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Influence of microporous membrane properties on the desalination performance in direct contact membrane distillation

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ABSTRACT

To evaluate the influence of membrane properties on direct contact membrane distillation (DCMD) performance, a variety of microporous hydrophobic flat sheet membranes of polyvinylidene fluoride (PVDF) and expanded polytetrafluoroethylene (ePTFE) were employed in this study over a range of hot brine temperatures, 65–85 °C. The membrane thickness was varied between 23 μm and 125 μm; the nominal pore size was varied from 0.05 μm to 0.45 μm; the porosity was generally high in the range of 0.7–0.8. Experiments were done using two different flat test cells, a stainless steel cell and a chlorinated polyvinyl chloride (CPVC) cell. Boundary layer heat transfer resistances in the membrane cell on both sides of the membrane and the two membrane surface temperatures were determined from the experimental data over a range of hot brine and cold distillate flow rates by the Wilson plot technique. Membrane properties such as the maximum pore size and tortuosity were characterized and employed in checking out model assumptions and model results for water vapor transport in the Knudsen regime and the transition region. Good agreements (within 5% deviation) of the membrane mass transfer coefficient of water vapor and the observed water vapor fluxes were obtained between the experimental values and the simulated results predicted for either the Knudsen regime or the transition region.

1. Introduction

Membrane distillation (MD) is a thermally-driven membrane separation process. In the MD process for desalination, hot brine is passed on one side of a porous hydrophobic membrane. Pure water vapor is recovered from the pores of the membrane in a number of ways. Four different methods carried out on the other side of the membrane to recover the water vapor define four types of MD: (a) In direct contact MD (DCMD), water vapor is in direct contact with a colder water; (b) in vacuum MD (VMD), water vapor is withdrawn by vacuum; (c) in sweep gas MD (SGMD), water vapor is swept by inert gas; (d) in air gap MD (AGMD), water vapor is condensed on a cold surface separated by a thin air gap [1,2]. MD process has a number of potential advantages, namely, low operating temperature and hydraulic pressure, very high rejection of non-volatile solutes, smaller footprint and potentially high permeate flux for example in DCMD compared to conventional thermal distillation processes. For such reasons, MD has been considered as an emerging desalination technology for producing fresh water from brines.

The DCMD configuration is the most studied one and desalination is its most important application. Water vapor transport mechanisms for DCMD have been extensively analyzed in the literature [3]. Different types of mechanisms have been proposed for the transport, namely, Knudsen flow model, viscous flow model, ordinary molecular diffusion model, and the combination thereof by the dusty gas model (DGM) [4–6] and those by Schofield et al. [7,8]. Surface diffusion is negligible because of the very limited adsorptive interaction between gas/vapor molecules and membrane polymer chains [9].

Using these models, there have been a number of studies which have modeled the transport of water vapor through a membrane in DCMD. In such cases, the heat transfer coefficients in the fluid were generally known so that the temperatures on the two surfaces of the membrane could be easily isolated. Knowing these temperatures one can determine the membrane mass transfer coefficients and check it against any proposed model. In real-life applications, the fluid mechanics on the two sides may be complex and the convective heat transfer coefficients unknown. It would be useful to demonstrate a general procedure to determine the membrane mass transfer coefficient under such conditions, and then check the utility of the existing mass transfer models.

Previous studies have generally focused on a few membranes with most limited variation in membrane pore size [10–12]. A variety of membranes are available with considerable variations in membrane thickness, pore size, pore size distribution, porosity,

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material etc. It will be useful if such a variety of membranes can be characterized and the usefulness of MD transport models verified. This is intimately connected with the loss of sensible heat in the hot brine to the distillate by heat conduction.

In this study, eight different flat membranes of two different materials, PVDF and ePTFE, have been investigated. The membrane thickness was varied between 23 μm and 125 μm; the pore size was varied from 0.05 μm to 0.45 μm. The porosity was generally high in the range of 0.7–0.8. The hot brine temperature was varied between 65 °C and 85 °C with the membrane mean temperature varying between 40 °C and 60 °C. We have employed models for Knudsen diffusion and the transition region to predict the membrane transport coefficient for water vapor. We have empirically characterized the heat transfer coefficients of the boundary layers on two sides of the membrane via the Wilson plot method. We have also simulated the behavior of the observed water vapor flux as a function of the flow conditions on two sides of the membrane, brine temperatures and membrane properties.

2. Modeling considerations

In DCMD – based desalination, hot brine passing over one side of a porous hydrophobic membrane creates a surface for vaporization of water, while cold distillate is passed over the other side of the membrane creating condensation of this water vapor (Fig. 1a). Vapor liquid interface occurs at every entrance of the membrane pores as a result of the hydrophobic nature of the porous membrane. The difference in water vapor partial pressure due to temperature difference on both sides of the membrane is the driving force for water vapor transfer.

2.1. Mass transfer

Mass transfer of water vapor through a membrane depends among others on the membrane pore size, porosity, thickness and tortuosity. In DCMD, both feed and permeate solutions are in direct contact with the membrane under atmospheric conditions. The total pressure is assumed to be maintained at ~1 atm; viscous flow is therefore negligible. Schofield et al. [13] have shown that in DCMD applications, the net flux of air across the membrane is extremely small relative to the flux of water vapor, and viscous flux can be neglected.

The mass transfer mechanisms strongly depend on the Knudsen number (K_n):

$$K_n = \frac{\lambda_{w-a}}{d_p} \tag{1}$$

where λ_{w-a} is the mean free path of water vapor and air and d_p is the nominal membrane pore diameter. For a binary mixture of water vapor and air, the mean free path is expressed by.

$$\lambda_{w-a} = \frac{k_B T_m}{\pi P_T \left(\frac{(\sigma_w + \sigma_a)}{2}\right)^2} \frac{1}{\sqrt{1+\frac{M_w}{M_a}}} \tag{2}$$

where k_B is the Boltzmann constant, P_T is the total pressure (1 atm), σ_w and σ_a are the collision diameters for water vapor (2.641×10^{-10} m) and air (3.711×10^{-10} m), respectively [14,15]; T_m is the membrane mean surface temperature, $T_m = ((T_1 + T_2)/2)$. Values of the mean free path for a binary mixture of water vapor and air at different membrane mean surface temperatures (T_m) are listed in Table 1 for a range of membrane pore size from 0.05 μm to 0.45 μm used in this study.

If the mean free path of the molecules is larger than membrane pore size ($K_n > 1$, $d_p < \lambda$), molecule – pore wall collisions are dominant and Knudsen diffusion model should be considered. If $K_n < 0.01$, $d_p > 100\lambda$, molecular diffusion is used to describe the mass transport in the continuum region; consider stagnant air trapped within membrane pores due to the low solubility of air in water. If $0.01 < K_n < 1$, $\lambda < d_p < 100\lambda$, the mass transport mechanism is in transitional region which could be described by combined Knudsen diffusion model and ordinary molecular diffusion flow model. Since mean free path for binary mixture of water vapor and air at T_m from 40 to 60 °C is around 0.11 μm, Knudsen diffusion or combined Knudsen/molecular diffusion model is considered for membranes having pore sizes in the range of 0.05–0.45 μm.

The general mass transfer expression for water vapor flux J in DCMD can be expressed by.

$$J = k_m(P_{w,1} - P_{w,2}) \tag{3}$$

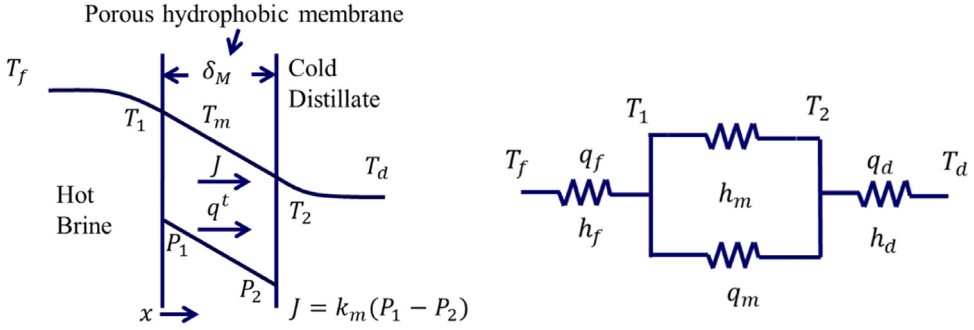
where $P_{w,1}$ is water vapor partial pressure at the brine side of the membrane surface; $P_{w,2}$ is water vapor partial pressure at the distillate side of the membrane surface; T_1 is the membrane surface temperature on the brine side of the membrane; T_2 is the surface temperature on the distillate side of the membrane. The values of $P_{w,1}$ and $P_{w,2}$ are calculated from T_1 and T_2 by Antoine equation (by neglecting the very limited effect of salt on water vaporization for 1 wt% brine used here).

$$\log_{10} P(\text{mmHg}) = 8.017 - \frac{1730.6}{233.426 + T(^\circ\text{C})} \tag{4}$$

The DCMD mass transfer model for Knudsen diffusion ($K_n > 1$, $d_p < \lambda$) can be expressed for a membrane of thickness δ_M by.

$$J = \frac{D_{Kn}}{RT_m} \times \frac{(P_{w,1} - P_{w,2})}{\delta_M} \tag{5}$$

where D_{Kn} is the Knudsen diffusivity,



a. Direct contact membrane distillation (DCMD). b. Heat transfer resistances in DCMD.

Fig. 1. (a) Direct contact membrane distillation (DCMD). (b) Heat transfer resistances in DCMD.