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INFLUENCE OF PORE STRUCTURE ON MEMBRANE WETTABILITY IN MEMBRANE DISTILLATION

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ABSTRACT

Amongst the vast variety of desalination technologies suitable to be coupled with solar energy, membrane distillation (MD) is recently being considered because of its feasible features for stand-alone systems and low operational requirements. MD is a thermally driven separation process that uses a hydrophobic membrane to create a liquid-vapor interface from which water evaporates. This vapor crosses the membrane and is condensed on the other side as salt-free distillate. One problem that faces MD systems is pre-mature wetting of the membrane, leading to operational interruptions. Pore wetting happens when feed liquid (seawater in desalination application) is subjected to pressure high enough to cause it to pass through the pores of the hydrophobic membrane. This pressure is termed Liquid Entry Pressure (LEP). Membrane wetting can be predicted using a basic force balance equation. However, MD operations have proven to be more complicated than what can be predicted for a membrane with simple cylindrical pores. In this study, we studied the impact of pore structure on pore wetting in MD membranes. Several interesting trends were observed and discussed. The ultimate goal of this research is to make better prediction of the conditions at which the membrane will start to wet and fail. This will enable a more sustainable MD operation.

Keywords: Membrane Distillation; membrane wetting; pore structure

1.INTRODUCTION

Membrane Distillation (MD) is a thermally driven separation process that can be used in desalination application. It uses a hydrophobic membrane to create a liquid-vapor interface from which water evaporates. This vapor crosses the membrane and is condensed on the other side as salt-free distillate. The hydrophobic porous membrane used in this process does not allow the liquid transfer until a certain pressure, known as the liquid entry pressure (LEP), is reached. LEP is defined as the pressure difference at which the liquid penetrates into the pores of the hydrophobic membrane [1], which is greatly important in membrane distillation desalination processes. During MD, liquid entry should be avoided or permeate water quality can be affected negatively.

To measure the LEP, pressure is gradually applied on the feed side of the membrane until the first drop of the feed solution appears on the permeate side or until a continuous permeate flow occurs. These LEP measurement guidelines have been described by Smolders and Franken [1] in detail and have been used by various researchers for both flat-sheet [2,3,4,5,6,7,8,9] and hollow-fiber membranes [10,11]. Other authors used conductivity changes on the permeate side in a membrane distillation set-up to determine the LEP [12].

LEP is correlated to the liquid surface tension, the contact angle of the liquid on the membrane surface, and the size and shape of membrane pores (especially the largest pore size). Operating temperature and feed solution composition can have a significant effect on the liquid contact angle (CA) and the liquid surface tension [13]. The maximum pore size of the membrane and the pore geometry are normally assumed to be constant for the same membrane under different operating temperatures (Typical MD desalination temperatures range between 30 to 85˚C). However, this study considers the possible effect of temperature on LEP via mechanisms other than its impact on CA and surface tension, namely through change in pore structure, despite the polymers' generally high thermal stability. Hence, in this study, the impact of membrane morphology on pore wetting in MD membranes is analyzed.

2. THEORY

Let F_E be the external applied force and F_γ be the force of surface tension. Such that (Figure 1)

$$F_\gamma = \gamma \, L \cos(\theta) \qquad \text{(Eq. 1)}$$

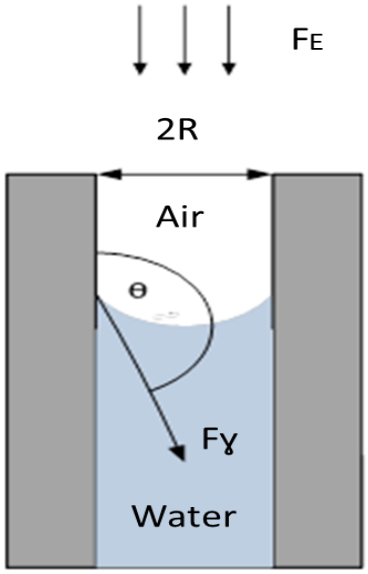

Figure 1-Pore wetting forces

Where γ is the surface tension of water, L is the pore perimeter in contact with water (Figure 2), A is the cross-sectional area of the pore (Figure 2), and θ is the contact angle of the water. In the case where $\theta > 90$, $\cos(\theta)$ will be negative, of which the absolute value needs to be taken.

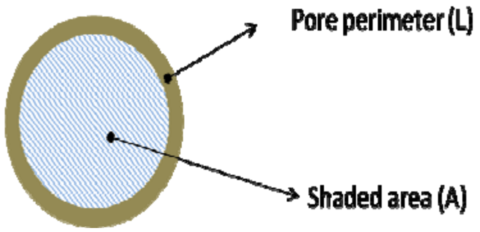

Figure 2-Cross-sectional view of pore

For a non-wetting liquid, the external pressure required to overcome the surface tension and capillary forces that hold the liquid outside the pores is defined as P_E .

The externally applied pressure (P_E) and pressure due to water surface tension (P_γ) can be defined as

$$P_E = \frac{F_E}{A} \qquad \text{(Eq. 2)}$$

$$P_\gamma = \frac{F_\gamma}{A} \qquad \text{(Eq. 3)}$$

Assuming the hydraulic pressures of the permeate and feed are both initially at atmospheric pressure. The minimum pressure above which pore wetting is observed occurs when

$$P_E = P_\gamma \qquad \text{(Eq. 4)}$$

Therefore, P_E can be defined as LEP and this can be expressed as

$$P_E = \frac{\gamma * \cos(\theta) * L}{A} = \text{LEP} \qquad \text{(Eq. 5)}$$

Let Z be the “morphology factor”, which is the pore perimeter (L) divided by its cross-sectional area (A). Thus, for a pore opening of any shape

$$\text{LEP} = \gamma \cos(\theta) * Z \qquad \text{(Eq. 6)}$$

In the case of a circular-shape pore, Z=2/R, where R is pore radius. So,

$$\text{LEP} = \frac{2\,\gamma \cos(\theta)}{R} \qquad \text{(Eq. 7)}$$

In some cases, Equation 7 is expressed in more general terms as equation 8 below, which is another form of Equation 3 [14]:

$$C = \frac{2\,B\,\gamma \cos\theta}{R} \qquad \text{(Eq. 8)}$$

Where B is often referred to as “the geometric factor”.

3. METHODOLOGY

3.1 Membrane samples tested

Three polytetrafluoroethylene (PTFE) membranes, obtained from GORE (USA), with a nominal pore size of 0.2 microns were tested. The membranes differed in their polypropylene (PP) backers, as shown in Table 1 below. These membranes were chosen because they are made by the same manufacturer, have the same nominal pore size and hydrophobic layer and only differ in their backer.

Table 1- Samples tested

	Hydrophobic layer	**Backer**
Sample 1	PTFE 0.2 microns	PP Scrim
Sample 2	PTFE 0.2 microns	PP non woven standard flow
Sample 3	PTFE 0.2 microns	non woven high flow

3.2 contact angle Measurements

EASY DROP® contact angle measurement instrument from Kruss (Germany) was used. A piece of membrane was placed on a platform situated in the thermostat chamber that was kept at constant temperature by an external liquid circulation thermostat. A microsyringe was used to manually generate a de-ionized water drop on the membrane surface. The contact angle was calculated from a digital image of the drop on the membrane using an image-processing program, which allowed the estimation of the contact angle from the circle fitting of the drop using the sessile drop method. The value of contact angle was averaged over at least six iterations for each membrane. The static contact angles were measured at 24 (room), 50 and 70 ˚C for each membrane. Each measurement was taken within less than 30 seconds from the time the drop was placed on the membrane surface in order to minimize the effects of variation in the contact angle due to evaporation of 3.3

3.3 LEP Measurements

A small chamber is filled with water and then set at the required temperature. The temperature is controlled via a thermal sensor connected to a heater. When the set temperature of the water is reached, the membrane sample is placed such that the PTFE (active hydrophobic layer) is in contact with the water (feed). The pressure is gradually increased at 1.5 psi/min on the feed water using compressed air. The test is then supervised visually. When the first small bubble appears on the backside of the membrane, the corresponding pressure is recorded as the liquid entry pressure (LEP). The appearance of the bubble means that water had flowed through the pore and penetrated to the other side of the membrane.

3.4 surface tension Measurements

The water surface tension of the deionized water used was assumed to be the same as the surface tension of pure water. Variation of surface tension of pure water with temperature was obtained from literature [15] as shown in Table 2.

Table 2- Surface tension of water with temperature

Temperature (˚C)	**Pure water surface tension (mN/m)**
25	71.99
50	67.94
70	64.47

4.RESULTS and DISCUSSION

4.1 Contact angle results

As shown in Table 3, the contact angle decreases with temperature for all three samples. The standard deviation for the contact angles was less than 2.5˚ for all the measurements taken.

Table 3-Contact angle measurements

	25˚C		**50 ˚C**		**70 ˚C**	
S#	**ө (˚)**	**SD (˚)**	**ө (˚)**	**SD (˚)**	**ө (˚)**	**SD (˚)**
1	130.00	0.80	129.71	2.15	123.46	1.93
2	130.5	2.23	129.90	2.12	128.25	1.55
3	132.27	1.75	129.18	1.715	126.81	0.87

4.2 LEP and Z Results

As expected, the minimum LEP went down with room temperature for all membranes, partially due to reduced surface tension and contact angle of water with increased temperature. Another reason behind the reduced LEP with temperature, and the variation in the reduction trend from one sample to another is due to morphological changes. Figure 3 shows that at room temperature, Sample 1 showed the highest LEP value. However, as the temperature was increased to 50 ˚C and 70 ˚C, the

LEP for sample 1 became closer to the LEP for sample 2. Meanwhile, sample 3 showed the steepest decrease in LEP value with temperature, as shown by the linear trend in Figure 3. At 70˚C, the LEP value for sample 3 dropped to as low as 17 psi compared to 35 psi for samples 1 and 2. This can be attributed to the significant variation in membrane pore morphology with temperature of the PP backer used for sample 3. Figure 4 shows that the calculated Z-values were not constant; rather the Z-value varied with temperature for all of the samples tested which indicates that not only the surface tension and contact angle vary with operating conditions but so does the porous membrane geometry, which consequently affects the overall predicted LEP value. For all temperatures, Sample 1 with scrim backer has the highest Z value, followed by Samples 2 and 3. Samples 1 and a 2 showed a relatively small decrease in Z value compared to Sample 3. With sample 3 a linear morphological decreases with temperature was observed. This decrease in Z value indicates that the pore shape is varying from the ideal circular shape with temperature.

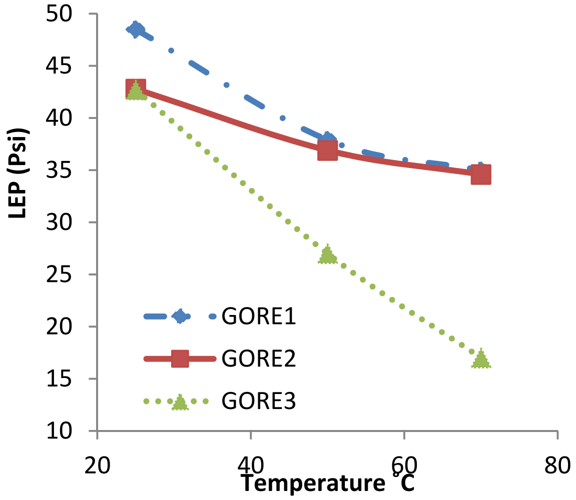

Figure 3- Measured minimum LEP values

5. CONCLUSIONS

Three PTFE membranes with different backers were examined. The contact angle and LEP was measured for each membrane at three different temperatures: 25˚C, 50 ˚C and 70 ˚C. The Z factor was calculated at each of the measurements.

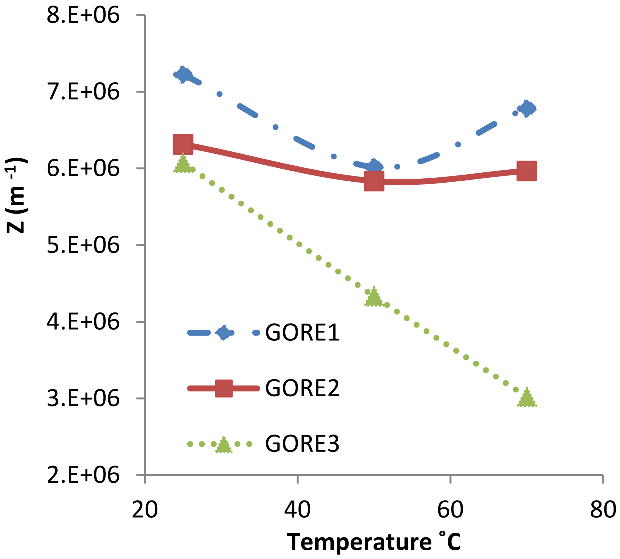

Figure 4- Calculated Z values

Unexpectedly, It was found that the Z value is not constant rather it decreases with temperature as the pore structure changes, and thus results in lower than predicted LEP values.

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