Effects of membrane structure and operational variables on membrane distillation performance

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Abstract

A bench-scale, sweeping gas, flat-sheet Membrane Distillation (MD) unit was used to assess the importance of membrane architecture and operational variables to distillate production rate. Sweeping gas membrane distillation (SGMD) was simulated for various membrane characteristics (material, pore size, porosity and thickness), spacer dimensions and operating conditions (influent brine temperature, sweep gas flow rate and brine flow rate) based on coupled mass and energy balances. Model calibration was carried out using four membranes that differed in terms of material selection, effective pore size, thickness and porosity. Membrane tortuosity was the lone fitting parameter. Distillate fluxes and temperature profiles from experiments matched simulations over a wide range of operating conditions. Limitations to distillate production were then investigated via simulations, noting implications for MD design and operation. Under the majority of conditions investigated, membrane resistance to mass transport provided the primary limitation to water purification rate. The nominal or effective membrane pore size and the lumped parameter $\varepsilon/\delta\tau$ (porosity divided by the product of membrane tortuosity and thickness) were primary determinants of membrane resistance to mass transport. Resistance to Knudsen diffusion dominated membrane resistance at pore diameters $< 0.3 \mu\text{m}$. At larger pore sizes, a combination of resistances to intra-pore molecular diffusion and convection across the gas-phase boundary layer determined mass transport resistance. Findings are restricted to the module design flow regimes considered in the modeling effort. Nevertheless, the value of performance simulation to membrane distillation design and operation is well illustrated.

Key Words: Sweeping Gas Membrane Distillation; Desalination; Flat Sheet Membrane; Heat and Mass Transfer

1   **Introduction**

2   Membrane distillation (MD) is a thermally driven desalination process in which vapor diffuses
3   through a porous membrane with at least one side in direct contact with the process liquids [1, 2].
4   Transmembrane transport depends on a gradient in the partial pressure of water vapor in the
5   membrane pores that is maintained by raising the temperature of the liquid feed stream and
6   continuously removing water vapor from the permeate side of the membrane. A hydrophobic
7   porous membrane retains the feed solution via surface tension, allowing water to cross the
8   membrane as a vapor [3]. Pore wetting does not occur if the transmembrane pressure differential
9   is lower than the liquid entry pressure (LEP), which is a function of pore size and the contact
10   angle of the membrane material [4, 5]. MD enjoys several advantages over other desalination
11   processes. MD operates at lower temperatures than conventional distillation/evaporation
12   processes and lower pressures than reverse osmosis. MD produces ~100% theoretical rejection
13   of ions [6]. Because vapor pressure is reasonably insensitive to ionic strength, permeate
14   production and energy requirements are weakly dependent on brine salinity. However, a
15   significant process limitation lies in the energy required to operate MD, which is dominated by
16   the energy necessary to evaporate water. The latent heat of water evaporation, ΔH , equals 2260
17   kJ/kg or 628 kWh/m³. At 10 cents per kWh, the energy cost to evaporate water is \$0.24 per
18   gallon, suggesting that recovery of energy or use of waste heat is essential to MD
19   competitiveness in many situations.

20   In SGMD, a flowing gas collects water vapor on the permeate side before exiting the module,
21   allowing pure water to be condensed externally. In addition to salt separation, SGMD has been
22   used to remove volatile solutes from aqueous solutions [7, 8]. Advantages specific to SGMD
23   include relatively low heat loss through the membrane, low resistance to mass transfer and a high

driving force for transmembrane transport that is maintained by continuous removal of vapor from the permeate side of the membrane [9]. Although SGMD offers the possibility of energy recovery through internal recondensation, in general SGMD systems require an external condenser and an air blower [10].

Mathematical modeling of SGMD based on coupled heat and mass balances has been used to determine the sensitivity of permeate flux to variations in operational parameters [7, 10, 11]. Charfi et al. (2010) performed a 2-D numerical simulation of SGMD using the Darcy–Brinkman–Forcheimer representation of momentum transport [7]. Experiment and prediction were in good agreement [7]. More recently, Karanikola et al. (2015) developed a model for SGMD using hollow-fiber modules [11]. The model was based on discretized forms of heat and mass balances in the membrane module, and it satisfactorily predicted permeate production rates, as well as temperature profiles through the module. In the mentioned studies, effects arising from mesh spacers were not considered.

Previous modeling and experimental efforts have not placed extensive effort on the assessment of effects of membrane structure on permeate production. In this work, flat sheet SGMD was modeled throughout the practical range of relevant physical membrane characteristics (pore size, thickness, porosity and tortuosity), incorporating the effects of spacers on heat and mass transfer. The validated model was used to explore the sensitivity of water production rate to membrane characteristics over a broad range of system operational variables, i.e., brine temperature and flow rate and sweep gas flow rate. Results are used to identify physical and operational limitations to rates of water purification via SGMD.

Materials and Methods

Membrane specifications are summarized in **Table 1**. All membranes were from Millipore. Except for a dual layer polytetrafluorethylene (PTFE) membrane supported by a polypropylene (PP) layer, all were monolayer polyvinylidene fluoride (PVDF) membranes. SEM micrographs are provided (**Figure 1**).

Top view of PTFE membrane $d_p = 0.45 \mu\text{m}$

Top view of PVDF membrane $d_p = 0.45 \mu\text{m}$

Cross section of PTFE, 30 μm membrane active layer and 130 μm PP support layer

Cross section of PVDF membrane, 110 μm uniform membrane active layer

Figure 1. Scanning electron micrographs of PVDF and PTFE membranes. The dual layer character of the PTFE membrane is clearly seen (lower left).

In the SGMD experimental setup (**Figure 2**), brine was heated and recirculated at velocities from 0.024 m/s to 0.11 m/s on the brine side of the hydrophobic porous membrane. Vapor pressure at

the brine/air interface was manipulated by varying the influent brine temperature. A plate and frame module with thermocouple monitoring was fabricated for bench-scale experiments (Figure 3).

Figure 2. Lab-scale experimental set up. Fluid flow pathways include the high-temperature brine/membrane loop (red) and the sweep gas pathway (blue). Condensate was collected in the permeate tank.

The module consisted of two Deldrin plates (21 cm × 16.5 cm × 3.8 cm each). Deldrin was selected for its low thermal conductivity ($\lambda_D = 0.33 \text{ W/m}\cdot\text{K}$) compared to stainless steel (common material for plate and frame modules) to minimize heat loss and amenability to computer controlled 3-D milling. Each plate had a milled chamber with dimensions 14.5 cm × 9.5 cm × 0.15 cm. The brine flow passed through one chamber, and air was swept through the other. The membrane that separated the two chambers had a working area of 0.015 m². Mesh

spacers were placed on both sides of the membrane for support and fluid mixing. Spacer characteristics are presented in **Table 2**.

Table 1. Membrane Specifications

Membrane Specifications	Membrane A	Membrane B	Membrane C	Membrane D
Membrane material ^a [--]	PVDF ^b	PVDF ^c	PTFE/PP ^b	PVDF ^c
Pore Size ^a d_p [μm]	0.22	0.45	0.45	0.65
Thickness δ [μm]	125	110	30/130	115
Porosity ^a ε [%]	75	70	75	70
Thermal conductivity ^a λ_m [W/m·K]	0.18	0.18	0.25/0.17	0.18
Contact Angle [$^\circ$]	109	150	120	150
Tortuosity ^d τ [-]	2.5	2	3.4/1.7	1.8
Membrane mass transfer coefficient ^e k_m [m/s]	0.042	0.070	0.075	0.054

^a Manufacturer's data (Millipore)

^b Hydrophobic

^c SuperHydrophobic

^d Fitted parameter

^e Calculated, see text.

In previous plate and frame studies [12, 13], air entered the permeate chamber via (i) a single point of entry (orifice) at one end of the module, or (ii) a 2-way distributor located in the middle of the chamber that contained a series of small orifices along its length. These geometries may have provided non-uniform flow conditions in the sweep gas over much of the air-side module chamber with attendant challenges for mathematical simulation. Consequently, the air-side chamber was designed so that air entered from a channel on one end and exited to a second channel at the other end in order to encourage uniform flow conditions across the chamber (**Figure 3**).

Figure 3. —Flat sheet module. Left: permeate side bottom plate. Arrows denote the direction of the sweep air flow and red dashed line denotes the inlet distribution and outlet channels. Right: air side top plate. Arrows show the direction of the air flow. Each side has an engraved chamber of L 14.5 cm x W 9.5 cm x D 0.15 cm.

Sweep air was pulled through the module chamber by a blower (Gast, ShopVac, 0.5 peak hp) countercurrent to the brine flow. The water content in air leaving the module was determined using the permeate collection and gas flow rates, assuming that the condenser exit gas was saturated at the condenser exit temperature. Cold water (15 °C) was provided continuously at 1.5 L/min to the condenser (Model # AB-404-85098, Thermal Transfer Products, interfacial area 0.57 m²).

Thermocouples were installed at the inlet and outlet of the module (two on both the water and air sides), the inlet and outlet of the condenser (two on each side) and the permeate collection tank.

Rotameters were present in the brine and air loops. Brine flow was regulated at the module entrance, and air flow was controlled after the permeate tank. Vacuum pressure gauges were placed in the air loop before and after the module, before the condenser and after the permeate tank.

The performance of the system was examined by varying the brine feed temperature and flow rate and the flow of sweeping gas. The effect of membrane structure was then established using the four membrane types described (**Table 1**) and extended via process simulation. Dependent variables included the flowrate and quality of permeate and pressures/temperatures at the points indicated. An Omega USB-4718 portable data acquisition module was used to translate the K-type thermocouple signals and transmit data to the computer. The nine thermocouples reported to a single data hub. The brine solution consisted of 0.05 wt% NaCl (Fisher Scientific) in Milli-Q (Merck Millipore) water. NaCl concentrations were calculated from measured electrical conductivity in the feed and permeate solutions using a benchtop thermal conductivity meter (inoLab® Cond Level 2).

Table 2. Spacer Specifications. Geometries illustrated in **Figure 5**.

Spacer Specifications	Mesh Angle θ [°] ^a	Spacer Filament Diameter d_f [mm] ^a	Spacer Mesh Size l_m [mm] ^a	Thickness H [mm] ^a
Feed Side Spacer	90	0.47	2.76	1.19
Permeate Air Side Spacer	90	1	4	1.2

^a Measured

Modeling Approach

A previously developed model for a hollow fiber SGMD module based on coupled energy and mass balances [11] was modified to simulate flat sheet module performance. The discretized mass and energy balances support calculation of the molar rate of water vapor transfer from liquid to gas and the partial pressure of water on the air side. If the partial pressure of water exceeds the vapor pressure at the gas-phase temperature, water condenses inside the module. However, due to the relatively short gas-phase path length in the bench-scale module,

recondensation in the module was neither predicted nor observed under the experimental conditions used (see below).

Control volumes for mass and energy balances consisted of finite sections through either the liquid or the gas phase contents of the module (**Figure 4**). Full development of heat and energy balances was provided previously [11]. Only details specific to the plate-and-frame configuration are provided here.

Figure 4. A magnified module section, Δz in thickness, consisting of a single membrane section to illustrate the basis of the local mass and energy balances. The right side dashed square denotes the control volume for local mass balance. $\Delta \dot{n}_{w,i}$ is the molar water vapor rate of transport through the membrane, $Q_{m,i}$ is the rate of energy transfer through the membrane, $Q_{c,i}$ is rate at which heat is released via condensation of the water vapor on the air side, $Q_{e,i}$ is the rate at which heat is lost from the liquid stream due to evaporation, $\Delta \dot{n}_{c,i}$ is the molar water vapor condensation rate in the section, T_a is the temperature of the air, T_b is the temperature of the brine, $T_{l,i}$ is the interfacial membrane pore temperature of the brine, $\dot{n}_c$ is the molar water condensation rate, $\dot{n}_w$ is the molar water rate of vapor at each section, $\dot{n}_b$ is the molar brine rate,

$\dot{n}_a$ is the molar air rate, q_a is the volumetric flowrate of air and q_b is the volumetric flowrate of the brine. Figure adapted from Karanikola et al. (2015).

The driving force for mass transfer across the membrane was the difference between the vapor pressure of water at the brine/gas interface in the membrane pores and the local partial pressure of water vapor in the bulk sweeping gas. Mass transfer resistances included the membrane resistance (due to molecular diffusion and/or Knudsen diffusion) and boundary layer resistance on the gas (permeate) side. The driving force for energy transfer to the liquid/gas interface was the difference between bulk brine temperature and the brine temperature at the interface. Resistance was provided by the brine-side thermal boundary layer. A second energy balance was necessary to account for energy transfer from the brine/gas interface into the sweeping gas. In that case, the driving force was the difference between interfacial and bulk gas-phase temperatures, and resistance was provided by the membrane material and membrane pores (in parallel) and the gas-phase thermal boundary layer. For mathematical details, see [11] and SI.

Resistance to mass transport.

Water mass balances in each section of the module have been presented elsewhere [11]. To assess the potential effect of membrane structure on water production during SGMD, it is necessary to summarize relationships governing resistance to trans-membrane mass transfer. The trans-membrane flux of water vapor through membrane pores in the i th section of the discretized module (**Figure 4**) was represented by J_i (mol/m² s), where

$$J_i = \frac{k_{tot}}{RT} (P_{l,i} - P_{w,i}) \quad (1)$$

In this equation, k_{tot} (m/s) is the overall mass transfer coefficient of water vapor, R is the gas law constant (8.314 J/mol K), T (K) is the average temperature between the brine and air streams at each section of the module, $P_{l,i}$ (atm) is the vapor pressure calculated from Antoine's equation using the local interfacial temperature ($T_{l,i}$) at the membrane pore entrance and $P_{w,i}$ (atm) is the partial pressure of water vapor in the sweep gas [11]. **Equation 1** shows that the driving force for water transport through the membrane is the difference between the local vapor pressure of the brine and the local partial pressure of water vapor on the air permeate side.

The overall mass transfer coefficient, k_{tot} , is related to mass transfer resistances in the system [14]. Water transport resistance on the brine side of the membrane was neglected due to the insignificant variations of the water concentration on the brine side (effects of concentration polarization were determined negligible) and the contribution of viscous transport through the membrane pores to transport was insignificant compared to the other transport mechanisms [11].

$$R_{tot} = \frac{1}{k_{tot}} = R_m + R_a = R_m + \frac{1}{k_a} \quad (2)$$

where R_m is the resistance to water vapor transport across the membrane, R_a is the resistance to mass transport in the air-side boundary layer, and k_a (m/s) is the mass transfer coefficient in the air-side boundary layer. R_m was represented as

$$R_m = \frac{\delta}{D_{eff}} \quad (3)$$

where δ (m) is the thickness of the membrane and D_{eff} (m²/s) is the effective diffusivity of water vapor in the membrane.

The effective diffusivity, D_{eff} , in a porous membrane is proportional to ε , the membrane porosity, and inversely proportional to τ , the effective tortuosity of pathways through the membrane,

$$D_{eff} = \frac{\varepsilon}{\tau} D \quad (4)$$

180 Porosity was obtained from membrane specifications, and tortuosity was treated as an adjustable
 181 parameter. D is the diffusivity of the vapor through the membrane, which is represented as the
 182 combination of Knudsen and molecular diffusion contributions; that is,

$$D^{-1} = D_{mol}^{-1} + D_{Kn}^{-1} \quad (5)$$

183 in which the molecular diffusivity, D_{mol} (m²/s) was estimated from the relation presented by [15]:

$$D_{mol} = \frac{0.926}{10^6 P_{tot}} \left(\frac{T^{2.5}}{T + 245} \right) \quad (6)$$

184 where P_{tot} is the total local pressure (kPa) and T (K) is the temperature of the feed side solution.

185 The Knudsen diffusivity, D_{Kn} (m²/s), was obtained from [16] as

$$D_{Kn} = \frac{2}{3} r_p \left(\frac{8RT}{\pi m_w} \right)^{1/2} \quad (7)$$

186 where r_p is the pore radius (m), T is the average temperature between the brine and air streams at
 187 each section of the module (K), and m_w is the molecular mass of water (kg/mol).

188 For the dual-layered membrane (membrane plus support; membrane **C** in **Table 1**), R_m was
 189 calculated as the sum of resistance to mass transport of the active membrane layer (R_{m1}) and the
 190 resistance due to molecular diffusion in the support layer (R_{m2}).

$$R_m = R_{m1} + R_{m2} \quad (8)$$

191

192 In the flat-plate apparatus, feed-side and permeate-side spacers were utilized for membrane
 193 support and improvement of mass/heat transfer characteristics. Spacers tend to reduce the
 194 boundary layer resistance to heat and mass transfer on the air or permeate side of the membrane

and resistance to heat transfer on the brine side. Values of the mass transfer coefficient on the permeate side, k_a (m/s), are related to the Sherwood number by

$$k_a = \frac{D_{mol} Sh}{d_{hs}} \quad (9)$$

The hydrodynamic diameter for a single rhombus of the mesh spacer (**Figure 5**), d_{hs} (m), was calculated per [17],

$$d_{hs} = \frac{4\varphi d_f H}{2d_f + 4(1-\varphi)H} \quad (10)$$

where d_f (m) is the diameter of one filament of the spacer, H (m) is the thickness of the spacer and φ is the spacer voidage, calculated from

$$\varphi = 1 - \left(\frac{\pi d_f^2}{2 l_m H \sin \theta} \right) \quad (11)$$

where l_m (m) is the mesh size, and θ ($^\circ$) is the orientation angle of the mesh (**Figure 5**). The characteristics of spacers used here were presented in **Table 2**.

Figure 5. Spacer Views. Spacer dimensions/properties were as illustrated.

The Sherwood number on the air side was estimated from an empirical relation that is specific for laminar flow [18]

$$Sh=0.664k_{dc} Re^{0.5} Sc^{0.33} \left(\frac{d_{hs}}{l_m}\right)^{0.5} \quad (12)$$

where k_{dc} is a correction factor for spacer geometry that was calculated from [17]

$$k_{dc}=1.654 \left(\frac{d_f}{H}\right)^{-0.039} \varphi^{0.75} \left[\sin\left(\frac{\theta}{2}\right)\right]^{0.086} \quad (13)$$

209

210 The Reynolds number is defined by

$$Re=\frac{u_a d_{hs} \rho_v}{\mu_v} \quad (14)$$

211 where u_a is the sweeping gas approach velocity (m/s), calculated by dividing the volumetric air
 212 flow rate by the cross-sectional area of the air side chamber of the module; ρ_v is the density of
 213 the gas phase (kg/m³); and μ_v is the viscosity of the gas (Pa s) on the permeate side. Reynolds
 214 numbers on both the air and feed sides of the membrane were always within the laminar regime.

215 The Schmidt number was obtained from:

$$Sc=\frac{\mu_v}{\rho_v D_{mol}} \quad (15)$$

216 From the foregoing, it is apparent that the internal membrane resistance has two components—
 217 resistance to Knudsen diffusion, which is proportional to $\delta\tau/\varepsilon$ and $d_p^{-1/2}$, and resistance to
 218 molecular diffusion, which is proportional to $\delta\tau/\varepsilon$ but independent of pore size. At constant
 219 temperature and pressure, the gas-phase boundary layer resistance is proportional to $u_a^{-1/2}$.
 220 Component resistances to trans-membrane flow of water vapor are additive.

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225 *Energy transport.*

226 The contributors to energy balances in each section of the module (**Figure 4**) were heats of
227 evaporation/condensation and the transmembrane transfer of heat from the hot brine to the cooler
228 gas phase.

229 Heat balances in the brine and air-side sections were used to calculate temperatures as a function
230 of position in the brine and air streams. The energy balance on the brine side for the i th section
231 (Figure 4) states that the energy lost by the brine is equal to the energy transferred to the
232 membrane surface,

$$\dot{n}_b c_{p,b} (T_{b,i} - T_{b,i-1}) = h_w A_i (T_{b,i} - T_{l,i}) \quad (16)$$

233 where $\dot{n}_b$ (mol/s) is the molar brine flow, $c_{p,b}$ (J/mol K) is the specific heat of the brine, $T_{b,i}$ and
234 $T_{b,i-1}$ (K) are the inlet and outlet brine temperatures in section i , respectively, h_w (W/K m²) is the
235 brine-side heat transfer coefficient (see below), and A_i (m²) is the area of the membrane section.
236 The energy transferred from the membrane interface to and through the membrane is described
237 by:

$$h_w A_i (T_{b,i} - T_{l,i}) = Q_{m,i} + Q_{e,i} \quad (17)$$

238 Where $Q_{m,i}$ (W) is the rate of heat transfer across the membrane section and is given by:

$$Q_{m,i} = h_{tot} A_i (T_{l,i} - T_{a,i}) \quad (18)$$

239 where $T_{a,i}$ is the section's air temperature, h_{tot} (W/K m²) is the overall transmembrane heat
240 transfer coefficient from the membrane to the air side (see below). In equation 7,

$$Q_{e,i} = \Delta \dot{n}_{w,i} \Delta H_{v,w} \quad (19)$$

in which $Q_{e,i}$ (W) is the rate at which heat is provided to evaporate liquid water from the brine stream, $\Delta\dot{n}_{w,i}$ (mol/s) is the rate of vapor or permeate production and $\Delta H_{v,w}$ (J/mol) is the latent heat of vaporization of water.

The thermal energy balance on the air side is given by

$$\dot{n}_a c_{p,a} (T_{a,i} - T_{a,i-1}) + \dot{n}_{w,i-1} c_{p,v} (T_{a,i} - T_{a,i-1}) + \Delta\dot{n}_{w,i} c_{p,v} (T_{a,i} - T_{a,i-1}) = Q_{m,i} + Q_{c,i} \quad (20)$$

where $c_{p,a}$ (J/mol K) is the gas-phase specific heat, $T_{a,i}$ and $T_{a,i-1}$ (K) are the inlet and outlet gas-phase temperatures at section i , and $c_{p,v}$ (J/mol K) is the heat capacity of water vapor.

$Q_{c,i}$ (W) is the energy released by condensation of water vapor in the section

$$Q_{c,i} = \Delta H_{v,w} \Delta\dot{n}_{c,i} \quad (21)$$

where $\Delta\dot{n}_{c,i}$ (mol/s) is the rate of vapor condensation in the air stream..

The membrane heat transport coefficient, h_{tot} , is expressed in terms of a sum of heat transfer resistances,

$$\frac{1}{h_{tot}} = \frac{1}{h_a} + \frac{\delta}{\lambda_{eff}} \quad (22)$$

where h_a (W/K m²) is the heat transfer coefficient on the air side of the membrane, δ (m) is the thickness of the membrane and λ_{eff} (W/m K) is the effective thermal conductivity of the membrane obtained from [19]

$$\lambda_{eff} = \lambda_v \varepsilon + \lambda_m (1 - \varepsilon) \quad (23)$$

where λ_v (0.0263 W/m K) is the thermal conductivity in the membrane void space (air + water vapor), and λ_m (W/m K) is the thermal conductivity of the membrane material (Table 1).

For a dual-layered membrane (membrane plus support) the effective thermal conductivity is calculated as follows [14]:

$$\lambda_{effd} = \frac{\delta_1 + \delta_2}{\frac{\delta_1}{\lambda_{eff1}} + \frac{\delta_2}{\lambda_{eff2}}} \quad (24)$$

where δ_1 (m) is the thickness of the active layer and δ_2 (m) is the thickness of the membrane support material. Since the support layer is considerably more porous than the active layer, $\lambda_{eff2} \sim \lambda_v$.

Values for the convective heat transfer coefficients in the permeate and brine-side boundary layers, h_a and h_w , were calculated using the Chilton-Colburn analogy [14] in terms of the Nusselt number,

$$h = \frac{\lambda Nu}{d_{hs}} \quad (25)$$

For the calculation of h_w (W/K m²), the thermal conductivity of water (λ_w) and the hydrodynamic diameter of the feed side spacer were used. For the calculation of h_a , the thermal conductivity of air (λ_v) and the hydrodynamic diameter of the permeate-side spacer were used. The Nusselt number was calculated from the correlation

$$Nu = k_{ac} 0.664 Re^{0.5} Pr^{0.33} \left(2 \frac{d_{hs}}{l_m} \right)^{0.5} \quad (26)$$

where the Reynolds number was obtained from equation (19) and the Prandtl number was obtained from

$$Pr = \frac{\mu_v C_p}{\lambda_v} \quad (27)$$

Results and Discussion

Model calibration/verification

The model was calibrated by comparing measured and predicted water production rates in response to variation in brine temperature ($50 < T_{b,in} < 80$ °C) (Figure 6). The temperature of the air going in the membrane module was ambient temperature ($T_{a,in} \sim 25$ °C). For each membrane type, membrane tortuosity was the sole fitting parameter (Table 1). It should be noted that for all experiments, the amount vapor that is not condensed after the condenser is less than 10% of the total amount of water produced.

Figure 6. Relationship between inlet brine temperature and permeate molar flux. Data points represent experiments at influent brine temperatures from 50 °C to 80 °C, 0.05 % NaCl, $u_a = 9.5$ m/s and $u_b = 0.11$ m/s that were used for model calibration. Points represent experimental data for membranes **A** (PVDF $d_p = 0.22$ μm , $\tau = 2.5$), **B** (PVDF $d_p = 0.45$ μm , $\tau = 2$) and **C** (PTFE $d_p = 0.45$ μm , $\tau = 2.5$) and **D** (PVDF $d_p = 0.65$ μm , $\tau = 1.8$). Solid lines represent model results. Error bars represent $\pm$ one standard deviation in the results of three repeat experiments at the conditions indicated.

Tortuosity values were selected to minimize the sum of squared error between the temperature-dependent predicted and measured water production rates. Model validation was then undertaken

using data representing the rate of permeate production as a function of the sweep gas flow rate and brine approach velocity for the four membrane types. Results (**Figures 7 and 8**) show that SGMD performance can be simulated over a broad range of operational conditions and membrane architectures, eliminating the need for a great many additional bench scale experiments. In all experiments, permeate conductivity was $< 20 \mu\text{S}/\text{cm}$ ($< 10 \text{ mg}/\text{L NaCl}$).

Figure 7. Dependence of permeate molar flux on the sweep air velocity at influent brine temperature = 70°C , salinity = 0.05% NaCl and brine velocity $u_b = 0.11 \text{ m/s}$. Points represent experimental data for membranes **A** (PVDF $d_p = 0.22 \mu\text{m}$, $\tau = 2.5$), **B** (PVDF $d_p = 0.45 \mu\text{m}$, $\tau = 2$) and **C** (PTFE $d_p = 0.45 \mu\text{m}$, $\tau = 2.5$) and **D** (PVDF $d_p = 0.65 \mu\text{m}$, $\tau = 1.8$). Solid lines are model predictions.

Figure 8. Effect of the brine flow rate and feed brine temperature on permeate molar flux for the PVDF membrane ($d_p = 0.22 \mu\text{m}$) at a sweep air velocity of 9.5 m/s. Solid lines represent model predictions.

Heat transfer considerations.

It was originally hypothesized that water production was constrained by a combination of heat and mass transfer limitations. Heat transfer to the brine/gas interface must continuously provide the heat of vaporization at the observed/predicted rate of water purification plus any heat that is transferred from the brine to the sweeping gas. The calculated difference between the bulk brine and brine/air interfacial temperatures, or driving force for energy transfer to the liquid/gas interface, is plotted as a function of position for three influent brine temperatures in **Figure 9**.

Figure 9. Temperature difference between the (bulk) brine and the membrane interface for three influent brine temperatures as a function of dimensionless distance from the air entrance to the module; $u_a = 9.5$ m/s and $u_b = 0.11$ m/s for the PVDF $d_p = 0.45$ μ m membrane.

In each case, temperature differences were greatest at the brine exit (air entrance) of the module.

In addition to motivating the transfer of heat energy across the liquid phase boundary layer, the temperature differences shown, reduce the temperature/vapor pressure at the brine/gas interface, and thus the driving force for mass transfer through the membrane. The figure shows, however, that most of the needed heat to support the observed evaporation rates can be provided with less than a degree difference. Thus heat transfer does not provide a significant limitation to water production under the operational conditions in these experiments. Heat transfer effects however, remain important as determinants of simulated temperature profiles on the air and water sides of the membrane.

For an experiment with inlet brine temperature $T_{bi} = 80$ °C, 87% of the energy transferred from the brine to the membrane is used to evaporate the water and 13% is transferred across the membrane/thermal boundary layer as sensible heat through conduction/convection. Energy

losses to the environment were neglected without sacrificing agreement between simulated and measured temperature profiles (data not shown).

Over the full range of conditions in these experiments, the calculated ΔT_p was ≤ 3.1 °C, reinforcing our assertion that heat transfer resistance within the thermal boundary layer was not a major determinant of evaporation and water production rates. This assertion is also supported by performance simulations in which the brine side spacer was eliminated (**Figure 10**). The figure shows that elimination of the brine-side spacer, which increases brine-side resistance to heat transfer, would have little consequence for the rate of water production. No such claim can be made for the air-side spacer.

Figure 10. Effects of spacers on calculated water production for PVDF $d_p = 0.45$ μm , $u_a = 9.5$ m/s and $u_b = 0.11$ m/s. Lines show results of simulations with spacers present on both sides of the membrane, air-side spacer only, brine-side spacer only and no spacer present. Data were collected with both spacers present.

A large drop in brine temperature between the brine inlet and outlet would also limit module performance. At the highest experimental temperature ($T_{b,in} = 80^\circ\text{C}$) and lowest brine flow rate

($u_b = 0.024$ m/s), ΔT_p was about 4 °C—again probably not enough to present a significant limitation to water production. Nevertheless, practical MD module designs that involve significantly larger in-module travel distance and longer brine retention times should consider the relationship between brine flow and temperature drop in order to maintain the brine vapor pressure over the entire length of the module.

It follows that rates of water production were largely limited by mass transfer, i.e., by (i) resistance to mass transport in the membrane, (ii) in the gas-phase boundary layer, (iii) near-saturation of the gas stream with water vapor ahead of the module exit, or (iv) some combination of these. To eliminate effects due to accumulation of water vapor in the gas stream over the length of the module, simulations were conducted in which water transfer rates were calculated while constraining the gas-phase concentration of water vapor to zero (curve labeled $P_w = 0$ in Figure 11).

Figure 11. Results of simulations in which the effect of accumulation of water vapor in the air flow was eliminated (by setting $P_w = 0$). In subsets of these simulations, either the air-side boundary layer resistance ($1/k_a$) or membrane resistance ($1/k_m$) was minimized. All calculations involved the 0.45 micron PVDF membrane.

Under those circumstances, there was very little increase in the predicted water purification rate when water vapor on the air side was eliminated, indicating that saturation effects were not the primary source of rate limitation (**Figure 11**).

The remaining constraints on water production include only membrane and air-side resistances to mass transfer. To separate these effects, each resistance was individually eliminated (separately) in subsequent simulations. Results (**Figure 11**) indicate that the membrane resistance is the primary source of water purification rate limitation in these experiments. This effect would be more pronounced for membranes with greater thickness or smaller pore size.

Membrane/Module Physical Characteristics.

Brine- and gas-phase spacers potentially affect water production rates (**Figure 10**). Brine side spacers increase the heat transfer coefficient and on the brine side of the membrane, enhancing heat transfer to the brine/gas interface. The permeate-side spacer reduces boundary layer resistance to both heat and mass transfer. As mentioned above, results of simulations indicate that the brine-side spacer is of little relevance to water production—i.e., that compression of the brine-side thermal boundary layer with consequent reduction of heat transfer resistance does not increase water production. It follows that resistance to heat transfer from the bulk fluid to interface does not effectively impede the process, and liquid-phase resistance to heat transfer will receive no further consideration here. Similarly, the resistance to mass transfer provide by the air-side boundary layer, although significant under some circumstances, will not be discussed in great detail.

Membrane characteristics that affect mass transfer are primarily the lumped parameter $\varepsilon/\tau\delta$ and d_p . The interdependence of membrane structural parameters and operational variables further illustrates the importance of simulations in determining the limits of module performance. Here the co-dependence of water production rates on $\varepsilon/\tau\delta$ or d_p (structural parameters) and sweep gas or brine flow velocities (operational variables) is illustrated in a series of contour plots (**Figures 12-14**) built from calculations with the model. Values used for the independent variables in these plots comprise the range of membrane characteristics and operating conditions of the experimental work.

Figure 12. Calculated permeate production flux as a function of sweeping gas velocity and the ratio of membrane porosity to tortuosity times thickness, for $u_b = 0.11$ m/s and brine inlet temperature of $T = 70$ $^{\circ}\text{C}$. Membrane pore size was $d_p = 0.45$ μm .

For the single-layer membranes, for example, water production is sensitive to u_a at high values of $\varepsilon/\tau\delta$ (or d_p) and low sweep gas velocities (**Figures 12 and 13**). In that region, resistance to

convective transport through the gas-phase boundary layer dominates the overall resistance to mass transport, potentially accounting for the observed relationship. Alternately, the exiting gas stream could approach saturation ahead of the module exit, in which case the water production rate would increase with gas flow rate. As previously shown (**Figure 11**), for the length of membrane module used in this study, saturation of the gas stream was not the primary source of limitation to water production. If a longer or hollow fiber membrane module were used, however, saturation of the gas stream might limit the water purification rate.

Figure 13. Calculated permeate production flux as a function of membrane pore size and sweeping gas velocity with $u_b = 0.11$ m/s, brine inlet temperature of $T = 70$ °C and $\varepsilon/\tau\delta = 3000$.

At $T = 70$ °C; $u_a = 9.5$ m/s; $u_b = 0.11$ m/s, water production was sensitive to membrane pore size and the lumped parameter $\varepsilon/\tau\delta$. The relationship is particularly acute at low values of $\varepsilon/\tau\delta$ or d_p (**Figures 13 and 14**), for which membrane resistance tends to restrict water purification rates.

Brine velocity is an important determinant of water production only brine approach velocities are low and $\varepsilon/\tau\delta$ is high (which implies low membrane resistance) (**Figure 14**). The result would be expected if high permeate flux and long brine retention times result in significant cooling of the brine before it exits the module. Large membrane pore size, which also lowers membrane resistance to mass transfer, should have a similar effect.

Figure 14. Calculated permeate production flux as a function of brine velocity and the ratio of membrane porosity to tortuosity times thickness with $u_a = 9.5$ m/s and brine inlet temperature of $T = 70$ °C. Membrane pore size was $d_p = 0.45$ μm .

The ratio of mass transfer resistances in the air-side boundary layer and membrane are presented as a function of pore diameter and sweep gas velocity (other operating conditions fixed) in **Figure 15**. At effective pore diameters < 0.3 μm , the effect of Knudsen resistance is readily apparent. At larger pore diameters, the Knudsen contribution is much reduced, and intra-membrane molecular diffusion becomes more important as a source of overall resistance to mass transfer. At the higher pore diameters, the resistance ratio is fairly sensitive to sweep gas

velocities at $u_a < 4$ m/s, where boundary layer resistance is relatively large, but sensitivity decreases at higher velocities.

Figure 15. Mass transfer resistance ratio of the air boundary layer to membrane as a function of sweeping gas velocity and membrane pore diameter with $u_b = 0.11$ m/s and brine inlet temperature of $T = 70$ °C.

Summary

Coupled heat and mass balances were used to predict permeate production during SGMD in a flat sheet module for four different membranes. Calibration was based on a single fitted parameter—the membrane tortuosity. The calibrated model was valid over a wide range of feed water temperatures, feed water flow rates, and sweep gas velocities. The validated model was then used to predict water production rates as a function of both operational variables and membrane characteristics. For the range of operating conditions in the study, performance simulations suggest that water purification rates were limited primarily by the membrane resistance to mass transfer, as opposed to resistance to mass transfer in the air-side boundary

446 layer, the accumulation of water vapor in the sweep gas, or heat transfer considerations. The
447 importance of MD simulations in identifying sources of performance limits is readily apparent
448 from the results presented. It is also important to note that results of this work cannot be
449 extended to practical membrane modules of vastly different dimension or type without model
450 reconfiguration and reapplication.

Abbreviations

A_i	surface area over a length of a section of the module	m^2
c_p	Heat capacity	J/mol K
d	Diameter	m
d_f	Diameter of spacer filament	m
d_{hs}	Hydrodynamic diameter	m
d_p	Pore diameter	m
D	Diffusivity	m^2/s
h	Heat transfer coefficient	$W/K\ m^2$
H	Spacer thickness	m
ΔH_v	Latent heat of vaporization	J/kg
J	Water vapor flux	$mol/m^2\ min$
k	Mass transfer coefficient	m/s
Kn	Knudsen number	
k_{dc}	Correction factor for spacer geometry	
L	Membrane length	m
Le	Lewis number	
l_m	Spacer mesh length	m
m	Molecular weight	kg/mol
$\dot{n}$	Molar flow	mol/min
Nu	Nusselt number	
P	Pressure	Pa
Pr	Prandtl number	
q	Volumetric flow	L/min
Q	Thermal content	J
r	Radius	m
R	Resistance	
Re	Reynolds number	
Sc	Schmidt number	
Sh	Sherwood number	
T	Temperature	K
z	Unitless length	
Greek Symbols		
δ	Thickness of membrane	m
$\Delta \dot{n}$	Vapor flow	Mol/min
ε	Porosity	Unitless

θ	Spacer mesh angle	degrees
λ	Thermal conductivity of fluid	W/m K
μ	Dynamic viscosity	kg/ m s
ρ	Density	kg/m ³
τ	Tortuosity	Unitless
φ	voidage	Unitless
ν	Kinematic viscosity	m ² /s

Subscripts

1	membrane first layer, active
2	membrane second layer, support
a	Air
b	Brine
c	Condensation
e	Evaporation
f	filament
eff	Effective single layer membrane
effd	Effective for dual layer membrane
Kn	Knudsen
m	Membrane
mol	Molecular
p	Pore
tot	total
v	Vapor
w	Water

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