DESALINATION BY MEMBRANE DISTILLATION

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Contents

1. Introduction
2. Membrane Distillation (MD)
3. MD configurations
3.1. Direct Contact Membrane Distillation (DCMD)
3.2. Air Gap Membrane Distillation (AGMD)
3.3. Sweeping Gas Membrane Distillation (SGMD)
3.4. Vacuum Membrane Distillation (VMD)
4. Membranes and modules used in MD
5. Application of MD technology in desalination
5.1. Effects of Membrane Characteristics
5.1.1. Effects of Membrane Porosity and Thermal Conductivity
5.1.2. Effects of Membrane Thickness and Pore Tortuosity
5.1.3. Effects of Membrane Pore Size and its Distribution
5.2. Effects of MD Process Conditions
5.2.1. Effects of Feed Temperature
5.2.2. Effects of Salt Concentration of the Feed Aqueous Solution
5.2.3. Effects of Feed Flow Rate
5.2.4. Effects of Permeate Conditions
5.3. Efficiency, Energy Analysis, Costs and MD Integrated Systems
6. Conclusions
Glossary
Bibliography
Biographical Sketch

Summary

Membrane distillation (MD) is a non-isothermal membrane separation process applied for desalination of seawater and brackish water. It is known since 1963 and is still being developed at desalination testing stages and not fully implemented in industry. The process is still under evaluation and different contradicted opinions exist concerning its future. Increasing attempts are being made for scaling-up MD systems and pilot plants have proved recently employing solar energy. MD exhibits various advantages over the industrially well-established reverse osmosis (RO) process in the field of water desalination. Aqueous solutions of salts with higher concentrations than seawater can be treated by MD and higher salts rejections have been achieved in MD compared to the pressure driven membrane process RO. The present chapter offers a comprehensive overview of MD applied in saline water desalination. Membranes and modules used in

MD, different MD configurations, heat and mass transport and effects of different parameters on the MD performance as well as energy consumption and integrated MD systems to other desalination processes are presented. Some key factors for the improvement of MD, aimed at MD industrialization, are highlighted.

1. Introduction

During the past fifty years, membrane technologies have been incessantly progressing because the demand for good quality drinking water is increasing steadily world-wide. Although over two thirds of the planet is covered with water, 99.3% of the total water is either too salty (seawater) or inaccessible (ice caps). Since water becomes potable if it contains less than 500 ppm of salts, much research has gone into finding efficient technologies for removing salt from seawater and brackish water called desalination processes.
Membrane technology is today well recognized as the most convenient desalination technology. Currently, it seems that there is no limit for the future progress of membrane processes. The growing interest towards membrane science and technology is evident. Most of membrane transport processes are isothermal and their driving forces are transmembrane hydrostatic pressures, concentrations, electrical potential, etc. For example the well known reverse osmosis (RO) used specially in desalination of seawater or brackish waters is an isothermal process. However, less membrane processes are non-isothermal technologies requiring a thermal driving force to establish the necessary transmembrane chemical potentials or transmembrane partial vapor pressures. Among these processes, one can find membrane distillation (MD) process that is applied also in desalination of seawater and brackish waters.

MD is a process mainly suited for applications in which water is the major component present in the feed solutions to be treated and refers to a thermally driven transport of vapor through non-wetted porous hydrophobic membranes. The driving force of this technology is the partial pressure difference between each side of the membrane pores.

The potential applications of MD are:

- Production of high-purity water, concentration of ionic, colloid or other non-volatile aqueous solutions and removal of trace volatile organic compounds (VOCs) from waste water.
- Desalination, environmental/waste cleanup, water-reuse, food, medical, etc.

The advantages of MD are:

- Lower operating temperatures than the temperatures normally applied in conventional distillation. The process can be performed at feed temperatures considerably lower than the boiling point of water (i.e., temperatures as low as 30ºC have been used). This permits the efficient use of low-grade or waste heat streams as well as the alternative energy sources (solar, wind or geothermal).
- Lower operating hydrostatic pressures than the pressure-driven processes, for example RO. The MD process can be performed at operating pressures generally near the atmospheric pressure.

- High rejection factors achieved when solutions containing no-volatile solutes (salts, colloids, etc.) are considered. This makes MD more attractive than other popular separation processes such as RO in the field of desalination as well as in nuclear desalination. MD can also be used in medical, pharmaceutical and semi-conductor sectors as water permeate is very pure.
- Less demanding membrane mechanical properties.
- Possibility to use equipments made of plastic material reducing or avoiding erosion problems.
- Membrane fouling in MD is less of a problem than in the pressure driven processes such as in RO.
- Possibility to use waste heat and renewable energy sources enabling MD technique to cooperate in conjunction with other processes in an industrial scale. Based on its high flexibility and compatibility, MD can be integrated in various important industrial production cycles increasing the efficiency of the whole process.

The disadvantages of MD include:

- Lack of membranes and modules designed specifically for MD. Compared to other membrane separation processes including RO only few research groups have considered the possibility of designing and manufacturing novel membranes for MD applications.
- Risk of membrane pore wetting. The pores of the hydrophobic membrane must be maintained always dry. Only water vapor and gases must be present inside the pores.
- Low productivity (i.e. permeate flux). Recently, for desalination purposes, permeate fluxes of some membranes developed for MD are “similar” to the ones achieved for RO process. Permeate fluxes higher than 100 kg/m^2h has been achieved in MD desalination with a salt rejection of nearly 100%, which are competitive with the fluxes typically observed in RO.
- Permeate flux decay with time due to fouling, membrane deterioration, etc.
- Uncertain and “high” energetic and economic costs. With respect to RO higher energy consumption is needed to establish the thermal membrane operation.
- Commercial membrane modules are still expensive.

Recently, interest in MD has increased significantly specially at academic levels, and various studies are reported in desalination field.

2. Membrane Distillation (MD)

Membrane distillation (MD) is a non-isothermal process known for more than forty years (First patent was filed by Bodell on 3rd June 1963, first MD paper was published 4 years later by Findley in the journal “Industrial & Engineering Chemistry Process Design Development”). Intense interests in MD process began in early 1980s when membranes such as Gore-Tex Membrane (expanded polytetrafluoroethylene, PTFE, porous membrane supplied by Gore & Associated Co.). During last three years, the number of papers published on MD and the research groups focusing on MD studies have been increasing. However, MD still needs to be developed for its industrial implementation.

The term MD comes from its similarity to conventional distillation (i.e. simple and multi-effect distillation). Both MD and conventional distillation technologies are based on the vapor/liquid equilibrium for salt separation from water and both require latent heat of evaporation to be supplied to the aqueous feed solution of salt.

The driving force in MD is the difference in partial vapor pressure of water across a membrane that must fulfill the following characteristics:

- Porous with high void volume fraction or porosity
- Pore size range may be from several nanometers to few micrometers
- Totally hydrophobic or at least the layer facing the salt aqueous solution is hydrophobic
- Not wetted by the aqueous solution of salt with sufficiently high liquid entry pressure (LEP)
- Does not alter the vapor/liquid equilibrium interfaces formed at the entrances of membrane pores
- Does not permit condensation to occur inside its pores
- Be maintained in direct contact with the hot feed aqueous solution of salt to be treated
- Low thermal conductivity of the membrane material with good thermal stability at temperatures as high as 100 ºC
- Membrane material of excellent chemical resistance permitting cleaning with case acid and base components is necessary
- Long life with a stable MD performance, permeability and salt rejection.

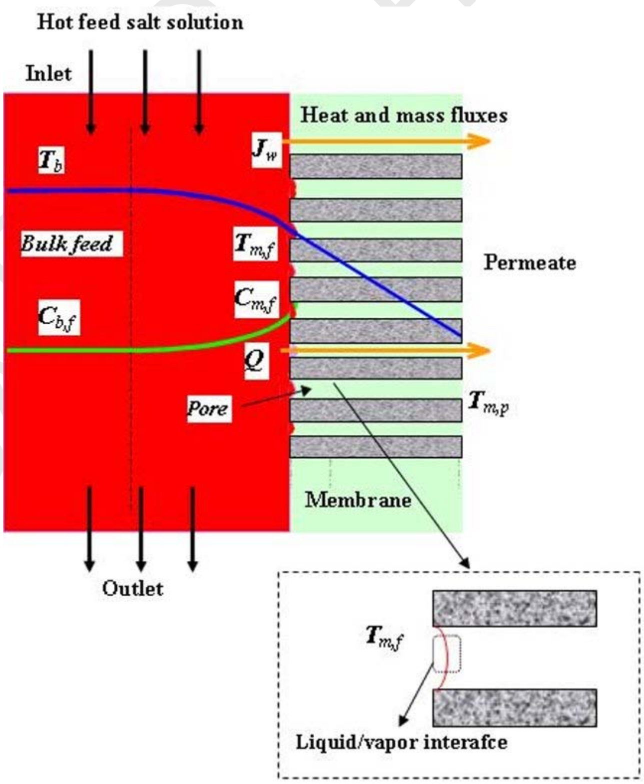

Figure 1. Schema of MD process at the feed salt aqueous solution

In this process, the membrane is maintained in contact with an aqueous salt solution on the feed or retentate side (Figure 1). The temperature of the feed solution is below its boiling point. It can vary between few degrees over the ambient temperature, about 30ºC, to 90 ºC. Feed pressures near atmospheric pressure are applied. The hydrophobic nature of the membrane prevents the feed solution to penetrate into the membrane pores creating vapor-liquid interfaces at the entrance of the membrane pores. Under these conditions, water molecules evaporate at the hot vapor/liquid interface, flow across the membrane pores in vapor phase, and finally condense at the cold side of the membrane module or removed out of the membrane module depending on the method applied to establish the driving force and to collect the permeate or distillate.

In MD process both heat and mass transfer phenomena occur through the membrane (Figure 1).

Mass transfer:

Water flux, J_{w}, which is dependent on the membrane characteristics and on the magnitude of the transmembrane driving force, Δp_{w}, is expressed as:

$$J_{\mathrm{w}} = B_{\mathrm{w}} \Delta p_{\mathrm{w}} \tag{1}$$

where B_{w} is the membrane permeability, which is a function of the applied temperature and the membrane properties such as pore size and effective porosity. This is proportional to the porosity and inversely proportional to the thickness and pore tortuosity.

The diffusion of non-condensable gases from the aqueous feed solution across the membrane can be neglected, as it is very small compared to the water vapor flux.

Eq. (1) can be simplified and rewritten depending on the considered MD configuration as will be explained in the next section.

The hydrophobic character of the used membranes as well as the proper use of the MD configuration permits to achieve very high salts rejection. Close to 100 % separation factors, α, were obtained when aqueous solutions of salts were employed as feed.
The separation factor, α, is calculated using the following expression:

$$\alpha = \left(1 - \frac{C_{\mathrm{b,p}}}{C_{\mathrm{b,f}}}\right) 100 \tag{2}$$

where $C_{\mathrm{b,p}}$ and $C_{\mathrm{b,f}}$ are the salts concentration in the permeate and in the bulk feed solution, respectively.

The concentrations of both permeate and feed solutions are determined at a temperature of 20 ºC, by a calibrated electrical conductivity meter (i.e. electrical conductivity *vs.* solute concentration). Temperature effect should be considered during the calibration of the electrical conductivity sensor.

Heat transfer:

The heat transfer is described by three steps: 1)- heat transfer through the feed boundary layer, 2)- heat transfer though the membrane and 3)- heat transfer through the permeate boundary layer depending on the considered MD configuration.

The total heat flux through the membrane, Q_{m}, is due to two mechanisms: 1)- conduction across the membrane material and its gas filled pores (Q_{c}), and 2)- latent heat associated to the water vapor molecules (Q_{v}). Therefore, the balance of energy is expressed as:

$$Q_{\mathrm{m}} = Q_{\mathrm{c}} + Q_{\mathrm{v}} \tag{3}$$

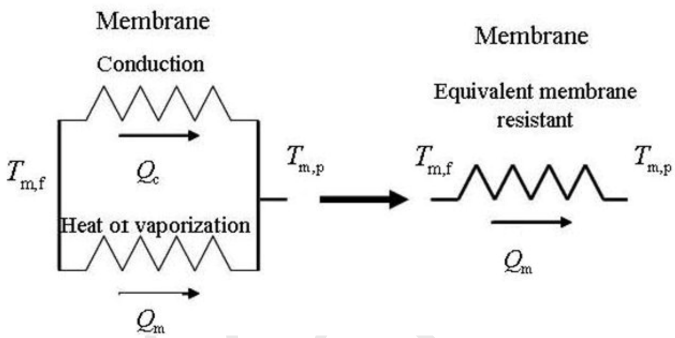

Figure 2. Heat transfer resistances of the membrane

The following integrated equation is normally used.

$$Q_{\mathrm{c}} = \frac{k_{\mathrm{m}}}{\delta}(T_{\mathrm{m,f}} - T_{\mathrm{m,p}}) \tag{4}$$

where δ is the membrane thickness and k_{m} is the thermal conductivity of the membrane. Various models have been considered to calculate k_{m}. In general the following expression has been used.

$$k_{\mathrm{m}} = \varepsilon\ k_{\mathrm{g}} + (1-\varepsilon)k_{\mathrm{p}} \tag{5}$$

where k_{p} is the thermal conductivity of the material forming the membrane matrix and k_{g} is the thermal conductivity of the gas filling the membrane pores.

The term Q_{v} is defined as:

$$Q_{\mathrm{v}} = J_{\mathrm{w}} \Delta H_{\mathrm{v,w}} \tag{6}$$

where $\Delta H_{v,w}$ is the evaporation enthalpy of water at the absolute temperature T of the transmembrane flux J_w.

Typically between 50 to 80 % is consumed as latent heat for water vapor production that is the useful heat (Q_v), while the remainder is lost by thermal conduction (Q_c).

The heat loss Q_c becomes less significant at high operating feed temperatures and the thermal efficiency, η, of a MD process defined by means of Eq. (7) is high.

$$\eta\ (\%) = \frac{Q_v}{Q_v + Q_c} \text{x}100 \qquad (7)$$

In Eq. (7), the heat used effectively in MD is the latent heat of evaporation associated with the mass flux (J_w), whilst the heat transferred by conduction across the membrane is considered as heat lost.

The first theoretical calculations on MD process, have been reported by Findley et al. in *AIChE J.* (volume 15, page 483) taking into account the membrane thermal conductivity and the film heat transfer coefficients. The study concerns heat and mass transfer of water vapor from a hot salt aqueous solution through a hydrophobic porous membrane to a cooled water condensate. Their experimental studies indicated that the major factor affecting the rates of heat and mass transfer was the diffusion through the stagnant gas (i.e. air) in the membrane pores.

3. MD Configurations

Four different MD configurations have been considered to apply the driving force (Δp_w in Eq. 1). The hot feed side that must be maintained in direct contact with one side of the membrane is similar for all possible modes (Figure 1). Changes are made only in the permeate side. There are four such possibilities as described below.

3.1. Direct Contact Membrane Distillation (DCMD)

An aqueous solution, normally tap or distilled water, colder than the feed aqueous solution is maintained in direct contact with the permeate side of the membrane. Both the feed and permeate aqueous solutions are circulated tangentially to the membrane surfaces. In this MD mode, the transmembrane temperature difference induces the required water vapor pressure difference between both membrane sides. Consequently, water molecules evaporate at the hot liquid/vapor interface, cross the membrane pores in vapor phase and condense in the cold liquid/vapor interface inside the membrane module.

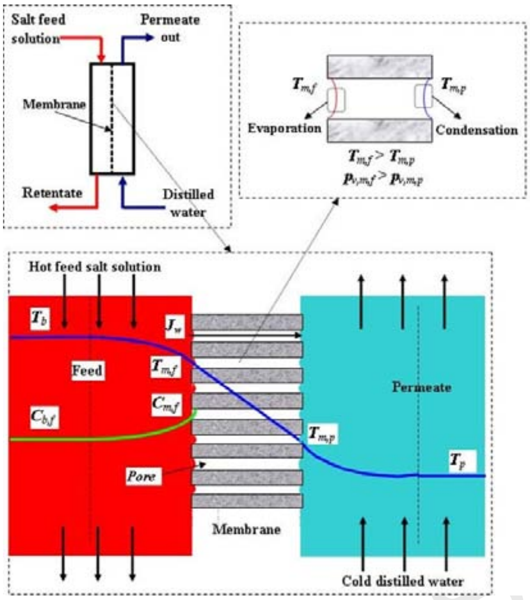

Figure 3. Schema of DCMD configuration

A typical laboratory DCMD system used for both flat sheet, capillary or hollow fiber membranes is presented in Fig. 4. Various membrane modules, plate and frame, shell and tube or spiral wound membrane modules can be employed. Different combinations in series or parallel (i.e. array of DCMD modules) can also be considered.

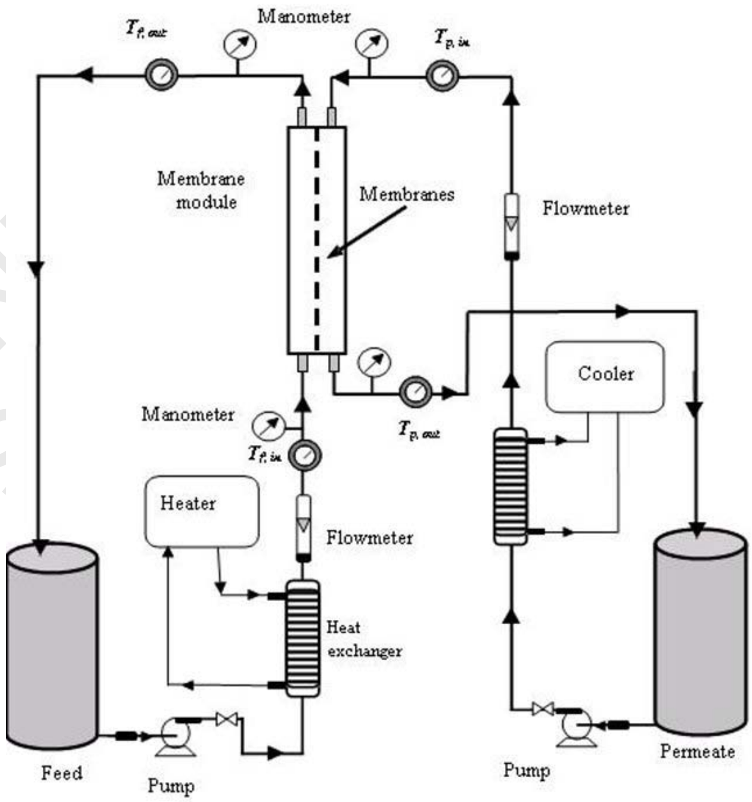

Figure 4. Typical DCMD system used for desalination

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K. Ohta, I. Hayano, T. Okabe, T. Goto, S. Kimura, H. Ohya, (1991) Membrane distillation with fluoro-carbon membranes, *Desalination* 81, 107-115. [This paper is about the application of a partially hydrophilic fluoro-carbon composite membrane for sea water desalination. Comparison of the fluoro-carbon membrane with the silicone membrane revealed that the permeability and thermal efficiency of the fluoro-carbon membrane were superior to those of the silicone membrane].

K. Schneider, W. Holz, R. Wollbeck, (1988) Membranes and modules for transmembrane distillation, *J. Membrane Sci*., 39, 25-42. [In this paper it is proved that aqueous solutions can be concentrated and pure water prepared via MD termed previously a thermal membrane separation process].

K.W. Lawson, D.R. Lloyd, (1996) Membrane distillation. I. Module design and performance evaluation using vacuum membrane distillation, *J. Membrane Sci*., 120, 111-121. [In this paper pure water VMD experiments were performed to evaluate the heat and mass transfer boundary layer resistances in a flat sheet membrane module. This paper also examines a new complete VMD model based on the dusty-gas model, which accounts for both Knudsen and viscous mass transport across the membrane. The new model was used to predict the performance of VMD with pure water and ethanol-water solutions].

K.W. Lawson, D.R. Lloyd, (1996) Membrane distillation: II. Direct contact MD, *J. Membrane Sci*., 120, 123-133. [DCMD process was used to measure the permeability parameter associated with the molecular diffusion in MD using pure water as feed. Dusty-gas model of gas transport through porous media has been applied showing good agreement with the experimental results. The obtained DCMD fluxes were two to three times higher than those reported in the literature for either DCMD or reverse osmosis RO].

K.W. Lawson, D.R. Lloyd, (1997) Review: membrane distillation, *J. Membrane Sci*., 124, 1-25. [This paper provides a state-of-the-art review of MD. An introduction to the terminology and fundamental concepts associated with MD as well as a historical review of the developments in MD are presented. Membrane properties, transport phenomena, and module design are discussed in detail. A critical evaluation of the MD literature is incorporated throughout this review].

K.Y. Wang, S.W. Foo, T.S. Chung, (2009) Mixed matrix PVDF hollow fiber membranes with nanoscale pores for desalination through direct contact membrane distillation, *Ind. Eng. Chem. Res.*, 48, 4474-4483. [This presents novel mixed matrix PVDF hollow fiber membranes prepared for desalination by DCMD using the dry/jet wet spinning method].

K.Y. Wang, T.S. Chung, M. Gryta, (2008) Hydrophobic PVDF hollow fiber membranes with narrow pore size distribution and ultra-skin for the fresh water production through membrane distillation, *Chem. Eng. Sci*., 63, 2587-2594. [PVDF hollow fiber asymmetric membranes with narrow pore size distributions have been fabricated by dry/jet wet spinning method. A permeate flux as high as 41.5 kg/m_2.h. with a 99.99% salt rejection factor have been obtained].

L. Basini, G. D´Angelo, M. Gobbi, G.C. Sarti, C. Gostoli, (1987) A desalination process through sweeping gas membrane distillation, *Desalination*, 64, 245-257. [Desalination by SGMD has been performed in this investigation using tubular porous hydrophobic membranes. A comprehensive mathematical model is also presented and the theoretical results were compared with the experimental ones].

L. Carlsson, (1983) The new generation in sea water desalination: SU membrane distillation system, *Desalination*, 45, 221-222. [A new patented process for desalination of sea water has been developed by Svenska Utvecklings AB (SU), the Swedish National Development Co. The system is called SU Membrane Distillation System. The modules can be combined in series to meet the need for larger capacities. The standard modules in large scale systems was claimed to produce about 5 m^3 per 24 h period and module].

L. Martínez, F.J. Florido-Díaz, A. Hernández, P. Prádanos, (2002) Characterization of three hydrophobic porous membranes used in membrane distillation: Modelling and evaluation of their water vapor permeabilities, *J. Membrane Sci.*, 203, 15-27. [This work is focused on the development of a theoretical model for DCMD process considering pore size distributions of three hydrophobic porous membranes. The common model of cylindrical capillaries was assumed for the membrane and flux equations including both diffusive and viscous mechanisms for gas transport in pores have been used].

L. Martínez, F.J. Florido-Díaz, A. Hernández, P. Prádanos, (2003) Estimation of vapor transfer coefficient of hydrophobic porous membranes for applications in membrane distillation, *Sep. & Pur. Tech*., 33, 45-55. [This estimates, based on the dusty gas model, water vapour transfer coefficients of porous hydrophobic membranes used in DCMD].

L. Martínez-Diez, M.I. Váquez-González, (2000) A method to evaluate coefficients affecting flux in membrane distillation, *J. Membrane Sci*., 173, 225–234. [This paper presents a method to evaluate the membrane mass transfer coefficient, the membrane heat transfer coefficient and the boundary layer heat transfer coefficient in a DCMD system].

L. Martínez-Diez, M.I. Vázquez-González, (1998) Effect of polarization on mass transport through hydrophobic porous membranes, *J. Ind. Eng. Chem. Res*. 37, 4128–4135. [In this work the temperature polarization and concentration polarization have been studied in DCMD using porous hydrophobic membranes].

L. Martínez-Diez, M.I. Vázquez-González, (1999) Temperature and concentration polarization in membrane distillation of aqueous salt solutions, *J. Membr. Sci.*, 156, 265–273. [This paper presents both experimental and theoretical DCMD studies using aqueous salts solutions. The objective is to analyze the temperature and concentration polarization effects].

L.F. Dumée, K. Sears, J. Schütz, N. Finn, C. Huynh, S. Hawkins, M. Duke, S. Gray, (2010) Characterization and evaluation of carbon nanotube Bucky-Paper membranes for direct contact membrane distillation, *J. Membrane Sci*., 351, 36-43. [New membranes supported by carbon nanotube (CNT) Bucky-Paper have been proposed for desalination by DCMD].

M. Gryta, (2005) Long-term performance of membrane distillation process, *J. Membrane Sci*., 265, 153-159. [DCMD experiments over 3 years have been considered in a system containing shell and tube hydrophobic capillary polypropylene membrane module. Tap water and permeate from RO process have been used as feed. No membrane wetting has been detected when using permeate from RO. However, precipitation of $CaCO_3$ on the membrane surface was observed when tap water was used directly as a feed with a partial wetting of the membrane].

M. Khayet, (2008) *Membrane distillation*, In: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura, (Eds.), Advanced Membrane Technology and Applications, John Wiley & Sons, Inc, New York, NY, USA, Ch. 5, pp. 297-370. [The chapter book offers a comprehensive MD state-of-the-art review covering an extended historical survey of MD, a wide range of commercial membranes, MD membrane engineering, their MD performance, transport mechanisms, experimental and theoretical modelling of different MD configurations as well as developments in MD].

M. Khayet, A. Velázquez, J.I. Mengual, (2004) Modelling mass transport through a porous partition: Effect of pore size distribution, *J. Non-Equilib. Thermodyn.*, 29, 279-299. [A new model for DCMD process has been developed taking into consideration the pore size distribution of porous hydrophobic membranes and the gas transport mechanisms through membrane pores based on the kinetic theory of gases. Different commercial membranes have been considered].

M. Khayet, A.O. Imdakm, T. Matsuura, (2010) Monte Carlo simulation and experimental heat and mass transfer in direct contact membrane distillation, *Int. J. Heat & Mass Transfer*, 53, 1249-1259. [A Monte Carlo (MC) simulation model is developed to study heat and mass transfer through hydrophobic membranes applying DCMD process. The membrane pore space is described by a three-dimensional network model of inter-connected cylindrical pores with distributive pore size. The simulated results were compared with the experimental ones of different membranes and the comparisons were found to be in excellent qualitative and quantitative agreement].

M. Khayet, J.I. Mengual, G. Zakrzewska-Trznadel, (2005) Direct contact membrane distillation for nuclear desalination. Part I. Review of membranes used in membrane distillation and methods for their characterization, *Int. J. Nuclear Desalination*, 1, 435–449. [The paper reviews the membranes commonly used in MD as well as the methods used for their characterization].

M. Khayet, J.I. Mengual, T. Matsuura, (2005) Porous hydrophobic/hydrophilic composite membranes: Application in desalination using direct contact membrane distillation, *J. Membrane Sci*., 252, 101-113. [This paper is focused on the fabrication and characterization of SMMs/polyetherimide flat sheet membranes in desalination].

M. Khayet, K.C. Khulbe, T. Matsuura, (2004) Characterization of membranes for membrane distillation by atomic force microscopy and estimation of their water vapor transfer coefficients in vacuum membrane distillation process, *J. Membrane Sci*., 238, 199-211. [Different types of fabricated PVDF flat sheet membranes and commercial membranes have been characterized by atomic force microscopy (AFM) to determine the pore size and roughness parameters. A theoretical model has been developed for VMD and the water vapour permeabilities of the membranes have been estimated and compared to experimental ones].

M. Khayet, M.P. Godino, J.I. Mengual, (2001) Modelling transport mechanism through a porous partition, *J. Non-Equilb. Thermodyn.*, 26, 1-14. [In this paper the mechanisms of mass transport through the pores of hydrophobic membranes used in DCMD have been analyzed using temperature polarization effects and the gas transport mechanisms through membrane pores based on the kinetic theory of gases. Different commercial membranes have been considered].

M. Khayet, M.P. Godino, J.I. Mengual, (2002) Thermal boundary layers in sweeping gas membrane distillation processes, *AIChE J.*, 48, 1488–1497. [SGMD process was analyzed in a plate and frame membrane module, and a method clarifying the contribution of the liquid and gas boundary layers separately was developed. The effects of different SGMD operating parameters on temperature polarization coefficients and permeate flux have been studied].

M. Khayet, M.P. Godino, J.I. Mengual, (2003) Possibility of nuclear desalination through various membrane distillation configurations: a comparative study, *Int. J. Nuclear Desalination*, 1, 30-46. [The 3 MD configurations, DCMD, SGMD and VMD have been studied using the same shell-and-tube capillary membrane module and NaCl aqueous solutions. A comparative study was made proposing MD as an alternative for liquid nuclear waste treatment].

M. Khayet, M.P. Godino, J.I. Mengual, (2003) Theoretical and experimental studies on desalination using sweeping gas membrane distillation method, *Desalination*, 157, 297-305. [In this paper SGMD was investigated as a possible technique for desalination using a shell-and tube polypropylene membrane module. The effects of different process parameters on the distillate flux have been investigated and a theoretical model that considers the heat and mass transfer through microporous hydrophobic membranes as well as the temperature and concentration polarization effects was developed and validated with the experimental data of distilled water and sat aqueous feed solutions].

M. Khayet, M.P. Godino, J.I. Mengual, (2004) Study of asymmetric polarization in direct contact membrane distillation, *Sep. Sci. & Tech.*, 39, 125-147. [The objective of this study was to analyze the polarization phenomena in each side of a microporous hydrophobic membrane using DCMD].

M. Khayet, P. Godino, J.I. Mengual, (2000) Nature of flow on sweeping gas membrane distillation, *J. Membrane Sci.*, 170, 243-255. [Based on the kinetic theory of gases through porous media, the physical nature of mass transport through the pore of hydrophobic membranes used in SGMD has been investigated using mean pore size. It was found that a combined Knudsen/molecular diffusion type of flow is the responsible of mass transport].

M. Khayet, P. Godino, J.I. Mengual, (2000) Theory and experiments on sweeping gas membrane distillation, *J. Membrane Sci*., 165, 261-272. [A theoretical model is presented that describes SGMD in a plate and frame membrane module emphasizing the importance of the heat fluxes in the directions parallel and perpendicular to the membrane surface and permits to obtain the temperature profiles inside the fluid phases. The theoretical predictions of the model have been applied to the obtained results and the accordance was considered good].

M. Khayet, T. Matsuura, (2001) Preparation and characterization of polyvinylidene fluoride membranes for membrane distillation, *Ind. & Eng. Chem. Res.*, 40, 5710-5718. [Various PVDF flat sheet membranes have been fabricated by the phase inversion technique using as non-solvent additive water. The membranes exhibit different porosities and pore sizes and used for VOCs removal from water by VMD configuration].

M. Khayet, T. Matsuura, (2003) Application of surface modifying macromolecules for the preparation of membranes for membrane distillation, *Desalination*, 158, 51-56. [This paper is the first paper in the series of fabrication and application of novel porous composite hydrophobic/hydrophilic membranes for DCMD fabricated by phase inversion method using surface modifying macromolecules, SMMs. Characteristics required by a membrane to be used in MD are outlined].

M. Khayet, T. Matsuura, (2004) Pervaporation and vacuum membrane distillation processes: Modeling and experiments, *AIChE J.*, 50, 1697-1712. [In this paper two separation processes, pervaporation (PV) and VMD were studied using fabricated PVDF flat-sheet membranes for the separation of chloroform–water mixtures. A new general model for VMD process that considers the pore size distribution and the solution/diffusion contribution through nonporous membrane portion was proposed. The contribution of each mechanism was analyzed. A comparative study was made between both membrane separation technologies].

M. Khayet, T. Matsuura, J.I. Mengual, (2005) Porous hydrophobic/hydrophilic composite membranes: Estimation of the hydrophobic-layer thickness, *J. Membrane Sci.*, 266, 68-79. [A theoretical model has been developed to estimate the thickness of the hydrophobic layer of porous composite hydrophobic/hydrophilic membranes fabricated using SMMs. DCMD process and temperature polarization effect have been considered].

M. Qtaishat, D. Rana, M. Khayet, T. Matsuura, (2009) Preparation and characterization of novel hydrophobic/hydrophilic polyetherimide composite membranes for desalination by direct contact membrane distillation, *J. Membrane Sci*., 327, 264-273. [A study on the effects of some casting conditions on the characteristics and DCMD performance of SMMs/polyetherimide flat sheet membranes].

M. Qtaishat, D. Rana, T. Matsuura, M. Khayet, (2009) Effect of surface modifying macromolecules stoichiometric ratio on composite hydrophobic/hydrophilic membranes characteristics and performance in direct contact membrane distillation, *AIChE J*., 55, 3145-3151. [This paper describes the effects of the stoichimetric ratio of SMMs on the characteristics and DCMD performance of porous composite hydrophobic/hydrophilic membranes].

M. Qtaishat, M. Khayet, T. Matsuura, (2009) Guidelines for preparation of higher flux hydrophobic/hydrophilic composite membranes for membrane distillation, *J. Membrane Sci*., 329, 193-200. [A mathematical model is presented in this paper to validate the use of hydrophobic/hydrophilic composite membrane concept in DCMD as well as to give guidelines for preparation of highly efficient DCMD membranes].

M. Qtaishat, M. Khayet, T. Matsuura, (2009) Novel porous composite hydrophobic/hydrophilic polysulfone membranes for desalination by direct contact membrane distillation, *J. Membrane Sci*., 341, 139-148. [Other porous composite hydrophobic/hydrophilic membranes have been fabricated in this study using another host polymer, polysulfone and applied in desalination by DCMD].

M. Qtaishat, T. Matsuura, M. Khayet, K.C. Khulbe, (2009) Comparing the desalination performance of SMM blended polyethersulfone to SMM blended polyetherimide membranes by direct contact membrane distillation, *Desalination and Water Treatment*, 5, 91-98. [The DCMD performances of SMMs porous composite hydrophobic/hydrophilic membranes prepared with different host polymers polyethersulfone and polyeterimide have been investigated in this paper and a comparison study has been carried out].

M. Tomaszewska, (1996) Preparation and properties of flat-sheet membranes from polyvinylidene fluoride for membrane distillation, *Desalination*, 104, 1-11. [In this work Flat sheet PVDF membranes have been prepared by the phase inversion method with different parameters for DCMD process].

M. Tomaszewska, M. Gryta, A.W. Morawski, (1998) The influence of salt in solution on hydrochloric acid recovery by membrane distillation, *Sep. Purif. Technol*., 14, 183–188. [This study presents the concentration and recovery of HCl by DCMD using PP capillary membrane module. The effect of acid concentration and salt present in the feed on HCl permeate flux was systematically studied].

M.C. García-Payo, C.A. Rivier, I.W. Marison, U.V. Stockar, (2002) Separation of binary mixtures by thermostatic sweeping gas membrane distillation. II. Experimental results with aqueous formic acid solutions, *J. Membrane Sci*., 198, 197-210. [Aqueous solutions of formic acid have been experimentally investigated in a thermostated SGMD membrane module. The effects of the relevant process parameters on the permeate flux and selectivity have been studied. The permeate fluxes and selectivity for aqueous formic acid mixtures have been calculated using the mathematical model previously described in Rivier et al. (2002). The model predictions were compared with the experimental data and good agreements were observed].

M.C. García-Payo, M. Essalhi, M. Khayet, (2009) Preparation and characterization of PVDF-HFP copolymer hollow fiber membranes for membrane distillation, *Desalination*, 245, 469-473. [In this paper poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP) hollow fiber membranes were prepared by the dry/wet spinning technique at different copolymer concentrations. Different techniques have been applied to study the structural and morphological characteristics of the hollow fibers].

M.C. García-Payo, M. Essalhi, M. Khayet, (2010) Effects of PVDF-HFP concentration on membrane distillation performance and structural morphology of hollow fiber membranes, J. Membrane Sci., 347, 209-219. [In this work PVDF-HFP hollow fiber membrane were fabricated for MD. The effects of PVDF-HFP content in the spinning solutions were studied by measuring the water entry pressure, porosity and DCMD permeate flux of the hollow fiber membranes].

M.E. Findley, (1967) Vaporization through porous membranes, *Ind. & Eng. Chem. Process Des. Dev*., 6, 226-237. [First paper published on MD using porous membranes].

M.E. Findley, V.V. Tanna, Y.B. Rao, C.L. Yeh, (1969), Mass and heat transfer relations in evaporation through porous membranes, *AIChE J.* 15, 483. [This paper is one of the first papers published on MD and it is focused on both experimental and theoretical calculations. The study concerns heat and mass transfer of water vapour from a hot salt aqueous solution through a hydrophobic porous membrane to a cooled water condensate. The membrane thermal conductivity and the film heat transfer coefficients in the feed and permeate sides have been considered in the theoretical model. Their experimental studies indicated that the major factor affecting the rates of heat and mass transfer was the diffusion through the stagnant gas (i.e. air) in the membrane pores. An empirical correction related to the possible internal condensation and diffusion along the membrane surfaces has been considered to perform the calculations].

M.M. Teoh, T.S. Chung, (2009) Membrane distillation with hydrophobic macrovoid-free PVDF-PTFE hollow fiber membranes, *Sep. Purf. Tech*., 66, 229-236. [In this work hydrophobic polyvinylidene fluoride–polytetrafluoroethylene (PVDF–PTFEPVDF–PTFE) hollow fiber membranes were fabricated for desalination via DCMD. PTFE particles (<1 μm) have been introduced into the PVDF polymeric matrix to enhance the hydrophobicity of the membranes].

M.N. Chernyshov, G.W. Meindersma, A.B. De-Haan, (2003) Modelling temperature and salt concentration distribution in membrane distillation feed channel, *Desalination*, 157, 315–324. [The paper attempts to modify an ultrafiltration model to be applied for a flat sheet AGMD module. The developed method allows solving hydrodynamic and heat transport equations without additional assumptions for decoupling the equations with permeation taken into account. Velocity and temperature distributions inside the membrane feed channel were obtained, as well as the concentration profiles of a sparingly soluble salt (barium sulfate)].

M.S. El-Bourawi, Z. Ding, R. Ma, M. Khayet, (2006) A framework for better understanding membrane distillation separation process, *J. Membrane Sci*., 285, 4-29. [A review paper on MD attempting to establish a framework for better understanding MD process considering all possible solutions developed so far to overcome the barriers of MD industrialization. The effects of different MD operating variables and membrane parameters on the permeate flux, membrane fouling and long-term MD performance are reviewed].

N. Couffin, C. Cabassud, V. Lahoussine-Turcaud, (1998) A new process to remove halogenated VOCs for drinking water production: vacuum membrane distillation, *Desalination*, 117, 233-245. [Removal of halogenated VOCs like chloroform, trichloroethylene (TCE) and tetrachloroethylene, from water has been carried out using VMD process and very dilute solutions].

P. A. Hogan, Sudjito, A. G. Fane, G. L. Morrison, (1991) Desalination by solar heated membrane distillation, *Desalination*, 81, 81–90. [This paper examines the feasibility of a solar powered MD plant for the supply of domestic drinking water in the arid/rural regions of Australia. Recovery of latent heat of vaporization has been taken into consideration and preliminary tests have shown the plant capable of achieving the required production capacity].

R.W. Schofield, A.G. Fane, C.J.D. Fell, (1987) Heat and mass transfer in membrane distillation, *J. Membrane Sci*., 33, 299-313. [Useful equations for heat and mass transfer in MD have been developed and tested experimentally].

R.W. Schofield, A.G. Fane, C.J.D. Fell, R. (1990) Gas and vapor transport through microporous membranes: II. Membrane Distillation, *J. Membrane Sci.*, 53, 173-185. [Deaeration was applied in DCMD observing an increase of 50% of the permeate flux. A new theoretical model shows that under these conditions, membrane permeability increased by around seven-fold, but temperature polarisation decreased the thermal driving force by five-fold. Heat loss by conduction across the membrane was shown to decrease with deaeration].

R.W. Schofield, A.G. Fane, C.J.D. Fell, R. Macoun, (1990) Factors affecting flux in membrane distillation, *Desalination*, 77, 279-294. [This paper summarises a model of the DCMD process as well as the factors affecting permeate flux including deaeration. Both salt and sucrose aqueous solutions at concentrations up to 25 and 30% respectively have been considered].

S. Al-Obaidani, E. Curcio, F. Macedonio, G.D. Profio, H. Al-Hinai, E. Drioli, (2008) Potential of membrane distillation in seawater desalination: thermal efficiency, sensitivity study and cost estimation, *J. Membrane Sci*., 323, 85-98. [In this work, an extensive analysis on DCMD performance was developed to estimate the mass flux and the heat efficiency, considering transport phenomena, membrane structural properties and most sensitive process parameters, with the aim to provide optimization guidelines for materials and methods. Exergy analysis, sensitivity study and economical evaluation were carried out to assess the feasibility of DCMD process].

S. Bandini, A. Saavedra, G.C. Sarti, (1997) Vacuum membrane distillation: experiments and modeling, *AIChE J.* 43-2, 398-408. [In this paper both experimental and theoretical studies have been conduced using VMD process for the VOCs removal from water].

S. Bonyadi, T.S. Chung, (2007) Flux enhancement in membrane distillation by fabrication of dual layer hydrophilic-hydrophobic hollow fiber membranes, *J. Membrane Sci*., 306, 134-146. [For the first time, co-extrusion was applied for the fabrication of dual layer hydrophilic–hydrophobic hollow fiber membranes for DCMD process. The effect of different non-solvents on the morphology of the PVDF membranes was investigated. Hydrophobic and hydrophilic clay particles were incorporated into the outer and inner layer dope solutions, respectively. Permeate fluxes as high as 55 kg/m^2 h were achieved].

S. Kimura, S. Nakao, (1987) Transport phenomena in membrane distillation, *J. Membrane Sci*., 33, 285-298. [The characteristics of polytetrafluoroethylene membranes used in MD were measured using both non-volatile and volatile solutes in water].

S.I. Andersson, N. Kjellander, B. Rodesjö, (1985) Design and field tests of a new membrane distillation desalination process, *Desalination*, 56, 345-354. [In this paper it is reported that a theoretical research and laboratory tests have resulted in a desalination module design. The produced modules have been subject to field tests].

S.T. Hsu, K.T. Cheng, J.S. Chiou, (2002) Seawater desalination by contact membrane distillation, *Desalination*, 143, 279-287. [This paper is focused on membrane fouling reported as one of the major obstacles in MD claiming that this is the reason why MD still cannot successfully compete with other conventional seawater desalination technologies. In this study, both the NaCl solution and real seawater were treated by MD to investigate the differences in permeate flux, product water quality and membrane fouling. An ultrasonic cleaning technique is found to be an effective way to restore the permeate flux of MD membranes].

T. Cath, V.D. Adams, A.E. Childress, (2004) Experimental study of desalination using direct contact membrane distillation: a new approach to flux enhancement, *J. Membrane Sci.*, 228, 5-16. [New MD configurations and a new membrane module were investigated to improve water desalination. Vacuum enhanced DCMD have been reconsidered].

Y. Fujii, S. Kigoshi, H. Iwatani, M. Aoyama, (1992) Selectivity and characteristics of direct contact membrane distillation type experiment: I. Permeability and selectivity through dried hydrophobic fine porous membranes, *J. Membrane Sci*., 72, 53-72. [This presents DCMD permeability and ethanol selectivity of fabricated hydrophobic porous membranes. Polarization of temperature and concentration and heat transport characteristics are also studied].

Y. Fujii, S. Kigoshi, H. Iwatani, M. Aoyama, Y. Fusaoka, (1992) Selectivity and characteristics of direct contact membrane distillation type experiment: II. Membrane treatment and selectivity increase, *J. Membrane Sci*., 72, 73-89. [The selectivity and characteristics of coated and uncoated PVDF hollow fiber membranes have been investigated considering DCMD process. Some coating materials and heat treatment of the PVDF membrane increased the selectivity].

Y. Kong, X. Lin, Y. Wu, J. Cheng, J. Xu, (1992) Plasma polymerization of octafluorocyclobutane and hydrophobic microporous composite membranes for membrane distillation, *J. Appl. Polym. Sci*., 46, 191-199. [This study is on the application of modified membranes by plasma polymerization of octafluorocyclobutane in MD].

Y. Wu, E. Drioli, (1989) The behaviour of membrane distillation of concentrated aqueous solution, *Water Treat.*, 4, 399–415. [This is the first paper reported on possible crystallization of salts solutes when treating high concentrated aqueous solutions by MD leading to membrane distillation crystallization, MDC].

Y. Wu, Y. Kong, X. Lin, W. Liu, J. Xu, (1992) Surface-modified hydrophilic membranes in membrane distillation, *J. Membrane Sci*., 72, 189-196. [In this work, hydrophilic cellulose acetate and cellulose nitrate membranes were modified into hydrophobic membranes by radiation grafting polymerization and plasma polymerization, and used in MD studies successfully].

Z. Al Suleimani, V.R. Nair, (2000) Desalination by solar-powered reverse osmosis in a remote area of the

Sultanate of Oman, Applied Energy, 65, 367-380. [Average cost of a solar-powered RO desalination plant has been estimated for brackish ground water over the 20 year life time of the equipment. It was demonstrated that solar-powered RO systems are particularly appropriate to remote locations that have limited or no access to supply services such as fuel, power or potable water].

Z.D. Hendren, J. Brant, M.R. Wiesner, (2009) Surface modification of nanostructured ceramic membranes for direct contact membrane distillation, *J. Membrane Sci*., 331, 1-10. [This work is on the application of different surface treatments for making ceramic membranes hydrophobic and suitable for application in DCMD].

Biographical Sketch

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- Director of the: *Membranes and Renewable Energy Group* (University Complutense of Madrid, UCM).
- Ph. D. (Physics): University Complutense of Madrid (1997).
- B.Sc. (Physics): University Cadi Ayyad of Marrakech, Morocco, (1990).
- Visiting Researcher at the Industrial Membrane Research Institute (2000/2001) in Ottawa, Canada.
- Visiting Researcher in various International Research Institutions (Institute of Nuclear Chemistry and Technology in Warsaw, Poland; Centre for Clean Water Technologies, University of Nottingham, UK, etc.)
- Author of more than 100 scientific papers to various international refereed journals, including among others, Journal of Membrane Science and Desalination. Various book chapters and 2 books.
- Author of 2 patents in the field of Membrane Science and Technology.
- Grants of various national and international projects.
- Supervision of various research studies (Ph.D. thesis, master and undergraduate students).
- Member of the European Desalination Society (EDS), European Membrane Society (EMS), North American Membrane Society (NAMS) and Real Sociedad Española de Física (RSEF).
- Conferences and lectures in various International Institutions for example in IBM Research, Zurich, University of Ottawa, University of Nottingham, etc.
- Participation in various national and international congresses and workshops.
- Referee of Journal of Membrane Science, Desalination, Polymer, Separation Science and Technology, International Journal of Heat and Mass Transfer, Industrial & Engineering Chemistry Research, etc.
- Member of the Editorial Board of the Journals: Desalination; Applied Membrane Science & Technology, Membrane Water Treatment (MWT), Polymers, and Membranes.