



Novel thermal efficiency-based model for determination of thermal conductivity of membrane distillation membranes



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ABSTRACT

Development and selection of membranes for membrane distillation (MD) could be accelerated if all performance-determining characteristics of the membrane could be obtained during MD operation without the need to recur to specialized or cumbersome porosity or thermal conductivity measurement techniques. By redefining the thermal efficiency, the Schofield method could be adapted to describe the flux without prior knowledge of membrane porosity, thickness, or thermal conductivity. A total of 17 commercially available membranes were analyzed in terms of flux and thermal efficiency to assess their suitability for application in MD. The model described the flux with an average %RMSE of 4.5%, which was in the same range as the standard deviation of the measured flux. The redefinition of the thermal efficiency also enabled MD to be used as a novel thermal conductivity measurement device for thin porous hydrophobic films that cannot be measured with the conventional laser flash diffusivity technique.

1. Introduction

It is estimated that up to 50% of industrial energy input in the US ends up as low-grade waste heat [1]. Many technologies have been developed or are under development to convert this low-grade heat into electricity or other useful end products. The state-of-the-art among many commercial applications is undoubtedly the organic Rankine cycle (ORC) [2]. Recently, more exotic heat engines have been proposed like osmotic [3–5], thermo-osmotic [6], colloidal [7] or electrochemical heat engines [8]. However, all these heat engines are limited by the Carnot efficiency, which at a temperature of 60 °C is only 14.6%. Furthermore, due to parasitic losses, practical efficiencies are often only a fraction of the Carnot efficiency, and as a result, the majority of the heat input remains unutilized [9]. More electricity use might actually be avoided than can be produced from low-grade heat by replacing electrically driven processes with thermally driven processes. Examples include cooling with absorption chillers [10], replacing resistance heating with heat transformers [11], or purifying water by thermal desalination instead of with pressure driven processes [12]. Considering that thermo-electric generation is responsible for 47% of water withdrawals in the US [13], which is more than agricultural and

industrial water use combined, it would be appropriate to preferentially allocate low-grade heat sources towards augmenting water supplies instead of generating an extraneous amount of electricity.

The vast majority of water use in thermo-electric power plants is for cooling, and by definition, the cooling load increases with decreasing thermal efficiency. Water footprint analysis (energy return on water investment) is commonly conducted to assess the viability of low efficiency heat engines [14–16]. However, water footprint of desalination technologies (*water return on water invested*) analysis could provide interesting insights. For example, the average water footprint of US thermo-electric generation in 2010, which constituted 90% of all electricity generation, was 71 m³ per MW h produced, of which 52 m³ was fresh water [17]. Average electricity consumption of reverse osmosis (RO) plants equipped with energy recovery devices ranges from 4 to 6 kW h m⁻³ [18]. As a result, for every 1 m³ of RO-desalinated water, up to 0.31 m³ (31% of fresh water input) is required for cooling during electricity generation. This number might be higher in reality due to regional differences in water footprints of electricity generation. Nevertheless, it constitutes a strong incentive to move away from electricity-intensive desalination technologies to decouple power and water demand.

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There are many commercialized thermal desalination technologies, including multistage flash distillation (MSF) and multi-effect distillation (MED). Both have similar or lower electricity consumption than RO. MSF has an *electrical energy* consumption of 2–5 kW h_e m⁻³ and MED has an *electrical energy* consumption of 2–2.25 kW h_e m⁻³ [18]; yet, both also have considerable *thermal energy* consumption. MSF and MED have been commercially deployed for several decades and for the most they are fully optimized.

Membrane distillation (MD) is a membrane-based distillation process that uses microporous hydrophobic membranes in conjunction with partial vapor pressure difference across the membrane to separate water from solutes. Electricity consumption as low as 0.6 kW h_e m⁻³ has been reported for the Scarab MD system, which is almost four times lower than state-of-the-art large-scale seawater RO [19,20]. On the other hand, thermal energy consumption of MD systems varies wildly from 5 to 350 kW h_{th} m⁻³, and it is generally higher than MSF (16–24 kW h_{th} m⁻³) or MED (12–19 kW h_{th} m⁻³) [18,20]. Yet, MED and MSF require higher brine inlet temperatures of 70 and 90 °C, respectively, while MD can produce water at any temperature difference; thus, MD can take advantage of a broader range of heat resources [18].

Even if MD does not demonstrate a pronounced advantage in terms of thermal efficiencies over MSF and MED, the fact that it is a membrane-based process with packing densities between 300 and 1000 m² of membrane per m³, enables it to be much more compact and thus can have a lower footprint [21]. In addition, the operation at lower temperatures enables utilization of less expensive materials (e.g., plastics) instead of metal. Lastly, the extent of heat recycling in the process and the properties of the membrane can have a substantial impact on process efficiency [22].

Thermal conductivity is an important property of the membrane; however, membrane manufacturers seldom provide it. It is also difficult to measure the thermal conductivity of very thin polymeric membranes (commonly done with a laser flash diffusivity method), because the membrane material would quickly disintegrate and the sample has to be self-supported, which is often not the case. This might be the reason why the thermal efficiency, which is the ratio between convective to total (conductive plus convective) heat transfer, is commonly not reported in the MD literature [23,24]. An accurate way of determining thermal efficiency in MD was developed in this study that does not require knowing the thermal conductivity of the membrane.

In this study the performance (water flux and thermal efficiency) of 17 commercially available hydrophobic microporous membranes was evaluated during direct contact membrane distillation (DCMD) experiments. The majority of these membranes are not marketed as MD membranes, but were selected based on their adequate hydrophobic nature and pore size. A novel method to accurately determine the thermal efficiency of the membranes based on the heat balance in the distillate channel is proposed. Despite its simplicity, the performance model developed by Schofield et al. [25] in 1987 still constitutes a surprisingly accurate description of mass and heat transport in MD. In the current study the Schofield model was adapted to incorporate the thermal efficiency instead of the thermal conductivity. As a result, the model does not require knowledge of the thermal conductivity of the membrane, nor its porosity or pore size. Lastly, owing to the redefinition of the thermal efficiency, MD can now be used to measure the thermal conductivity of porous hydrophobic membranes.

2. Theory: thermal efficiency-based model

MD is a separation process where mass and heat transfer occurs concurrently through a porous membrane. Water flux through the membrane (J_v) is driven by the difference in vapor pressure between the feed and distillate streams, at the membrane surfaces [25]:

$$J_v = C_m(p_{f,m} - p_{d,m}) \quad (1)$$

where C_m is the membrane mass transfer coefficient, and $p_{f,m}$ and $p_{d,m}$ are the vapor pressures at the membrane surface of the feed side and the distillate side, respectively. The membrane mass transfer coefficient C_m is a function of the characteristics of the membrane, including thickness, nominal pore size, pore size distribution, porosity, and pore tortuosity [26]. Because measuring vapor pressure is not straightforward, Eq. (1) is often rewritten as a function of temperature by linearizing the vapor pressure-temperature dependence:

$$J_v = C_m \left. \frac{dp}{dT} \right|_{T_m} (T_{f,m} - T_{d,m}) \quad (2)$$

where dp/dT is the derivative to the temperature of the Antoine equation evaluated at the mean temperature of the membrane (T_m), and $T_{f,m}$ and $T_{d,m}$ are the temperature at the membrane surface of the feed side and the distillate side, respectively (all in Celsius). The temperature derivative of the vapor pressure is determined by the Clausius-Clapeyron equation:

$$\left. \frac{dp}{dT} \right|_{T_m} = \frac{p_0 \lambda}{RT_m^2} \quad (3)$$

where λ is the heat of vaporization of water (slightly dependent on temperature), p_0 is the vapor pressure of pure water, and R is the ideal gas constant. λ can be determined by Eq. (4), which was generated with OLI Stream Analyzer (OLI Systems, Morris Plains, NJ):

$$\lambda = 2502800 - 2438.18 T_m \quad (4)$$

For the dilute aqueous solutions used in this study, the vapor pressure is adequately described by the Antoine equation:

$$p_0 = \exp\left(23.238 - \frac{3841}{T_m + 228.15}\right) \quad (5)$$

For more concentrated solutions this vapor pressure needs to be multiplied by a solute-specific expression of the activity coefficient and the molar concentration of the solute.

Due to heat transfer resistance, the temperature at the membrane surface differs from the temperature in the bulk feed (T_f) or distillate (T_d) in the flow channels. The ratio of the temperature difference across the membrane to the bulk temperature difference is defined as the temperature polarization coefficient (TPC) (τ):

$$\tau = \frac{(T_{f,m} - T_{d,m})}{(T_f - T_d)} \quad (6)$$

Finally, the water flux through the MD membrane can be calculated based on the bulk temperature difference:

$$J_v = C_m \left. \frac{dp}{dT} \right|_{T_m} (T_f - T_d) \tau \quad (7)$$

By conducting a heat balance over the membrane, an expression for the TPC can be derived as a function of the different heat transfer coefficients. The total heat transfer through the membrane (Q_{total}) is equal to the sum of the convective and the conductive heat transfer:

$$Q_{total} = J_v \lambda + \frac{k_m}{\delta} (T_{f,m} - T_{d,m}) \quad (8)$$

where k_m and δ are the thermal conductivity and the thickness of the membrane, respectively. Substituting Eq. (2) for vapor flux yields:

$$Q_{total} = \left(C_m \left. \frac{dp}{dT} \right|_{T_m} \lambda + \frac{k_m}{\delta} \right) (T_{f,m} - T_{d,m}) \quad (9)$$

The first component on the right side of Eq. (9) constitutes the total heat transfer coefficient of the membrane (H):

$$H = \left(C_m \left. \frac{dp}{dT} \right|_{T_m} \lambda + \frac{k_m}{\delta} \right) \quad (10)$$

and the total heat transfer through the membrane equals the total heat

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