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Theoretical assessment and experimental analysis of liquid entry pressure in membrane distillation process

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ABSTRACT

Liquid entry pressure (LEP) of membrane is crucial in the process of membrane distillation (MD) to ensure the quality of distillate since the whole operation will be contaminated as soon as the feed liquid starts to penetrate the hydrophobic membrane. Assuming standard condition (i.e., ambient temperature, hydrostatic pressure, etc.), experimental LEP values were inconsistent compared with theoretical LEP, thus rigorous analysis attempt was made to help understanding the wetting phenomena in MD. We first conducted an experiment with LEP device under various temperature of the feed water. Scanning electron microscopy images were taken to visualize the pore size transition and the results were proved with capillary flow porometry of each membrane after the experiments. Effects of different flow rate have also been studied, yet the results showed no significant difference. As a natural result, LEP is temperature dependent; however, other factors which are not reflected in the LEP equation also exist. Experiments show that the wetting at pressure above LEP may not only wet the membrane but also affect membrane properties. Therefore, in the MD process, the importance of preventing wetting exceeds the necessity of recovering after wetting.

Keywords: Membrane distillation; Liquid entry pressure; Wetting; Membrane deformation

1. Introduction

Membrane distillation (MD) is a thermally driven process utilizing a porous hydrophobic membrane to produce clean water in vapor forms separating from a liquid mixture. MD best shows its applicability when used in desalination field because of its unique mechanism. Since only water molecule as vapor form will penetrate the membrane, salt rejection rate can reach up to 100% in theory [1,2]. Comparable with other thermally driven desalination processes such as multi-stage flash and multi-effect distillation, MD uses less energy since temperature of the feed water does not have to be increased up to boiling temperature to produce water [3,4]. Moreover, concentration of feed solution is reported to have less effect in efficiency on MD than on reverse osmosis, the most widely used desalination technology [5–7].

Despite of its advantages, MD technology still faces many problems with one of them being wetting phenomena. The driving force depends on the vapor pressure difference as mass transfer through the hydrophobic membrane only takes place in the vapor phase [1,2]. However, the membrane loses hydrophobicity when wetting occurs, and the whole process can be contaminated [8]. The feed liquid containing the contaminants can be contained and prevented from penetrating the membrane when the hydrophobicity of the membrane is not lost so that quality of the produced water remains pure. Since hydrophobic membrane allows volatile components to pass through, amount of volatile organic compounds and any components with low surface tension that can possibly wet the membrane more easily should be monitored.

The minimum transmembrane pressure at where liquid penetrates the membrane is called liquid entry pressure (LEP). LEP is calculated by using Young–Laplace capillary

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equation. The equation under standard condition (i.e., ambient temperature, hydrostatic pressure, etc.) assumes that the pore is perfectly cylindrical and the surface is smooth. However, membrane pores are not perfectly cylindrical, and other operation parameters are not considered when calculating LEP according to Young–Laplace equation.

LEP measurement is frequently used as one of critical criteria for hydrophobic membrane manufacturers since high LEP may indicate high applicability and superior performance of their membranes. LEP measuring device reported by most of the related papers utilizes static LEP device which find it difficult to imitate actual environment where the pressure applied is not static for an example. Consequently, LEP acquired in the field has shown some inconsistencies from theoretical LEP, thus rigorous analysis attempt was made to help understanding the wetting phenomena of MD.

2. Materials and methods

2.1. Theory

The difference at the liquid–vapor interface is expressed with Young–Laplace equation. The equation assumes that the pore is uniform, cylindrical, and sufficiently small which supposes constant curvature of radius [9–11]. LEP is a pressure when the first drop of feed solution penetrates through the largest pore in the hydrophobic membrane. Its critical parameters include interfacial tension, contact angle at the membrane surface (at pore entrance), pore size, and pore morphology.

Franken et al. [9] have suggested a model which determined LEP derived from Young–Laplace equation as:

$$\text{LEP}_w = \frac{-2B\gamma_l\cos\theta}{r_{\max}} \tag{1}$$

where LEP_w is the liquid entry pressure of deionized (DI) water, B is the dimensionless factor of membrane pore geometry ($B = 1$ for ideal cylindrical pores and $0 < B < 1$ for unideal pores), γ_l is the surface tension of the solution, θ is the angle of contact between the solution and the membrane surface in N/m, and $r_{\max}$ is the largest pore radius in m. Temperature affects the surface tension of the liquid. Surface tension of DI water, γ_w, is modified using the following Eq. (2) as:

$$\gamma_w = 235.8\left(1-\frac{T}{T_c}\right)^{1.256}\left[1-0.625\left(1-\frac{T}{T_c}\right)\right] \tag{2}$$

where both water temperature T and the critical temperature $T_c = 647.096$ K are expressed in Kelvin [12].

2.2. Materials and equipment

2.2.1. Membrane properties

DI water was used as feed solution of all LEP tests. The LEP module was employed in the experiment to embed membranes. Polyvinylidene fluoride (PVDF) flat-sheet membrane having a pore size of 0.45 μm was used. Table 1 shows detailed specifications of the membrane.

Table 1
Properties of the membrane

Material	PVDF
Type	Flat-sheet
Produced by	Millipore
Pore size, μm	0.45
Porosity, %	75
Thickness, μm	115
Membrane area, m^2	0.004275

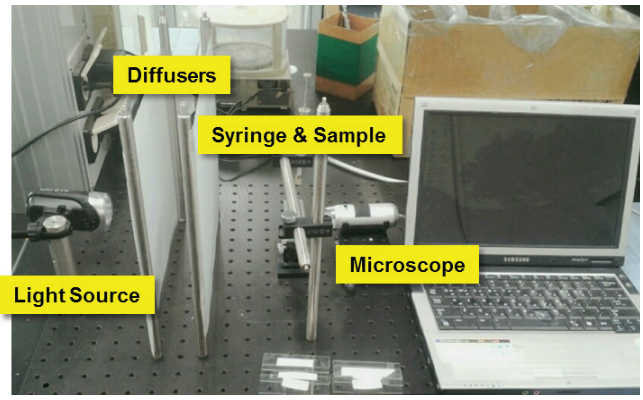

Fig. 1. Custom built contact angle apparatus.

2.2.2. Contact angle measurement

To measure the contact angle between the liquid and the membrane surface, a custom measuring apparatus was built and used (Fig. 1). Chemicals with known surface tension (i.e., diiodomethane and water) were deposited on the membrane through syringe. Light source and diffusers help the droplet image taken by microscope more visible. The contact angle was measured 5 min after the deposition of the droplet. The size of the droplet was decided and controlled to minimize distortion of droplet caused by gravity [13]. An image analyzing program utilized axisymmetric drop shape analysis method to show the results.

2.2.3. Dynamic LEP device

To control the temperature and to apply different concentration of liquid, static LEP device was not going to suffice. A schematic of custom built dynamic LEP device is shown in Fig. 2. Both inlet pressure and outlet pressure were measured as well as the temperature. A digital gear pump with flow rate control (Cole-Parmer, Korea) supplied pressure up to 700 kPa on the membrane. The pump flow rate was first set to 5 mL/s which translates to a similar flow velocity of 0.03 m/s. A needle valve installed at the end of the outlet provided additional flow and pressure control to the system. A vacuum pump at the end was installed for possible cases where gear pump pressure could not overcome LEP of the membrane. The pressure when the liquid penetrates the membrane is recorded by the digital scale. The experiment continued, maintaining the same pressure, to record wetting rate of the membrane. After certain pressure point where linear trend of pressure is recorded along the pressure vs. mass flux graph, the pressure was lowered by both releasing the needle valve and lower the flow rate of the pump until the pressure reaches zero.

2.2.4. Static LEP device

The equipment, as shown in Fig. 3, was designed to measure the LEP of hydrophobic membrane. This equipment is widely used to measure the LEP as shown in other papers [1,10]. The device was composed of a reservoir, a rubber piston, a digital pressure gauge, and a pressure regulator. The reservoir was filled with DI water. Its volume was 25 mL excluding the rubber volume. A membrane was 7.5 cm in diameter and effective area of membrane was 9.62 cm^2. A thin steel plate with hole was adopted to support. Nitrogen gas (99.99%) was used to apply static pressure which was controlled by precision pressure regulator (CM2-B515-DW, TANAKA). An applied pressure measurement was used and the digital pressure gauge with a maximum allowable pressure up to 10 bar (PSA-1, Autonics) which measures relative pressure to the atmospheric pressure.

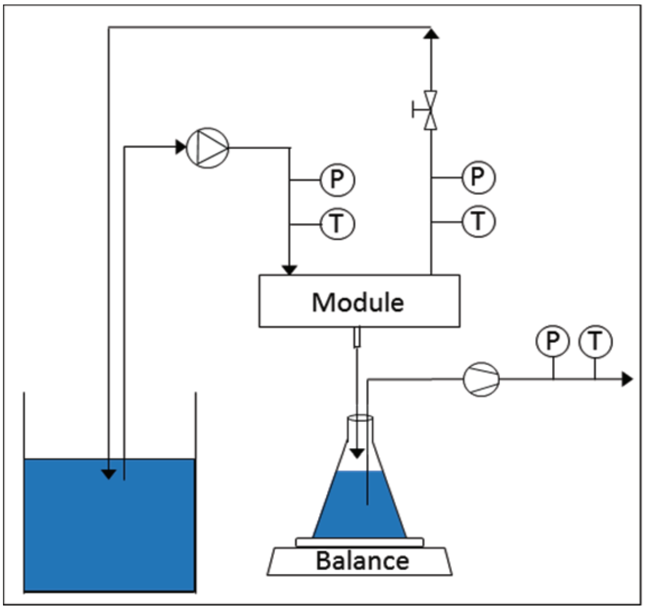

Fig. 2. Custom built dynamic LEP device.

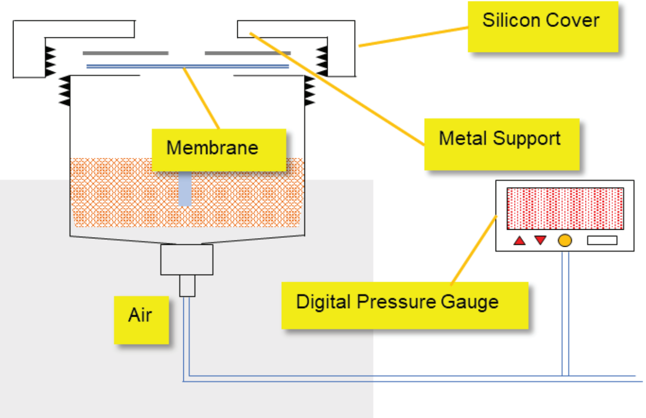

Fig. 3. Schematics of static LEP device.

2.2.5. Scanning electron microscopy measurements of membranes

The membrane surface morphologies are evaluated by scanning electron microscopy (SEM; NOVA Nano SEM 450, FEI). The SEM analysis was used to visualize surface deformation of operated membranes in comparison with raw membranes.

3. Results and discussion

3.1. LEP measurements using custom made device

The theoretically derived LEP value was judged to be different from the actual value obtained in the field. For example, the thickness of membrane is excluded from this equation, however, is known to affect LEP [14,15]. Therefore, the experiment was carried out to imitate MD module with controlling operational parameters as in the field which may have not been well expressed in theoretical LEP.

3.1.1. Effects of flow rate on LEP

First, dynamic LEP experiment was performed to find out whether flow rate influences LEP. According to the experimental results as shown in Fig. 4, LEP with flow rate of 10 mL/s was the lowest where an experiment with 5 mL/s was the highest. Although, the difference between the highest and the lowest LEP recorded were observable, the pressure was increased by 0.05 bar for every 2 min; therefore, it is reasonable to conclude that there is no significant effect caused in LEP value by flow rate.

The flow rate should be considered though to make sure the pressure created by the flow rate is lower than LEP of the membrane. Some researchers reported that continuous operation of MD – although the hydrostatic pressure is comparably low – has damaged the membrane causing membrane deformation, and ultimately, wetting the membrane more easily [16]. Intensive study to see the effects of flow rate on membrane integrity should be done in the future.

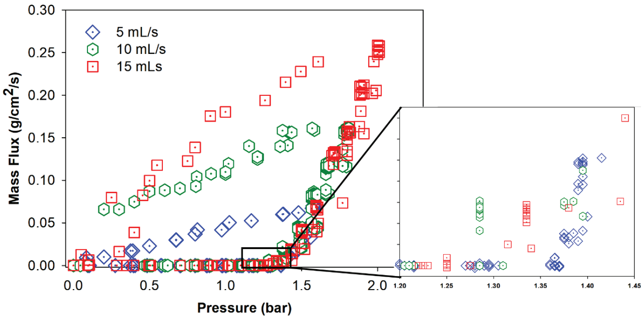

Fig. 4. LEP of PVDF (0.45 μm) membrane with various flow rate (at 20°C).

3.1.2. Effects of temperature on LEP

Since MD operation always involves high temperature on one side of the membrane, the effects of temperature on LEP value needed to be evaluated. The experiments were done with 10 mL/s. The experiment to find the relationship between LEP and the temperature (Fig. 5) confirms that the LEP decreases with increasing temperature. Similar results have been reported by Garcia-Payo et al. [17]. This can be attributed to the decrease in the water surface tension via increasing temperature as well as the decrease of the contact angle on the membrane (Table 2). Also, the theoretical LEP and the dynamic LEP values are different with each other. The difference may have been caused by factors which have not been considered in the Young–Laplace LEP equation, for example, the membrane thickness, the porosity, and manufacturing method. Therefore, theoretical LEP value alone may provide misleading information for MD operation when operational parameters are omitted.

3.2. Membrane deformation via wetting over LEP

To visualize influence of wetting on the membrane, indirect analysis on membranes after static LEP experiments was carried by analyzing multiple SEM images as shown in Fig. 6. Comparing Fig. 6(a) with Fig. 6(c), membrane deformation which was not present in the raw membrane was observed. Deformation tends to be shown sporadically throughout membrane after the wetting. Deformation as shown in Fig. 6(d) reveals that LEP experiments have deformed the membrane which will greatly decrease the LEP if the membrane was to be recovered and reused. When membrane is subjected to pressure, it is deformed and considered that the physical properties (such as pore size and pore geometry) are changed and difficult to recover. The results may lead to a conclusion that the membrane should be prevented from being wetted rather than recovering wetted membrane since wetted membranes will likely experience permanent damages.

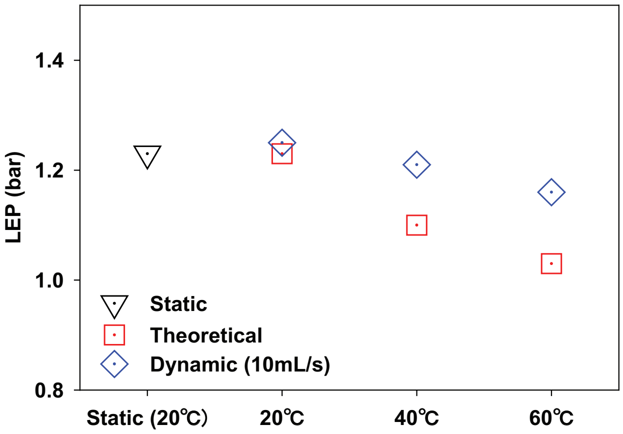

Fig. 5. LEP value comparison of static, theoretical, and dynamic LEP.

Table 2
LEP values affected by temperature on PVDF (0.45 μm) membrane (10 mL/s)

Temperature, °C	20	40	60
Contact angle, °	113.5	112.0	111.6
Surface tension, mN/m	72.7	69.6	66.2
Theoretical LEP, bar	1.23	1.10	1.03
Experimental LEP, bar	1.25	1.21	1.16

When the membrane is wetted the first time, various technique to restore hydrophobicity of the membrane can be introduced and then reuse the membrane. However, as shown in Fig. 6, whether the recovery is successful, it will not ensure the membrane integrity to be restored as well. Also, repetitive operation may induce permanent damage on the membrane. Therefore, repetitive wetting experiment using dynamic LEP device was conducted.

The dynamic LEP experiment was repeated several times with the same membrane. The SEM images from Fig. 6 further support the theory as shown in Fig. 7. A similar deformation on the membrane surface subjected to overpressure on dynamic LEP is shown. However, in the case of dynamic LEP test, the degree of the damage to the membrane was not clearly shown in the first experiment, unlike the membrane subjected to the static LEP test (Figs. 6(d) and 7(a)). As the membrane was repetitively wetted, the SEM image shows that the stretching of the membrane is gradually increasing as compared with the initial membrane (Fig. 7(b)). That is, when the membrane wetting occurs under dynamic pressure, the physical properties (i.e., pore size, pore geometry, etc.) of the membrane are permanently changed. Therefore, membrane damage occurs beyond whether the LEP by static or dynamic experiment. As a result, the measured LEP tended to decrease continuously as the wetting frequency increased (Fig. 8).

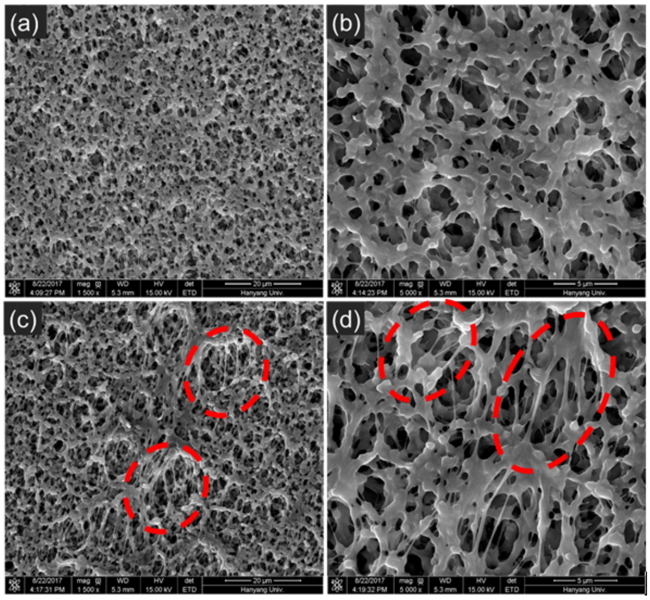

Fig. 6. SEM images of static LEP experiment of PVDF (0.45 μm) membrane of (a) raw (×1,500), (b) raw (×5,000), (c) after wetting (×1,500), and (d) after wetting (×5,000).

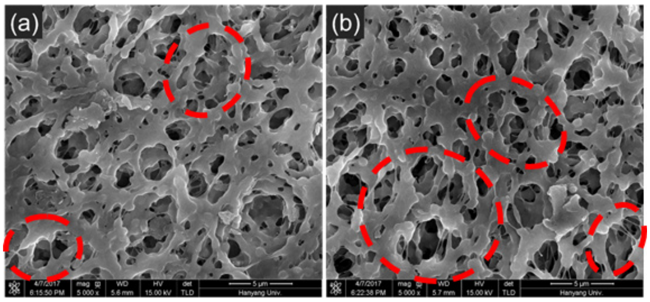

Fig. 7. SEM images (×5,000) of dynamic LEP experiment of PVDF (0.45 µm) membrane (a) after operated once and (b) operated for three consecutive experiment.

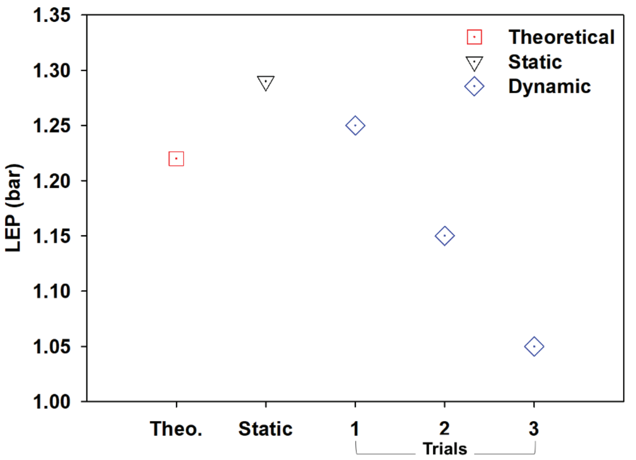

Fig. 8. Difference in LEP after multiple trials of membrane wetting experiment.

In other words, it can be regarded as a basis for failing to maintain the performance of the membrane that was initially tested.

4. Conclusion

In this study, we conducted set of experiments to see the effect of various components on the membrane when the wetting occurs. This study can be summarized into three major points:

1. There is no change in LEP regarding flow rate in MD process. Therefore, the flow rate can be increased up to known LEP of the membrane when operating MD.
2. LEP is temperature dependent. This is a natural result. However, the difference between the theoretical LEP and the measured LEP may also have been influenced by other factors not reflected in the LEP equation.
3. Wetting at pressure above LEP may not only wet the membrane but also affect membrane properties. Therefore, the importance of preventing wetting exceeds the importance of recovery of wetted membrane in the MD process.

Acknowledgments

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