From low-pressure effusion to membrane distillation

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Thu August 3, 2017
# Membrane Distillation Processes

## Types and Specifics

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Distillate</th>
<th>Phase</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DCMD</strong></td>
<td>hot water</td>
<td>cold water</td>
<td>liquid</td>
<td>feasible</td>
</tr>
<tr>
<td><strong>SGMD</strong></td>
<td>hot water</td>
<td>sweeping gas</td>
<td>@~1 atm</td>
<td>higher flux</td>
</tr>
<tr>
<td><strong>VMD</strong></td>
<td>hot water</td>
<td>(low) vacuum</td>
<td>@1-3% atm</td>
<td>highest flux</td>
</tr>
<tr>
<td><strong>AGMD</strong></td>
<td>hot water</td>
<td>cold surface</td>
<td>solid</td>
<td>low cost</td>
</tr>
</tbody>
</table>

- **DCMD**: Direct Contact Membrane Distillation
- **SGMD**: Swept Gas Membrane Distillation
- **VMD**: Vacuum Membrane Distillation
- **AGMD**: Air Gap Membrane Distillation
Membrane Distillation ← Heat Exchanger

- Module Structure
  - Flat Sheet ← Plate and Frame
  - Hollow Fiber ← Shell and Tube

- Goal of MD in HT
  - To maximize convective (↑) and minimize conductive (↓) \( Q \).
  - So, if vapor flux (↑), total heat flux (↑): latent heat

<table>
<thead>
<tr>
<th>Process</th>
<th>Phase</th>
<th>Thermal Conductivity ( \kappa ) [mW/m·K]</th>
<th>Example Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGMD</td>
<td>Cold solid surface</td>
<td>( O(10^3 - 10^5) )</td>
<td></td>
</tr>
<tr>
<td>DCMD</td>
<td>Liquid water</td>
<td>561 – 679</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solid membrane part</td>
<td>100 – 300</td>
<td></td>
</tr>
<tr>
<td>SGMD</td>
<td>Humid air</td>
<td>20 – 30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Membrane (solid + gas)</td>
<td>20 – 40</td>
<td></td>
</tr>
<tr>
<td>VMD</td>
<td>Vacuum</td>
<td>4 – 8</td>
<td></td>
</tr>
</tbody>
</table>
From low-pressure effusion to membrane distillation

Introduction

Length Scale Analysis

A hollow fiber membrane module, supplied by Econity Inc. (17 cm)

Length scales of HF MD: \( \times (1000)^3 = 10^9 \)

<table>
<thead>
<tr>
<th>Objects</th>
<th>Length Order</th>
<th>In meter</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF length, ( L_{\text{fiber}} )</td>
<td>0.20 – 0.50 m</td>
<td>( O(10^{-1}) )</td>
</tr>
<tr>
<td>HF inter-spacing, ( h_{\text{gap}} )</td>
<td>(~ O(10^{-1} – 1) ) mm</td>
<td>( O(10^{-4} – 10^{-3}) )</td>
</tr>
<tr>
<td>HF Dims., ( (d_o &gt; d_i &gt; \delta_{th}) )</td>
<td>(~ O(10^{-1}) ) mm</td>
<td></td>
</tr>
<tr>
<td>Pore diameter, ( d_{\text{pore}} )</td>
<td>( \leq O(10^{-1}) ) \mu m</td>
<td>( O(10^{-7} – 10^{-6}) )</td>
</tr>
<tr>
<td>Water molecule (( \text{H}_2\text{O} ))</td>
<td>(~ 0.1 ) nm</td>
<td>( O(10^{-10}) )</td>
</tr>
</tbody>
</table>
Why VMD?

Basic configuration

Example (Pros)
1. Highest production rate
2. Less wetting vulnerability
3. Less significant $\Delta T$ effect

Example (Cons)
1. High $e^{-}$ power req.
2. Vacuum pump req.
3. External **condenser** req.
Ocean Thermal Energy Conversion (OTEC) in Hawaii

At the French Academy of Science in Nov. 15, 1926

Georges Claude (24 September 1870 – 23 May 1960)

Masayuki Mac Takahashi, Deep Ocean Water as Our Next Natural Resource.
Retrieved from http://www.terrapub.co.jp/e-library/dow/
"Twenty thousand Leagues Under the Sea" by Jules Verne (1870). Captain Nemo and his assistant discussed ...

OC OTEC = evaporation of \( \sim 30^\circ \text{C} \) surface seawater using \( \sim 5^\circ \text{C} \) deap seawater.

Why don’t we replace the huge evaporator by VMD modules?\(^1,2\) → Estimated footprint reduced to \( \sim 10\% \).

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Conventional Governing Equations for VMD

**Phenomenological equations, implicitly using \( \epsilon, \tau \) and \( \kappa_s \)**

\[
Q_m = Q_{\text{cond}} + Q_{\text{conv}} \ [J_w] \quad (1)
\]

\[
J_w \propto D_{\text{effective}} \times \nabla P_{\text{partial}} \quad (2)
\]

\[
\frac{1}{D_{\text{effective}}} = \frac{1}{D_B} + \frac{1}{D_K} \quad \text{(Bosanquet’s relationship?)} \quad (3)
\]

**Brownian \rightarrow \text{Empirical}**

\[
D_B = \frac{k_B T}{3 \pi \eta d_w} \rightarrow BT^{2.072} \quad (4)
\]

\[
B = \frac{1.895 \times 10^{-5}}{P_T} \quad (5)
\]

**Knudsen (for rarified gas)**

\[
D_K = \frac{1}{3} d_{\text{pore}} \bar{v} \propto T^{\frac{1}{2}} \quad (6)
\]

\[
\bar{v} = \sqrt{\frac{8RT}{\pi M_w}} \quad (7)
\]
Knudsen number analysis (B vs. K)

\[ \text{Kn} = \left( \frac{\lambda_w}{d_{\text{pore}}} \right) \]  

(8)

where \( \lambda_w \) is the mean free path of vapor molecules, and \( d_{\text{pore}} \) is the pore diameter.

From continuum liquid to rare gas

<table>
<thead>
<tr>
<th>Flow regime</th>
<th>Kn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Continuum</td>
<td>( \text{Kn} &lt; 10^{-3} )</td>
</tr>
<tr>
<td>2. Slip (on walls)</td>
<td>( 10^{-3} &lt; \text{Kn} &lt; 10^{-1} )</td>
</tr>
<tr>
<td>3. <strong>Transition</strong></td>
<td>( 10^{-1} &lt; \text{Kn} &lt; 10^{+1} )</td>
</tr>
<tr>
<td>4. Free molecular</td>
<td>( 10^{+1} &lt; \text{Kn} &lt; \infty )</td>
</tr>
</tbody>
</table>

*Table: Dominant transport mechanisms with respect to Kn.*
Introduction

Saturation Pressure of Water

Figure: Variation of (a) water vapor pressure and (b) concentration versus temperature.

- $P_v(80^\circ C) = 0.467 \text{ atm} \rightarrow \sim 50 \% \text{ gas concentration, Knudsen?}$
- $P_v(25^\circ C) = 0.031 \text{ atm} \rightarrow \sim \text{ vacuum pressure}$
Problem Statement

Thermodynamic dilemma in a (straight) pore

1. Mass transport: *Saturation pressure* or *Ideal gas law*?

   \[ J_w = -D_{\text{eff}} \nabla C = -B_{\text{eff}} \nabla (P_v \text{ or } P_{\text{sat}}) \]

   \[ = -B_{\text{eff}} \left( \frac{dP_v}{dT} \right) \nabla T \]

   \[ = -B_{\text{eff}} \nabla (RT\bar{C}) \] (9)

2. If Brownian diffusion\(^3\) only and \( \nabla T \neq 0 \):

   \[ J_w = -D_B \nabla C \rightarrow -\frac{D_B}{T} \nabla (CT) \] (11)

Questions\(^4\)

1. What is the true driving force?
2. How do we deal with the effective (combined) diffusion?
3. Isn’t there any analogous phenomenon in statistical physics?


The true driving force for VMD may be the gradient of the incidence rate $\nu$:

$$\nu = \frac{1}{4} n \bar{v} = \frac{P}{\sqrt{2\pi M_w RT}} \propto \frac{P}{\sqrt{T}} \quad (12)$$

- Governing equations for MT and HT (using enthalpy $H_\nu$) can be

$$J_w = \frac{4}{3} d_p \nabla \nu \propto \nabla \left( \frac{P}{\sqrt{T}} \right) \quad (13)$$

$$Q_{\text{conv}} = \frac{4}{3} d_p \nabla (H_\nu \nu) \neq H_\nu J_w \quad (14)$$
Combined transport through a straight pore may be calculated using Molecular Kinetics and Statistical Mechanics.

Example (Straight pore)

- Top: pore inlet

- Bottom: middle cross-section

Number of vapor molecules colliding with

- a pore wall → Knudsen
  \[
  dN_m = d\Omega \cdot dB_\perp \cdot \nu e^{-\rho/\lambda} \quad (15)
  \]

- an adjacent molecule → Brownian
  \[
  dN_g = d\tau d\psi ds \frac{\cos \alpha}{\pi \rho^2} \frac{\nu}{\lambda} e^{-\rho/\lambda} \quad (16)
  \]

- and the total
  \[
  dN_{total} = dN_m + dN_g \quad (17)
  \]

Before passing through the bottom middle cross-section.
From low-pressure effusion to membrane distillation

Theoretical

Flux contributions

- **Knudsen flux:**

\[
J_m = \frac{N_m}{\frac{1}{4} \pi d_p^2} = \frac{1}{\pi^2} \int_0^{2\pi} d\phi \cdot \int_{-\hat{h}_p}^{+\hat{h}_p} d\zeta \cdot \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} d\psi \cdot \int_0^1 d\omega \times \left( \frac{dv}{dz} \right) \left[ \frac{\zeta^2 \omega^2 \cos^4 \psi \cdot e^{-\rho/\lambda}}{(\cos^2 \psi \omega^2 + \zeta^2)^2} \right]
\]  

(18)

- **Brownian flux:**

\[
J_g = \frac{N_g}{\frac{1}{4} \pi d_p^2} = \frac{8}{\pi d_p^2} \int_{-\pi/2}^{+\pi/2} d\psi \int_0^{s_{\text{max}}} sd\xi \int_0^\pi d\alpha \int_0^{s \cdot \csc \alpha} d\rho \times \left( \frac{dv}{dz} \right) \left( \frac{\rho}{\lambda} \right) \cos^2 \alpha \cdot \sin \alpha \cdot e^{-\rho/\lambda}
\]  

(19)

- **Total flux:**

\[
J_w = J_m + J_g
\]
Regional Governing Equations for a HF membrane

- **Lumen region**
  1. Momentum Transport: NS eq. $\rightarrow$ constant $\langle u \rangle$
  2. HT: Thermal diffusion = Thermal convection

\[ \nabla \cdot (\kappa_{lmn} \nabla T_{inr}) = \frac{\partial}{\partial z} \left( \rho_w c_{pw} u T_{inr} \right) \]  

- **Shell region**
  1. Continuity equation: $\nabla \cdot \langle \rho v \rangle = 0$
  2. Energy balance equation: $\rho c_v v \cdot \nabla T + p \nabla \cdot v = 0$
  3. Euler’s equation: $\rho v \cdot \nabla v + \nabla p = 0$
  4. State equation (ideal gas law): $p = nk_B T = CRT$

- **Membrane region**
  1. Continuous $T$ and $P$
  2. $J_w = \langle v \rangle$ of gas
Mean molecular speed under $T$ gradient, $v^\dagger$

- From the new general definition of vapor flux:

$$J_w = -\frac{1}{3} d_p \nabla (n\bar{v})$$  \hspace{1cm} (21)

- Effective mean molecular speed $v^\dagger$ from $\nabla (n\bar{v})$: proportional to the linear momentum density:

$$\nabla (n\bar{v}) = v^\dagger \nabla n$$  \hspace{1cm} (22)

$$v^\dagger = \sqrt{\left(\frac{8RT}{\pi M_w}\right)\left(1 + \frac{\ln T_1/T_2}{\ln n_1/n_2}\right)}$$  \hspace{1cm} (23)
Example: $v^+$ in DCMD

Figure: Ratio of the effective and mean molecular speed, $v^+ / \bar{v}$, with respect to the feed $T$ ranging from 26 °C to 90 °C at cold distillate $T$ at 25 °C.

- The minimal influence of the temperature gradient on $\bar{v}$ because

$$\frac{\ln T_1 / T_2}{\ln n_1 / n_2} \ll 1$$

so that $v^+ \sim \bar{v}$ even if $\nabla \neq 0$.  

(24)
Results and Discussions

Experimental verifications

Experimental setup

Figure: Schematic of vacuum membrane distillation operation using cold deepsea water.
## Experimental Parameters

<table>
<thead>
<tr>
<th>Variables</th>
<th>Values</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore diameter, $d_p$</td>
<td>0.10</td>
<td>μm</td>
</tr>
<tr>
<td>Membrane porosity, $\epsilon$</td>
<td>0.70</td>
<td>[-]</td>
</tr>
<tr>
<td>Thermal conductivity, $\kappa$</td>
<td>0.2</td>
<td>W/m K</td>
</tr>
<tr>
<td>Contact angle, $\theta_c$</td>
<td>105 ± 5</td>
<td>°</td>
</tr>
<tr>
<td>Inner diameter, $D_i$</td>
<td>0.70</td>
<td>mm</td>
</tr>
<tr>
<td>Outer diameter, $D_o$</td>
<td>1.20</td>
<td>mm</td>
</tr>
<tr>
<td>Thickness, $\delta_m$</td>
<td>0.25</td>
<td>mm</td>
</tr>
<tr>
<td>Number of fibers, $N_{hf}$</td>
<td>180</td>
<td>ea.</td>
</tr>
<tr>
<td>Fiber length (ea.), $l_f$</td>
<td>0.17</td>
<td>m</td>
</tr>
<tr>
<td>Total fiber length, $L_f$</td>
<td>30.6</td>
<td>m</td>
</tr>
<tr>
<td>Total surface area</td>
<td>$A_{mi} = 0.0673 \ (w/ \ D_i)$</td>
<td>m²</td>
</tr>
<tr>
<td></td>
<td>$A_{mo} = 0.1154 \ (w/ \ D_o)$</td>
<td>m²</td>
</tr>
</tbody>
</table>

**Table:** Characteristics of hollow fiber membranes.
Results and Discussions

Experimental verifications

Experimental conditions

<table>
<thead>
<tr>
<th>Operation</th>
<th>Variables</th>
<th>Values</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum (shell) pressure, $P_{\text{vac}}$</td>
<td>$0.031 - 0.037$</td>
<td>bar</td>
<td></td>
</tr>
<tr>
<td>Feed (lumen) temperature, $T_f$</td>
<td>$26 - 61$, $\Delta T = 5$</td>
<td>$^\circ C$</td>
<td></td>
</tr>
<tr>
<td>Feed flow rate, $q_f$</td>
<td>1.0</td>
<td>liter/min</td>
<td></td>
</tr>
<tr>
<td>Feed flow speed, $u_f$</td>
<td>0.24</td>
<td>m/sec</td>
<td></td>
</tr>
<tr>
<td>Condenser Temperature, $T_c$</td>
<td>$4.5 \pm 0.5$</td>
<td>$^\circ C$</td>
<td></td>
</tr>
</tbody>
</table>

Table: Experimental factors using low-temperature feed stream.

1. $P_{\text{vac}} = 0.031$ bar equivalent to $T_{\text{dist}} \approx 25^\circ C$ in DCMD.

2. $T_{\text{feed}} \approx 26^\circ C$ about sea surface temperature in tropical areas.
Saturation pressure of seawater: \( P_v(C,T)/P_v(0,T) \)

- Empirical correlations reported: ML\(^5\), EJ\(^6\), and WP\(^7\).

- In Weiss and Price’s work, \( P_v \propto \ln C \).

\(^6\) Emerson and Jamieson, Desalination, 3 (1967), 207–212.
Diffusive Tortuosity

1. Maxwell\textsuperscript{8} originally used the concept of tortuosity to compare the electric conductivity of a medium with and without non-conducting spheres (for high $\epsilon$): $\tau = 1 + \frac{1}{2} (1 - \epsilon)$

2. Mota et al.\textsuperscript{9} conducted an empirical study on the tortuosity of binary mixtures with $\beta = 0.4$: $\tau = 1 - e^{-\beta}$

3. Iversen and Jørgensen\textsuperscript{10} provided a similar correlation to Maxwell’s theoretical expression with $q = 2$: $\tau = 1 + q(1 - \epsilon)$.

4. Beekman\textsuperscript{11} developed an analytical approach to model the nature of highly interconnected pores: $\tau = \epsilon / [1 - (1 - \epsilon)^{1/3}]$

5. For a various arrangement of cylinders\textsuperscript{12} ($\mathcal{P} = 1$) and spheres\textsuperscript{13} ($\mathcal{P} = 2$): $\tau = 1 - \mathcal{P} \ln \epsilon$

\textsuperscript{8} A Treatise on Electricity and Magnetism, Clarendon Press, Oxford, 1873.
\textsuperscript{13} Geochimica et Cosmochimica Acta, 60, (16) (1996) 3139-3142
VMD experiment using cold deepsea water

**Figure**: Comparison with experimental observation and theoretical prediction for salinity 0.0, 32.0, and 64.0 g/kg using HF VMD module consisting of $N_{\text{fiber}} = 180$ fibers. ($d_p = 0.10 \, \mu m$, $\epsilon = 0.70$, $\kappa = 0.10 \, W/\, m \, K$, $a_f = 0.35 \, mm$, $b_f = 0.6 \, mm$, and $l_f = 0.17 \, m$, $P_v = 0.031 - 0.037 \, \text{bar}$, $T_{\text{vacum}} = 4.5 \pm 0.5^{\circ} \, C$, and $\langle u \rangle = 0.24 \, m/s$).
Heat flux insensitive to salt concentrations

Figure: Heat transfer rate simulations using the same parameters of Fig. 4.
Effects of $T_{\text{vac}}$ on mass and heat fluxes: $\propto \nabla (P / \sqrt{T})$

**Figure:** As $T_{\text{vac}}(\uparrow)$, $J_w(\uparrow)$ and $Q(\downarrow)$
On-going work: module-scale CFD simulations

MD as pseudo-conductive heat transport:

\[ Q_{\text{total}} = Q_{\text{conductive}} + Q_{\text{convective}} \]  \hspace{1cm} (25)
\[ = -\kappa_m (\kappa_s, \epsilon) \nabla T - \frac{4}{3} d_p \nabla (\nu H_w) \]  \hspace{1cm} (26)
\[ = -\tilde{\kappa}_m (\kappa_s, \epsilon, H_w, T) \nabla T \]  \hspace{1cm} (27)

1. \( Q_{\text{conductive}} \): CFD using an **impermeable** membrane
2. \( Q_{\text{total}} \): CFD using **pseudo-thermal** conductivity \( \tilde{\kappa}_m \)
3. \( Q_{\text{convective}} = \text{Total} - \text{Conductive} \)
Undergraduate students’ posters: VMD & DCMD

- Flat sheet module: 20 cm × 10 cm × 2.010 cm
- CFD package: OpenFOAM (customized)
Conclusions

1. The fundamental transport quantity primarily controlling the mass and heat fluxes is the incidence rate: \( \propto \nabla v \).

2. In VMD, both vacuum-side \( P_{\text{vac}} \) as well as \( T_{\text{vac}} \) can be controlling factors.

3. Saline concentration does not significantly influence the vapor flux: \( P_v(C, T) \approx P_v(0, T) \).

4. Mass transport in VMD must be in the transition region between Brownian and Knudsen diffusion (in review): \( 0.1 < \text{Kn} < 10 \).
Thanks for enough(?) FoodEnergyWater.

Thanks You!