heterogenized on hydrophobic fluorine hyflon]

Cassano A., Adzet J., Molinari R., Buonomenna M.G., Roig J., Drioli E. (2003) Membrane treatment by nanofiltration of exhausted vegetable tannin liquors from the leather industry. *Water Research* 37, 2426–2434 [Technical aspects of NF treatment of wastes from leather industry]

Fontananova E., Donato L., Drioli E., Lopez L., Favia P., d'Agostino R. (2006). Heterogenization of polyoxometalates on the surface of plasma modified polymeric membranes. *Chemistry of Materials* 18, 1561-1568 [Membranes are modified by plasma treatments on the surface to graft N-containing polar groups that are able to act as binding sites with phosphotungstic acid]

Gryaznov V. (1999). Membrane catalysis. *Catalysis Today* 51, 391-395 [An overview on the catalytic membrane processes with emphasis on hydrogenation and dehydrogenation reactions]

Helal A.M., El-Nashar A.M., Al-Katheeri E.S., Al Malek S.A. (2004). Optimal design of hybrid RO/MSF desalination plants. Part II: Results and discussion. *Desalination* 160, 13-27 [This paper provides some technical data on the possible combination of thermal and membrane desalination technologies]

Jiao B., Cassano A., Drioli E. (2004). Recent advances on membrane processes for the concentration of fruit juices: a review *Journal of Food Engineering* 63, 303–324 [A review on the potentialities of membrane operations in agrofood industry]

Kujawski W. (2000). Application of Pervaporation and Vapor Permeation in Environmental Protection, *Polish Journal of Environmental Studies* 9, 13-26 [A survey on the applications of pervaporation at industrial level]

Larmine J., Andrews D. (2000) *Fuel Cell Systems Explained*. John Wiley & Sons, Ltd.: Chichester [An introductory book to fuel cells world]

Ludwig H. (2003). Hybrid systems in seawater desalination-practical design aspects, status and development perspectives. *Desalination* 157, 31-32 [A technical and economical assessment on hybrid desalination systems]

Melin T., Jefferson B., Bixio D., Thoeue C., De Wilde W., De Koning J., van der Graaft J., Wintgens T.

(2006). Membrane bioreactor technology for wastewater treatment and reuse, *Desalination* 187, 271-282 [Potentiality and perspectives of MBR in municipal water treatment]

Miachon S., Dalmon J.-A. (2004). Catalysis in membrane reactors: what about the catalyst?. *Topics in Catalysis* 29, 59-65 [Role and properties of the catalysts in membrane reactors]

Osman A. H.(2005). Overview of hybrid desalination systems — current status and future prospects. *Desalination* 186, 207–214 [A comprehensive review about the hybrid systems in seawater desalination]

Paul D., Sikdar S.K. (1998). Clean production with membrane technology. *Clean Products and Processes* 1, 39–48 [Membrane applications for a sustainable and eco-friendly industrial development]

Tanaka K., Yoshikawa R., Ying C., Kita H., Okamoto K. (2001). Application of zeolite membranes to esterification reactions. *Catalysis Today* 67, 121–125 [Potentialities and performance of zeolite membrane reactors in esterification process]

Biographical Sketches

Enrico Drioli

Professor of Chemistry and Electrochemistry at the School of Engineering of the University of Naples (since 1968) and Full Professor at the School of Engineering of the University of Calabria (since 1981).

- Dean of the School of Engineering of the University of Calabria (1982-1985).
- Director of the Institute on Membrane Technology of the National Research Council (former Research Institute on Membranes and Modelling of Chemical Reactors - IRMERC) (since 1993).
- President of the European Society of Membrane Science and Technology (1982 - 1998).
- Chairman of the Working Party on Membranes of the European Federation of Chemical Engineering (since 1985).
- Doctorate *Honoris Causa* in Chemistry and Chemical Technology from Russian Academy of Science (February 1992).
- Honorary Professor at the China Northwest University in Xi'an, Shaanxi, People's Republic of China (Sept. 1991).
- Honorary Founding President of the European Membrane Society (from 1999).
- Honorary Member of the A. V. Topchiev Institute of Petrochemical Synthesis at the Russian Academy of Sciences, Moscow (from 1999).
- Patron Member of the Indian Membrane Society.
- Member of the Advisor Board of the UNESCO Center on Membrane Science and Technology at the New South Wales University, Australia.
- Member of the European Communities Chemistry Council (E.C.C.C.).
- Member of Executive Council of the European Federation of Chem. Engineering (from 1996)
- Member of the Interim Board of Governors of the Middle East Desalination Research Center, Oman, Muscat (1994 - 1996); Member and Moderator of the Research Advisory Council of the Middle East Desalination Research Center , Oman, Muscat (from May 1997)
- Member of the NATO/CCMS Pilot Study on "Clean Products and Processes"
- International Scientific Counselor of the Membrane Industry Association of China
- Member of the Editorial Boards of the: *Chemical Engineering and Processing Elsevier*; *Desalination – Elsevier*; *Journal of Membrane Science – Elsevier*; *Journal of Molecular Catalysis (1982–1992) – Elsevier*; *Chemical Engineering and Technology Journal - Wiley-VCH*; *Industrial & Engineering Chemistry Research (from Jan. 2002) – American Chemical Society*; *Journal of Clean Products and Processes - Springer-Verlag*; *Acqua-Aria – Arti poligrafiche europee*; *Chimica Oggi - TeknoScienze*; *La Chimica e L'Industria - Editrice di chimica*; *Orizzonti Tecnologici - CESVITEC*; *Water Treatment - China Ocean Press*; *Anales de Fisica - La Sociedad*; *Russian Journal of Physical Chemistry - MAIK Nauka, Interperiodica Publ.*; *Journal of Separation and Purification Technology - Childwall University Press*; *Membrane Science and Technology – Lanzhou (China)*

Author of more than 450 scientific papers and 14 patents in the field of Membrane Science and Technology:

Efrem Curcio

He received his Degree and Ph.D in Chemical Engineering at the University of Calabria in 1999 and 2005, respectively.

Researcher at the Department of Chemical Engineering and Materials of the University of Calabria. Since 1999 he is associate researcher at the Institute on Membrane Technology (ITM-CNR) of the Italian Research National Council, where he developed his expertise on membrane science and technology.

His present research interests concern: development of membrane crystallization devices and advanced membrane contactors, design and optimization of integrated membrane desalination systems, implementation of new brine disposal strategies, development of membrane bio-reactors for hepatocyte cells culture.

He is co-author of the book “Membrane Contactors: fundamentals, applications and potentialities” (Elsevier, 2005), author of more than 30 papers in international journals, and several proceedings of international scientific conferences and workshops. Dr. Curcio received the European Membrane Society Award for the best published paper in Membrane Science and Engineering on 2004.

Enrica Fontananova

Graduated *cum laude* in Chemistry at the University of Calabria (Rende (CS), Italy) in 2001.

Contract Researcher at the Engineering Faculty of the University of Calabria and at the Institute on membrane Technology (ITM-CNR) (since 2001).

Research interests: membrane preparation and application in membrane reactor, membrane contactor, fuel cell and stereoselective recognition in membrane separation processes.

Tutor of Chemistry at the Engineering Faculty of the University of Calabria (since 2001).

Author of about 20 research papers in international journals and numerous presentations in international scientific meetings on membrane science and technology.

1st Prize for “New ideas for industrial applications” NanoMemPro Awards - Euromembrane 2006, Giardini Naxos (ME), Italy; 24-28 September 2006.