A standardized approach for permeance assessment in direct contact membrane distillation

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A standardized approach for permeance assessment in direct contact membrane distillation

Sarah Almahfoodh, Sofiane Soukane, Khalid Alhamdan, Ingo Pinnau, Noreddine Ghaffour

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Highlights

- Flux fails to reflect MD membranes performance; permeance reveals intrinsic properties.
- A new methodology captures MD membrane intrinsic permeance accurately.
- Reproducible and reliable estimation of membrane permeance in DCMD is demonstrated.
- The experimental protocol can lead to a standardization of MD membrane assessment.
A standardized approach for permeance assessment in direct contact membrane distillation

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Abstract

Membrane distillation (MD) is a separation technology for many industries including desalination, pharmaceuticals, and food processing. However, MD technology readiness has not reached the required level to penetrate the desalination and water treatment market. One of the challenges to commercialization is the limited development and inaccurate assessment of MD-specific membranes. In fact, measuring the performance of MD membranes is challenging because it is dependent on process parameters, making it difficult to separate the individual influences of the process operating conditions and the membranes’ intrinsic properties. These shortcomings drive the need for a standardized methodology to compare and report membrane performance independently of the process parameters. In this work, we propose a standardized methodology for measuring the permeance of MD membranes using a reduced scale direct contact membrane distillation (DCMD) setup. This methodology has the potential to streamline membrane assessment and support ongoing efforts in MD membrane development and process scale-up.
Keywords: Membrane distillation performance, permeance, standardization, membrane permeability, porous membranes

1. Introduction

Membrane distillation (MD) is an emerging thermal-membrane hybrid separation process driven by the vapor pressure difference between two streams. The streams are physically separated by a hydrophobic porous membrane, which sustains this non-equilibrium condition causing a transfer of vapor from hot feed to cold permeate side [1, 2]. Because of the potential of MD to utilize low-grade energy, operate at low pressure, and allow high solute rejection [1, 3-5], it is used in a number of applications, including desalination [6-8], industrial wastewater treatment [9-11], and food processing [1, 12].

The most studied MD configuration is the direct contact membrane distillation (DCMD), owing to its simple design and operation [13, 14]. Other configurations, such as air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), and vacuum membrane distillation (VMD) [15, 16], employ permeate-side modifications to increase the thermal efficiency of the module.

The properties of the membranes used in MD are central to the process efficiency. As such, lab-scale development of membranes specific to MD has been increasing, using various techniques such as electro nanofiber spinning of polymeric membranes [17-19], nano-particle deposition of photothermal materials [20, 21], and hydrophobization of inorganic membranes [17, 18]. Additionally, commercial microfiltration membranes are often used in experimental MD studies [18, 22, 23]. As more MD-specific membranes are developed, it becomes increasingly important to assess their performance accurately. Assessment of the membrane performance in MD literature relies on the flux and salt rejection measurements without properly considering the entire test system. The absence of a common basis for comparison makes it difficult to objectively quantify the improvements of novel membranes. The reasons for this difficulty stem from the flux dependence on not only the membrane, but on module design and process parameters as well.

From the process standpoint, transport limitations, which govern the extent of temperature polarization (TP) in MD, can lead to erroneous estimates of the membrane performance. This is because the driving force is defined by the difference of vapor
pressures estimated at the membrane surface temperature, not the bulk. Hence, depending on the hydrodynamic conditions, the TP effect can vary, resulting in different flux values for the same membrane and bulk temperature (Figure 1a and Table S1) [24]. For instance, despite operating the same membrane at the same bulk feed and permeate temperatures, Fortunato et al. [25] showed that the resulting flux increased from 23 to 42 kg m\(^{-2}\) h\(^{-1}\) when the feed flow rate increased from 15 to 45 L/h, respectively [25]. Moreover, because the driving force is the difference in vapor pressure across the membrane, which involves exponential functions of temperature, it is used to normalize the flux (area-specific production) instead of the temperature difference. For instance, a \(\Delta T\) of 10 °C can result in significantly different driving forces depending on the absolute temperatures defining the temperature difference (Figure 1b). Hence, reporting the flux without considering the vapor pressure difference between feed and permeate is generally misleading.

From the design standpoint, geometric considerations have a direct impact on the flux estimates. Because the driving force across the membrane changes along the flow direction due to conduction and TP [8, 26, 27], longer modules yield lower flux values. Hence, the module length should be selected carefully such that it is long enough to yield stable measurements, but short enough to not influence the driving force.
Figure 1. (a) The effect hydrodynamic conditions on temperature polarization and the driving force of a DCMD process at low cross-flow velocity (top) and high cross-flow velocity (bottom) (b) water vapor pressure as a function of temperature showing the exponential dependence.

These shortcomings drive the need for a standardized methodology to compare and report membrane performance, especially when novel materials and membranes are developed. Specifically, the flux must not be used as an indicator of the membrane’s productivity. Instead, the permeance, which is the flux normalized by the driving force (vapor pressure difference), should be used [28, 29]. Similar conclusions were reported in the field of pervaporation, wherein permeance provides a process-independent measure of the membrane performance [28, 29]. Permeance is defined as the ability of a fluid to flow through a permeable medium without specifying thickness [30].

Several methods to estimate the permeance of gases through porous materials are reported in the literature [22, 31-34]. The pure gas permeation method, which relies on an inert gas and corrects for water vapor, was found to overestimate the vapor permeance [22]. Similarly, the American Society for Testing and Materials (ASTM) cup method, which relies on the measurement of vapor permeation rate through the porous material at controlled temperature and relative humidity, was designed for low to moderately permeable materials and is inaccurate for highly porous MD membranes [31-33]. A mixed gas permeability setup [34] yields accurate measurements of vapor permeation through membranes, but the system is complex, and the flow parameters require tedious tuning.

Furthermore, a methodology designed specifically for the measurement of MD membranes permeance was presented by Dao et al. ten years ago [22]. The measurements obtained using a VMD process (i.e., sub-atmospheric conditions) eliminate the presence of air in the membrane pores, yielding the intrinsic membrane permeance. However, their methodology has not been adopted in MD research, due to the methodology requirement of a finely tuned VMD system, which is complex and not commonly available in MD research laboratories.

In light of these complexities, it is clear that a simple and practical experimental method for permeance measurements of MD membranes is required. Thus, we distinguish our
work by developing a straightforward experimental methodology for permeance measurements using a standard DCMD laboratory system, tested using commercial composite and isotropic membranes. The methodology proposed in this work could pave the way towards a standardized process for the evaluation of the permeance of MD membranes and an accurate representation of their performance.

2. Materials and methods
The experiments are performed in a typical DCMD apparatus (Figure S1). In all experiments, ultrapure water at 20 °C is used as permeate. Furthermore, we focus our analysis on two commercial membranes with the properties shown in (Table S2). This choice is motivated by the availability of the membranes and the consistency of their properties, which could offer better reproducibility compared to membranes fabricated and developed in-house. Detailed description of the materials and instruments is provided in section 2 of the SI document.

2.1. Permeance measurement and process metrics
Given the standard definition of the flux, a process- and membrane-dependent property:

\[
Flux = \frac{\text{mass of product}}{\text{area of membrane} \times \text{time}} = \frac{\Delta m_{\text{product}}}{A \Delta t}
\]

The permeance, which is the flux normalized by the driving force (membrane-dependent) can be written as [35]:

\[
Permeance = \frac{\text{flux}}{\text{driving force}} = \frac{\Delta m_{\text{product}}}{A \Delta t \Delta P_{\text{sat}}}
\]

where the driving force is the partial pressure (concentration) difference across the membrane [28, 29, 36].

The permeance measurement methodology introduced in this work involves two stages. In the first stage, the flow rates (and consequently the velocity) are increased to minimize temperature polarization (TP) until a maximum stable flux is achieved. Because increasing the velocity increases the potential of pore wetting, it is important to observe whether wetting is detected at the flow conditions that yield the maximum flux. In the second stage, the feed temperature (T_F) is varied at a fixed flow rate to validate the
permeance results. Summarized step-by-step methodology can be found in Section 1 of the SI document.

**Stage 1: Minimization of TP**

TP can be mitigated by enhanced mixing, use of flow promoters or spacers, or interfacial heating [15, 22, 24, 37, 38]. To keep the system simple and eliminate secondary effects of spacers and localized heaters, we choose to mitigate TP by increasing the flow rate within the channel. Although the temperature boundary layer is reduced by increasing the flow rate (i.e. cross-flow velocity) in the fluid channel, the potential of pore wetting at high cross-flow velocities poses a practical limitation. Because of this drawback, the cross-flow velocities in MD literature are maintained low enough to prevent wetting [38, 39]. However, at these low velocities, the TP effect is severe, which affects the accurate determination of membrane permeance. Hence, careful consideration must be taken when assessing the suitability of the membrane to MD.

In this analysis, we monitor experimentally the pore wetting response while maximizing the flow rate to minimize the TP. We use a 3.5%wt NaCl solution as feed and ultrapure water as permeate. During the experiments, any increase in the electroconductivity of the permeate stream is an indication of pore wetting. The feed and permeate flow rates are kept identical and varied between 350-950 mL/min in 200 mL/min increments (Table S3). In this set, the feed temperature is kept at 60 °C and 70 °C, while the permeate is kept at 20 °C.

**Stage 2: Verification of TP**

Upon minimization of the TP, the measured flux is essentially dependent on the membrane only. Hence, normalizing the flux by the driving force (vapor pressure difference) at any ΔT should yield the same value for permeance. Based on the results from Stage 1, the highest flow rate that does not cause wetting is selected as the flow rate for the feed and permeate streams. Moreover, to eliminate any concentration and salinity effects, ultrapure water is used for both streams. In our experiments, the permeate temperature was kept at 20 °C, while the feed temperature was varied between 40-70 °C in 10 °C increments.
3. Results and discussion

3.1. Minimization of TP limitations

To minimize the TP, the thickness of the thermal boundary layer is reduced by increasing the flow rates of the feed and permeate streams. The flux results depicted in Figure 2 illustrate the increase of flux with increasing flow rate for M1 and M2 at feed temperature of 60 °C. The electroconductivity of the permeate remained constant throughout the experiments, indicating the absence of pore wetting at these operating conditions. In all cases, the flux increases with flow rate until 750 mL/min (cross-flow velocity 0.42 m/s), at which it reaches a plateau. This plateau indicates that at these operating conditions, the TP was minimized, so the effective temperature at the membrane surfaces was identical to the temperature in the bulk fluid [22, 38]. Hence, the flux observed at the plateau was dictated solely by the properties of the membrane (e.g. morphology, porosity, tortuosity, thickness). This observation is crucial for two reasons:

1. It indicates that beyond 750 mL/min (0.42 m/s), there is no significant increase in the flux. This threshold value is crucial for preventing potential wetting of the membrane when operating at higher velocities than necessary to minimize TP. Nevertheless, in a scaled-up process, higher flow rates may be required to achieve the same velocity condition in a longer module, leading to potential pore wetting.

2. The true membrane performance (permeance) is detected at these operating conditions, while at flow rates lower than 750 mL/min (i.e., velocities lower than 0.42 m/s) the effect of TP is included. Relying on flux values measured at velocities lower than the threshold velocity will lead to erroneous estimates of membrane’s permeance.
Figure 2. Flux response to increasing the flow rate (i.e., cross flow velocity) for M1 and M2 membranes at \( T_F = 60 \, ^\circ\text{C} \).

3.2. Variable driving force

When TP effect is minimized, the transport rate of vapor is governed by the membrane [15, 37]. In this case, while flux is expected to increase with increasing feed temperature (i.e. driving force), the permeance (flux normalized by driving force) should be constant. This requirement is verified by setting the feed and permeate flow rates at 950 mL/min (0.53 m/s), while the feed temperature is varied between 40-70 °C. The resulting flux of both membranes (Figure 3a) exhibits an exponential increase with temperature, consistent with the increase of the driving force. In contrast, the permeance (Figure 3b) is found to be relatively constant at an average of \( 6.0 \times 10^{-7} \) and \( 3.6 \times 10^{-7} \, \text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa} \) with a standard deviation of 6.1 and 6.7% for M1 and M2, respectively. These results confirm that it is practically feasible to reach operating conditions at which the membrane dictates the process.
Now that we have a reliable measure of the membrane intrinsic permeance, it can be used to determine the flux at any given vapor pressure difference (driving force) using the same system (e.g. module, flow conditions) or used in advanced numerical models where TP can be predicted [40]. Furthermore, erroneous permeance estimates can be detected if they fail to predict the flux at a given driving force using the same system. More importantly, since this methodology is performed in the DCMD process and does not require complex instrumentation, it provides a more accessible approach to measuring the permeance of MD membranes. Nonetheless, this methodology could be further refined in future works to address potential pore wetting, which was not encountered in this work.

3.3. Considerations for future work

The methodology presented in this work provides a guideline for standardizing DCMD membrane performance evaluation (summarized in Section 1, SI document). Specifically, membrane manufacturers and academic researchers could consider permeance as a standard quantity to evaluate membrane performance. Moreover, while this methodology
could streamline DCMD membrane development efforts, it also presents potential research avenues to address important questions, including:

i) Determination of a standard membrane length for permeance measurements. Because the driving force varies along the length of the membrane, the flux calculations (which normalize the production by the specific area) are directly impacted. Hence, a standard cell design with a short length is required for accurate comparison of membranes.

ii) Addressing potential pore wetting at the plateau flow rate. While we did not detect pore wetting in the membranes used in this analysis, it is possible that other membranes (commercial or novel) would suffer pore wetting before reaching the critical velocity and minimizing the TP effect. Because there is a tradeoff between module length and maximum flow rate, a shorter module could be used if wetting is observed. In such cases, careful consideration of the module geometry must be taken to ensure an acceptable accuracy of permeate measurements.

4. Conclusion
The aim of this work was to establish a standard straightforward protocol for the measurement of MD membrane permeance. We demonstrate that a flux-based estimation is process-dependent and does not reflect the membrane’s performance accurately. Instead, we utilize permeance, a function of the intrinsic properties of the membrane and the fluid passing through it. The methodology described in this work provides reproducible and reliable estimates of the membrane permeance in DCMD. The main steps can be summarized as:

1. Determination of the threshold flow rate at which TP effects become negligible, including screening for wetting at that operation condition.
2. Variation of the driving force by performing DCMD experiments at different feed temperatures.
3. Normalization of the experimental flux by the vapor pressure difference (based on the bulk temperature measurements) to calculate permeance.
The versatility and straightforwardness of our methodology streamline the evaluation of MD membranes in a process-independent way, which can be utilized to aid the efforts in MD membrane development, and process scale-up. Additionally, the simplicity of the system described herein leverages the use of this methodology in any MD research laboratory without the need for spacers, heaters, or complex vacuum systems.

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References


Graphical abstract

Without minimization of \( T_{f,\text{bulk}} \), bulk conditions yield an overestimated driving force.
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Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.