

Introduction to Membrane Distillation

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Membrane Science and Technology has made a tremendous progress during the last decades and membrane processes have become competitive to the conventional separation methods in a wide variety of applications. Different membrane separation processes have been developed during the past half century and new membrane applications are constantly emerging from industries or from academic and government laboratories. Membrane Distillation (MD) is one of the emerging *non-isothermal* membrane separation processes known for about 47 years and still needs to be developed for its adequate industrial implementation. It refers to a thermally driven transport of vapour through non-wetted porous hydrophobic membranes, the driving force being the vapour pressure difference between the two sides of the membrane pores. As in other membrane separation processes, the driving force is the chemical potential difference through the membrane thickness. Simultaneous heat and mass transfer occur in this process

and, as will be explained later, different MD configurations such as (i) direct contact membrane distillation, (ii) sweeping gas membrane distillation, (iii) vacuum membrane distillation and (iv) air gap membrane distillation, can be used for various applications (desalination, environmental/waste cleanup, water-reuse, food, medical, etc.)

The involved simultaneous heat and mass transfer phenomena through the membrane, the different MD configurations and the various MD applications make MD attractive within the academic community as a kind of didactic application. Additionally, the possibility of using waste heat and/or alternative energy sources, such as solar and geothermal energy, enables MD to be combined with other processes in integrated systems, making it a more promising separation technique for an industrial scale. Furthermore, the lower temperatures than in the conventional distillation, the lower operating hydrostatic pressures than in the

pressure-driven processes (i.e., reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF)), the less demanding membrane mechanical properties and the high rejection factors achievable especially during water treatment containing non-volatile solutes make MD more attractive than any other popular separation processes.

Benefiting from the low temperature and transmembrane hydrostatic pressure required to perform MD operations, several approaches to make the MD a viable separation technique were proposed. These approaches ranged from finding new areas of MD applicability and the cooperation of MD with other processes as a pre-treatment or post-treatment step, to researches devoted to preparation of membranes together with MD modules and studies of factors affecting MD production associated with the application of some enhancement techniques.

MD has been the subject of worldwide academic studies by many experimentalists and theoreticians. Unfortunately, from the commercial stand point, MD has gained only little acceptance and is yet to be implemented in the industry. The major barriers include MD membrane and module design, membrane pore wetting, low permeate flow rate and flux decay as well as uncertain energetic and economic costs.

CONCEPT OF MD

MD is a process mainly suited for applications in which water is the major component present in the feed solution. As stated earlier, MD is a thermally driven process, in which only vapour molecules are transported through porous hydrophobic membranes. The liquid feed to be treated by MD must be maintained in direct contact with one side of the membrane without penetrating its dry pores unless a transmembrane pressure higher than the membrane liquid entry pressure (i.e., breakthrough

pressure, *LEP*, explained in Chapter 8) is applied. The hydrophobic nature of the membrane prevents liquid solutions from entering its pores due to the surface tension forces. As a result, liquid/vapour interfaces are formed at the entrances of the membrane pores. Various MD modes differing in the technology applied to establish the driving force can be used. The differences between them are localized only in the permeate side as can be seen in Fig. 1.1.

The MD driving force may be maintained with one of the four following possibilities applied in the permeate side:

- i) An aqueous solution colder than the feed solution is maintained in direct contact with the permeate side of the membrane giving rise to the configuration known as Direct Contact Membrane Distillation (DCMD). Both the feed and permeate aqueous solutions are circulated tangentially to the membrane surfaces by means of circulating pumps or are stirred inside the membrane cell by means of a magnetic stirrer. In this case the transmembrane temperature difference induces a vapour pressure difference. Consequently, volatile molecules evaporate at the hot liquid/vapour interface, cross the membrane pores in vapour phase and condense in the cold liquid/vapour interface inside the membrane module. A DCMD with liquid gap is another DCMD variant, in which a stagnant cold liquid, frequently distilled water, is kept in direct contact with the permeate side of the membrane (Fig. 1.1).
- ii) Vacuum is applied in the permeate side of the membrane module by means of a vacuum pump. The applied vacuum pressure is lower than the saturation pressure of volatile molecules to be separated from the feed solution. In this case, condensation takes place outside of the membrane module. This MD configuration is termed Vacuum Membrane Distillation (VMD).

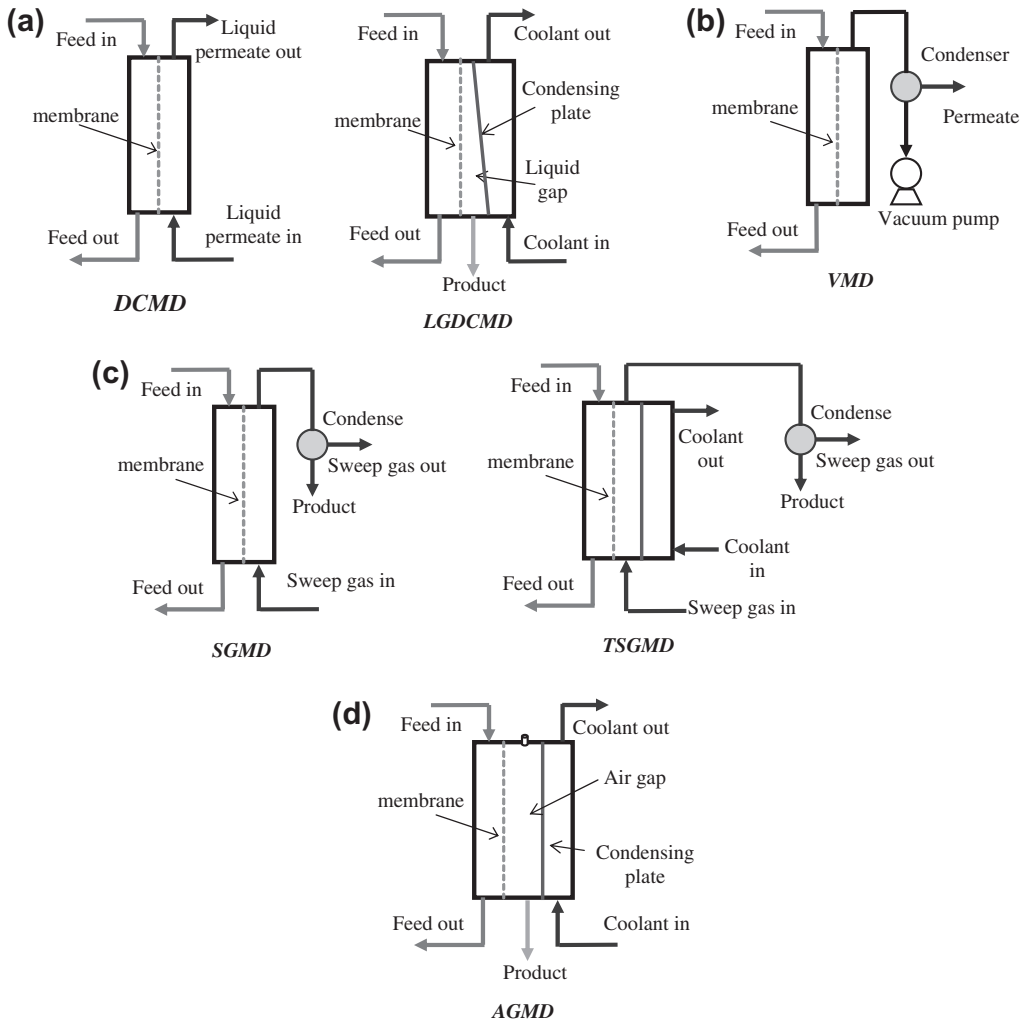


FIGURE 1.1 MD process configurations: (a) DCMC and DCMC with liquid gap; (b) VMD; (c) SGMD and thermostatic SGMD; (d) AGMD.

iii) A stagnant air gap is interposed between the membrane and a condensation surface. In this case, the evaporated volatile molecules cross both the membrane pores and the air gap to finally condense over a cold surface inside the membrane module. This MD configuration is called Air Gap Membrane Distillation (AGMD).

iv) A cold inert gas sweeps the permeate side of the membrane carrying the vapour molecules and condensation takes place outside the membrane module. This type of configuration is termed Sweeping Gas Membrane Distillation (SGMD). In this configuration, due to the heat transferred from the feed side through the membrane,

the sweeping gas temperature in the permeate side increases considerably along the membrane module length. A SGMD variant termed Thermostatic Sweeping Gas Membrane Distillation (TSGMD) has been proposed recently. In this mode of SGMD the increase in the gas temperature is minimized by using a cold wall in the permeate side.

Each one of the above MD configurations has its advantages and inconveniences for a given application as will be explained later in this book. Two examples are given below:

- i) To solve the problem of heat loss by conduction through the membrane, which leads to relatively low efficiency of the MD process, an air gap was placed inside the membrane module between the permeate side of the membrane and the condensing surface. This reduces considerably both the heat loss by conduction and temperature polarization, thereby improving the separation effect. However, the permeate flux has to overcome the air barrier and therefore it is drastically reduced depending on the effective air gap width. On the other hand, because permeate is condensed on a cold surface rather than directly on membrane surface, AGMD can be applied in fields where the DCMD is limited such as the removal of organic compounds from aqueous solutions.
- ii) Generally, in VMD, membranes of smaller pore size (i.e., less than $0.45\ \mu\text{m}$) than in the other MD configurations are used because in this case vacuum is applied and the risk of pore wetting is high.

NOMENCLATURE IN MD

Various authors involved in MD investigations often abbreviate DCMD term to MD and SGMD is named Membrane Air Stripping

(MAS). To avoid misconceptions the adequate term should be used as explained below.

Following the 1996 International Union of Pure and Applied Chemistry (IUPAC) recommendations [1], the 21st term 'Membrane Distillation' was defined as 'distillation process in which the liquid and gas phases are separated by a porous membrane, the pores of which are not wetted by the liquid phase'. In fact, the term MD comes from the similarity of the MD to conventional distillation as both processes are based on the vapour/liquid equilibrium (VLE) for separation and both processes require heat to be supplied to the feed solution in order to achieve the required latent heat of vapourization. Before the Workshop on Membrane Distillation held in Rome on 5 May 1986, various terms had been used to identify MD, such as transmembrane distillation, thermo-pervaporation, pervaporation, membrane evaporation and capillary distillation.

The terminology for MD was first discussed by the committee formed by six members during the Workshop on Membrane Distillation held in Rome on 5 May 1986: V. Calabro (University della Calabria, Calabria, Italy), A.C.M. Franken (Twente University, Enschede, Netherlands), S. Kimura (University of Tokyo, Tokyo, Japan), S. Ripperger (Enka Membrana, Wuppertal, Germany), G. Sarti (Universita di Bologna, Bologna, Italy) and R. Schofield (University of New South Wales, Kensington, Australia). Terms, definitions and symbols related with MD have been discussed, standardized and lately reported in [2,3].

Mainly, MD should be applied for non-isothermal membrane operations in which the driving force is the partial pressure gradient across the membrane that complies with the following characteristics:

- i) Porous.
- ii) Not wetted by the process liquids.
- iii) Does not alter the VLE of the involved species.

- iv) Does not permit condensation to occur inside its pores.
- v) Is maintained in direct contact at least with the hot feed liquid solution to be treated.

A HISTORICAL SURVEY OF MD

On 3 June 1963, Bodell filed the first MD patent [4] and four years later Findley published the first MD paper in the international journal *Industrial & Engineering Chemistry Process Design Development* [5]. Within the 16 cited references throughout the paper, Findley did not mention the first Patent made by Bodell [4]. Findley used the DCMD configuration using various types of membrane materials (paper hot cup, gum wood, aluminum foil, cellophane, glass fibres, paper plate, diatomaceous earth mat and nylon). Silicone and Teflon have been used as coating materials to achieve the required membrane hydrophobicity. Based on the obtained MD experimental results, Findley outlined the most suitable membrane characteristics needed for a MD membrane discussed in Chapter 2 and stated throughout the paper the following: 'calculations indicate possible economical performance, especially at high temperatures, if high temperature, long life and low cost membrane are obtainable'. Findley also suggested the possibility of using infinite-stage flash evaporation through porous membranes.

In 1967 another U.S. patent was filed by Weyl on 14 May 1964 [6] claiming an improved method and apparatus for the recovery of demineralized water from saline waters also using DCMD. It was stated that the two bodies of water may be stationary or moving, that is passing with respect to the membrane, and the process may be effected in a single stage or may be multi-staged. The membrane used was a polytetrafluoroethylene (PTFE) membrane having a thickness of 3175 μm , an average pore size of 9 μm and a porosity of 42%. In this patent, the use of other suitable hydrophobic

membranes made of polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) was suggested. As it was considered recently and discussed in the present book in Chapter 7, Weyl [6] also stated that membranes may be constructed of non-hydrophobic material coated with a hydrophobic substance, for example, by liquid or vapour impregnation. In this patent, an alternate geometrical form for multi-stage operation was presented by having the membrane coiled up into a cylinder giving rise to the actual known DCMD with liquid gap in the spiral wound module.

A year later, in 1968, a second U.S. patent was made by Bodell [7], partly as a continuation of his first U.S. patent [4]. Bodell described a system and a method to convert impotable aqueous solutions to potable water using a parallel array of tubular silicone membranes having a 0.3 mm inner and 0.64 mm outer diameter. No membrane characteristics such as pore size and porosity were presented. Air was circulated through the lumen side of the tubular membranes and condensation was carried out in an external condenser, giving rise to the actual known Sweeping Gas Membrane Distillation (SGMD) configuration. The patent provided novel apparatus and methods for desalting seawater in an economical manner. The improved apparatus was also provided for extracting potable water from brine, sewage, urine, wastewater, bacteria-containing water and other impotable water sources. Bodell recommended the water vapour pressure in the air side of the SGMD system to be at least 4 kPa below that of the aqueous medium. Moreover, Bodell suggested, for the first time, an alternative means of providing low water vapour pressure in the tubes by applying vacuum leading to the actual known VMD configuration [4,7].

A second MD paper has been published by Findley and co-authors [8] without mentioning any of the previous cited U.S. patents [4,6,7]. The study concerns heat and mass transfer of

water vapour from a hot salt solution through a hydrophobic porous membrane to a cooled water condensate. Their experimental studies indicated that the major factor influencing the rates of transfer was the diffusion through the stagnant gas (i.e., air) in the membrane pores. First theoretical calculations have been reported taking into account the membrane thermal conductivity and the film heat transfer coefficients. An empirical correction related to the possible internal condensation and diffusion along the surfaces has been considered to perform their calculations [8].

In Europe, a seawater desalination 'SGMD' process using dry air was also proposed by Van Haute and Henderyckx [9,10] in the 2nd European Symposium on Fresh Water from the Sea held in Athens (Greece) in May of 1967. The authors stated that the proposed apparatus can utilize waste hot water and it should be possible to use it for solar distillation; but it has not been further developed.

After this short period of time, interest in the MD process has faded quickly losing its brightness due partly to the observed lower MD production compared to that of reverse osmosis (RO) process. Rodgers [11,12], in his successive patents related to distillation, presented a system and a method of desalination using a stack of flat sheet membranes separated by non-permeable corrugated heat transfer films and working under DCMD configuration. A temperature gradient is applied over the membrane stack, and the latent heat passing from feed to distillate is recovered by heat transfer to a lower temperature feed. Thus the latent heat of vapourization may be used several times, as with multiple effect evaporation. The feed liquid supplied was subjected to treatment including heating and deaeration. The main object was to provide an improved economical desalination system and method of desalination. It was disclosed in the aforementioned patents that the distillation unit comprises a multiplicity of sheet-like elements all

substantially rectangular having the same dimensions and arranged with their edges in alignment so that the distillation unit takes the form of a relatively thin parallelepiped. It was also indicated that the suitable materials for the membranes are those which permit the formation of microporous membranes having high porosity, that is 70–80%, uniform pore size distribution and must be either poorly wettable or non-wettable (i.e., hydrophobic) by the used liquids or can be treated to render them non-wettable. The cited polymers were polycarbonates, polyesters, polyethylene, polypropylene and the halogenated polyethylenes, particularly the fluorocarbons. Particular mention has been made of polyvinylidene fluoride (PVDF) as a preferred membrane material and the so called 'solvent–non-solvent' casting process as the preferred method of forming the membranes. The use of cellulose nitrate, cellulose acetate and cellulose triacetate microscopic porous filter media coated with silicone water repellent to provide a non-wetting porous membrane was also mentioned.

MD process has recovered much interest within the academic communities in the early 1980s when novel membranes with better characteristics and modules became available [13–23].

A Gore-Tex membrane, which is an expanded PTFE membrane having a thickness of 50 μm and 0.5 μm pore size, has been used first by Esato and Eiseman [13] as a biologically inert membrane oxygenator, and later was proposed by Gore & Associated Co. under the name 'Gore-Tex Membrane Distillation' for MD application in a spiral-type module using the liquid gap DCMD configuration (Fig. 1.1) [14]. The proposed Gore-Tex membranes are made of PTFE having a thickness as low as 25 μm , porosity up to 80% and a pore size of 0.2–0.45 μm .

Other types of MD membranes, method and apparatuses have been proposed by Cheng and Wiersma in a series of U.S. patents [15–18]. The object of the first patent [15], filed by Cheng on 14 February 1979, was to provide an

improved thermal membrane distillation process with continuous distillate production over a prolonged period of time. A desalination system with three cell stages has been presented. Multiple-layered (i.e., composite) membranes have been proposed comprising a thin hydrophobic microporous layer or membrane and a thin hydrophilic layer or membrane. The hydrophilic layer was maintained adjacent to the distilland (i.e., salt water) whereas the hydrophobic layer was kept adjacent to the distillate (i.e., fresh water). The proposed composite porous membrane was formed by clamping the hydrophobic/hydrophilic layers closely together to form a cell with a suitable support backing to maintain the integrity of the composite membrane. The evaporation and condensation phenomena took place within the micropores of the hydrophobic layer while the hydrophilic layer prevents intrusion of distilland into the pores of the hydrophobic layer. It was reported that, in the case of salt water distillation, generally higher distillate production rates have been observed in composite membranes with the smaller pore sizes in the hydrophilic layer than in the hydrophobic layer. The best results have been obtained with the hydrophobic layer having a mean pore size smaller than $0.5\ \mu\text{m}$. It was also reported that the hydrophilic layer can be non-porous. The proposed hydrophobic materials for the composite membrane include PTFE and PVDF, whereas the proposed hydrophilic materials included cellulose acetate, cellulose nitrate, mixed esters of cellulose and polysulfone.

The following patents [16–18] filed by Cheng and Wiersma claimed the use of composite membranes having a thin microporous hydrophobic layer and one or two thin hydrophilic layers with the hydrophobic layer sandwiched between the two hydrophilic layers. It was stated that the two hydrophilic layers may be of different materials (cellulose acetate, mixed esters of cellulose, polysulfone and polyallylamine) and the composite membrane could be formed

by coating the hydrophilic layers on the hydrophobic layer. It was found that fresh water production rate for a distilland bulk temperature 62.8°C and distillate temperature 56.7°C was $75.2\ \text{kg}/\text{m}^2\cdot\text{day}$. For the same distilland and distillate temperature conditions a composite membrane of similar structure except with non-hydrophilic layer on the distillate side of the hydrophobic membrane yielded a fresh water production rate of $51.3\ \text{kg}/\text{m}^2\cdot\text{day}$. In other words, it was reported that the addition of the hydrophilic layer of the distillate side of the hydrophobic membrane increased the fresh water production rate by almost 50%.

In the fourth patent, [18] filed by Cheng and Wiersma on 4 March 1982, an improved apparatus and method for MD was proposed using a composite membrane comprising a microporous hydrophobic layer having deposited thereon an essentially non-porous hydrophilic coating. The hydrophobic layer of the membrane had either asymmetrical or symmetrical shaped micropores. Fluoro-substituted vinyl polymers, which are suitably hydrophobic, were proposed as ideal materials for the microporous hydrophobic layer of the composite membrane. The coating material and method were selected taking into account the adequate adhesion to the hydrophobic substrate, its resistance to both mechanical abrasion and chemical damage from the distilland, its ability to be coatable as a thin continuous layer on the surface of the porous substrate and to allow certain liquids to pass through to the hydrophobic layer of the membrane. Examples were plasma polymerized allylamine, dehydrated polyvinyl alcohol and polyacrylic acid.

At the same time, the Swedish National Development Co. (Svenska Utvecklings AB) developed the plate and frame membrane module applying the AGMD configuration [19,20]. The German company Enka AG presented polypropylene (PP) hollow fibre membranes in tubular modules at the Europe–Japan Joint Congress on Membranes

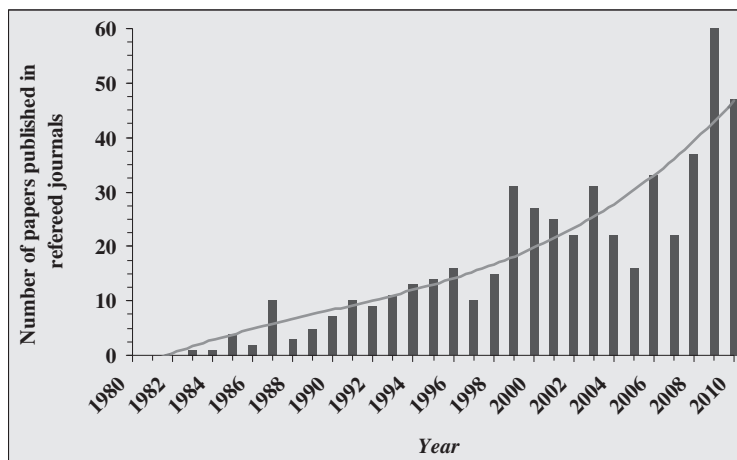


FIGURE 1.2 Growth of research MD activity up to the year 2010 represented as a plot of number of papers published in refereed journals for each year.

and Membrane Processes, held at Stresa (Italy) in 1984 [21]. Their experiments using DCMD process with heat recovery took more academic orientation by publication of their results in international journals [22,23]. In the same congress, other papers on MD have also been communicated [24,25]. More MD papers were presented at the Second World Congress on Desalination and Water Reuse in 1985, held in Bermuda. This renewed interest is a result of the development of various types of porous hydrophobic membranes used in different MD configurations [26–30]. Since then, numerous studies have been carried out but taking more academic interest rather than industrial. Most of those studies are published in national and/or international journals such as *Journal of Membrane Science and Desalination* as will be shown later in this book. Recently, interest in MD has increased significantly as can be seen in Fig. 1.2, presenting the number of published papers in journals per year in the MD field.

It must be stated that the number of MD papers referenced in the 1997 MD review by Lawson and Lloyd [31] was below 87 and that mentioned in the recent MD review (2006)

by El-Bourawi et al. [32] is 168; however, actually the number of MD papers published in international journals is more than 500.

It is worth quoting that within the published papers in international journals, DCMD is the most studied MD configuration, as it is illustrated in Fig. 1.3, although the heat loss by conduction through the membrane matrix is higher than in the other MD configurations. 63.3% of the MD studies are focused on DCMD as in this configuration condensation step is carried out inside the membrane module leading to a simple operation mode. In contrast, SGMD is the least studied configuration, only 4.5% of the MD published papers. This is due to the fact that SGMD requires external condensers to collect the permeate and a source for gas circulation.

Most of the considered publications in Figs 1.2 and 1.3 are concerned with theoretical models of MD and experimental studies on the effects of the operating conditions. 50.4% of the MD publications dealt with theoretical models (i.e., 40.6% for DCMD, 48.4% for AGMD, 40.3% for VMD and 72.2% for SGMD) whereas only about 16.7% of the MD papers

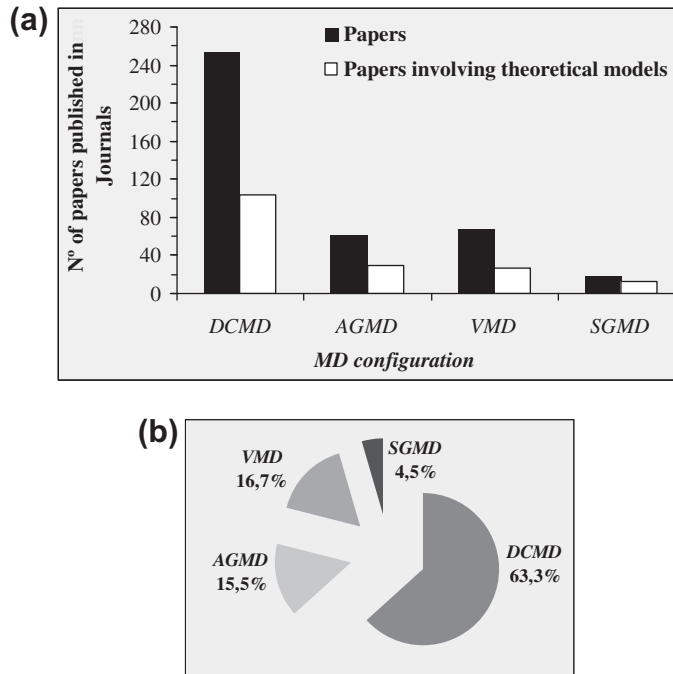


FIGURE 1.3 Number of MD papers published in refereed journals for each configuration including the papers presenting theoretical models (a) and percentages of each MD configuration (b).

reported in journals are focused on the preparation of MD membranes. Few authors have considered the possibility of manufacturing novel membranes and membrane module designs specifically for MD applications [33]. As a matter of fact, commercial microporous hydrophobic membranes available in capillary or flat sheet forms have been used in MD experiments although these membranes were prepared initially for other purposes, for example MF. Discussions on this subject are given in the next chapter.

MECHANISM OF MD TRANSPORT

In MD process, both heat and mass transfer through porous hydrophobic membranes are

involved simultaneously. The mass transfer occurs through the pores of the membrane whereas heat is transferred through both the membrane matrix and its pores. The heat transfer within the membrane is due to the latent heat accompanying vapour or gas flux and the heat transferred by conduction across both the membrane material and the gas-filled membrane pores. One must pay attention that only water vapour or volatile compounds are transported through the membrane pores from the feed side to the permeate side as the membrane is hydrophobic. In addition, there is a presence of fluid boundary layers adjoining both the feed and permeate membrane sides giving rise to the phenomena called *temperature polarization* and *concentration polarization*. These phenomena are explained in this book for each MD configuration.

The transport of gases and vapours through porous media has been extensively studied and theoretical models have been developed based on the kinetic theory of gases to predict the MD performance of the membranes depending on the MD configuration used. The different types of mechanisms proposed for the mass transport are Knudsen flow model, viscous or Poiseuille flow model, ordinary molecular diffusion model and/or the combination thereof often summarized as the dusty gas model. The governing quantity which provides a guideline in determining the operating mass transport mechanism in a given pore under given experimental conditions is Knudsen number (Kn) defined as the ratio of the mean free path, λ , of the transported molecules to the pore size of the membrane. The mean free path (λ_i) for a species i can be calculated using the following expression:

$$\lambda_i = \frac{k_B T}{\sqrt{2\pi} \bar{p} \sigma_i^2} \quad (1.1)$$

where σ_i is the collision diameter (2.641 Å for water vapour), k_B is the Boltzmann constant, \bar{p} the mean pressure within the membrane pores and T the absolute temperature.

For the binary mixture (i and j) in air, the mean free path can be evaluated by the following equation:

$$\lambda_{i/j} = \frac{k_B T}{\pi \bar{p} ((\sigma_i + \sigma_j)/2)^2} \frac{1}{\sqrt{1 + M_j/M_i}} \quad (1.2)$$

where σ_i and σ_j are the collision diameters and M_i and M_j the molecular weight of the components i and j , respectively.

In DCMD, the mean free path for water vapour at 50 °C under atmospheric pressure is approximately 0.14 μm, which is around the pore sizes of the membranes used in MD. However, in VMD, the mean free path value is

higher due to the low pressure in the permeate side. This indicates that the physical nature of mass transport may be different when using the same membrane under different MD configurations. Furthermore, for the membrane having a pore size distribution, different mechanisms may occur simultaneously.

In AGMD configuration, the transport of vapours through the membrane was assumed to be described by the theory of molecular diffusion admitting the presence of air inside the pores of the membrane and in the gap width as a stagnant film. Stefan diffusion and binary type relations (i.e., Fick's equation of molecular diffusion) as well as Stefan–Maxwell equations were used to describe the multicomponent mass transfer in AGMD systems [34–39]. In all these theoretical models, the pore size was not considered although experimental studies proved the dependence of the AGMD flux on this parameter [40,41]. Recently, attempts were made to predict the AGMD performance process using the dusty gas model that takes into account all membrane parameters to describe the simultaneous Knudsen diffusion, molecular diffusion and viscous flow models [42,43].

In MD theoretical studies, generally a membrane of uniform and non-interconnected cylindrical pores is assumed. The pore size distribution of MD membranes rather than their uniform pore size has been considered to a lesser extent in DCMD configuration [44–47], in VMD configuration [48] and in SGMD configuration [49]. A three-dimensional network of interconnected cylindrical pores with a pore size distribution was considered for Monte Carlo simulation of DCMD [50,51] and VMD [52]. The agreements between the predicted MD permeate fluxes and the experimental ones were found to be good.

It must be pointed out that the presence of air within the membrane pores between the feed and permeate liquid/vapour interfaces hinders the mass transfer resulting in a reduction of

the DCMD flux. Deaerated DCMD systems were proposed [22,53–55]. This can be carried out by lowering the pressure of the liquid streams hence controlling the maximum pressure of gas within the membrane pores. For membranes having small pore sizes, Knudsen flow is predominant and the removal of air results only in a small increase in the DCMD flux; however, for membranes having larger pores a substantial increase in the DCMD flux can be achieved by deaeration.

In MD processes, the transport of molecules through the membrane matrix (i.e., surface diffusion) is neglected due to the fact that the diffusion area of the membrane matrix is small compared to the pore area. For hydrophobic MD membranes, the ‘affinity’ between water and the membrane material is very low and it may be allowed to neglect the contribution of transport through the membrane matrix especially for porous membranes with large pore sizes and high porosities. Nevertheless, when other compounds are present in the aqueous feed solution especially for compounds having strong ‘affinity’ with the membrane material, the transport mechanism through the matrix of the membrane may have a significant effect. Systematic studies are needed to clarify this point in MD. It was reported that surface diffusion may affect MD performance in membranes with small pore sizes ($< 0.02 \mu\text{m}$) [56,57]. A theoretical model considering mass transport through the membrane matrix by solution–diffusion mechanism has been proposed for VMD and an extensive comparative study between pervaporation separation process (PV) and VMD employing the same membrane material (PVDF) has been carried out [48]. This is explained in detail in Chapter 12.

As stated above, the heat transfer within the membrane is due to the latent heat accompanying vapour flux and the heat transferred by conduction across both the membrane material and the gas-filled membrane pores. The

following equation was applied in various studies.

$$Q_m = \frac{k_m}{\delta}(T_{m,f} - T_{m,p}) + \sum_{i=1}^s J_i^t \Delta H_{v,i} \quad (1.3)$$

where k_m is the thermal conductivity of the membrane, δ is the membrane thickness, $\Delta H_{v,i}$ is the evaporation enthalpy of the species i of the transmembrane flux J_i^t , s is the number of permeated components, $T_{m,f}$ is the temperature of the feed aqueous solution at the membrane surface and $T_{m,p}$ is the temperature of the permeate at the membrane surface.

It is worth quoting that of the total heat flux transferred through the membrane, typically 50–80% is consumed as latent heat for permeate production, while the remainder is lost by thermal conduction. In fact, the heat loss by conduction through the membrane matrix becomes less significant when the MD system works under high operating temperatures, which are lower than the boiling point of the feed aqueous solution. This may be considered one method to minimize heat loss through the membrane, which is one of the inconveniences of MD process, in general, and DCMD, in particular.

In VMD, the boundary layer resistance in the permeate side and the contribution of the heat transported by conduction through the membrane are frequently neglected [31,32, 58,59]. This makes VMD of pure water useful to determine the temperature of the feed solution at the membrane surface ($T_{m,f}$) as it cannot be measured directly and therefore the boundary layer heat transfer coefficients in the membrane module can be evaluated [60]. This procedure has been used for selecting the adequate empirical heat transfer correlation of a given MD system, which is a complex task when developing theoretical models to determine the temperature polarization coefficients. In fact, the use of empirical heat transfer correlations in MD was

questioned and even criticized as these correlations were developed originally for only heat exchangers.

ENGINEERING ASPECTS: MD APPLICATIONS

The MD process is currently applied mostly at the laboratory scale and the MD applications are very appropriate for environmental, chemical, petrochemical, food, pharmaceutical and biotechnology industries. Recently, some pilot plant applications have been proposed for desalination and nuclear desalination but are still under experimental tests and their use is not fully extended [61–67].

The major MD application has been in desalination for production of high purity water. Near 100% rejection of non-volatile electrolytes (i.e., sodium chloride, NaCl; potassium chloride, KCl; lithium bromide, LiBr; etc.) and non-electrolytes (i.e., glucose, sucrose, fructose, etc.) solutes present in aqueous solutions was achieved. A quality water as low as 0.8 $\mu\text{S}/\text{cm}$ electrical conductivity with 0.6 ppm TDS (total dissolved solids) was produced [68]. As the permeate product is very pure it is suitable for use in medical and pharmaceutical sectors. In fact, in the case of a solution with non-volatile components only water molecules flow through the membrane pores. It must be mentioned here that Weyl [6] was the first in conducting desalination by DCMD. However, the obtained permeate fluxes were up to $1 \text{ kg}/\text{m}^2 \cdot \text{h}$, which were lower than the RO permeate fluxes ($20\text{--}75 \text{ kg}/\text{m}^2 \cdot \text{h}$). Actually, due to MD membrane module improvement, the MD production begins to be competitive to RO process in the field of desalination with nearly total rejection factors, which can not be accomplished by RO at high permeate fluxes.

MD has been applied successfully to wastewater treatment at a laboratory scale, either to produce a permeate less hazardous to the

environment or to recover valuable compounds. MD has been tested for the treatment of pharmaceutical wastewater containing taurine, textile wastewater contaminated with dyes such as methylene blue, aqueous solutions contaminated with boron, arsenic, heavy metals, ammonia (NH_3), coolant liquid (i.e., glycols), humic acid and acid solutions rich in specific compounds, oil-water emulsions, olive oil mill wastewater for polyphenols recovery and radioactive wastewater solutions. It was proved that DCMD is feasible to process low and medium-level radioactive wastes giving high decontamination factor in only one stage and can be applied for nuclear desalination [62,69,70]. Recently, DCMD was proposed for wastewater reclamation in space in a combined direct osmosis system [71].

Due to the fact that MD can be conducted at relatively low feed temperatures, it was successfully tested in many areas where high temperature applications lead to degradation of the process fluids especially in food processing. It was demonstrated that MD can be used for the concentration of milk [30], for the recovery of volatile aroma compounds from black currant juice [72], for the concentration of must (i.e., the juice obtained from grape pressing containing sugars and a wide variety of aroma compounds) [73] and for the concentration of many other types of juices including orange juice, mandarin juice, apple juice, sugarcane juice, etc. It was concluded that the utilization of either osmotic distillation (OD) and/or MD in the food industry for concentration or separation is promising especially at high feed concentration degrees. This will be discussed in Chapter 10.

MD also has potential applications in biotechnology. As an example, MD has been used for the removal of toxic products from culture broths. The application of DCMD unit connected to a laboratory bioreactor for the selective recovery of ethanol from the culture medium has been reported [74]. The experiments were

run at a constant temperature of 38 °C on anaerobic cultures of *fragilis*. MD was also applied for the concentration of biological solutions such as bovine plasma and bovine blood [75,76]. It was demonstrated that MD was suitable for stable removal of solute free water from blood with a haematocrit of 45%. DCMD was applied to the direct concentration of protein (0.4% and 1% bovine serum albumin at pH 7.4) aqueous solutions at low temperatures and found that fouling effects were practically absent, while the limiting factor of the process was the temperature polarization [77].

It is known that azeotropic mixtures are impossible to be separated by simple distillation. Thus, the application of MD for breaking azeotropic mixtures was proposed and tested for the separation of hydrochloric acid/water, propionic acid/water and formic acid/water azeotrope mixtures [78,79]. It was demonstrated that MD is of potential interest in breaking azeotropic mixtures. The effect of the inert gases, helium, air and sulfur hexafluoride, in breaking the formic acid/water azeotropic mixtures was studied [80]. The selectivity was found to be larger and near unity when using helium (around 0.96), followed by that in air (about 0.9) and then in sulfur hexafluoride (0.85–0.86). The results were related with the different diffusivities of the components in the inert gas.

MD has been proposed for the extraction of volatile organic compounds (VOCs) from dilute aqueous solutions. Various types of dilute binary mixtures containing VOCs at different concentrations were tested by different MD configurations and membrane modules. Values of the selectivity different from those calculated on the basis of the corresponding VLE data were found. Removal from water of alcohols such as methanol, ethanol, isopropanol and n-butanol; halogenated VOCs such as chloroform, trichloroethylene and tetrachloroethylene, benzene, acetone, acetonitrile, ethylacetate, methylacetate and methyltertbutyl ether among others were

studied. The potential advantage of MD for ethanol recovery from fermentation broth was also reported [34]. It must be mentioned here that the addition of salt such as magnesium chloride ($MgCl_2$) during the treatment of aqueous alcohol feed solutions was found to increase the alcohol selectivity significantly with only a slight decrease in the total permeate flux. This was attributed to the reduction in water vapour pressure leading to a decrease in the water mass transfer through the membrane [36,78].

The concentration of aqueous solutions containing sodium hydroxide (NaOH) and the strong mineral acid, sulfuric acid (H_2SO_4), at different pH values has been investigated [30]. Comparable MD permeate flux and electrical conductivity to those obtained using sodium chloride (NaCl) aqueous solutions was noticed. MD separation of aqueous solutions containing volatile solutes such as nitric acid (HNO_3) and hydrochloric acid (HCl) have been conducted and similar trends for both components were found, different from that of the aqueous solutions containing non-volatile solutes [30]. Attempts were made for the concentration of hydrogen iodide (HI) and sulphuric acid aqueous solutions in relation to hydrogen energy production from water using DCMD and AGMD [81].

Details are given in the following chapters of the present book.

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