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Characterization and performance evaluation of commercially available hydrophobic membranes for direct contact membrane distillation

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HIGHLIGHTS

- 24 commercial membranes are evaluated for DCMD.
- Different porosity and pore size measurement techniques are evaluated.
- A membrane characterization procedure is developed
- Realistic conditions are selected as reference lab scale test conditions.
- A benchmark is proposed depending on salinity (0–23 wt% NaCl).

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ABSTRACT

Membrane distillation (MD) uses a microporous hydrophobic membrane for the separation of non-volatile solutes from liquid streams. The microporous structure should be designed for optimal vapor transport through the membrane, whereas the hydrophobicity is required to retain the liquid phase. Currently, different types of commercially available hydrophobic microfiltration membranes are used for membrane distillation. However, no comparison is available between these membranes, complicating the selection of a proper membrane and the evaluation of new membranes. In this study, over 20 (semi-)commercial hydrophobic membranes are characterized and tested in a lab scale direct contact membrane distillation set-up. These membranes include the standard PTFE, PVDF and PP membranes, but also less known PE and PES membranes. These membranes are synthesized using the phase inversion technique, stretching or electrospinning, resulting in a wide variety of membrane structures. In this study, a method is proposed to evaluate the suitability of membranes. The membrane performance in MD is evaluated with a performance chart including flux and energy efficiency using realistic process conditions. From this chart a benchmark performance is proposed, which depends on the salt concentration.

1. Introduction

An increasing fraction of the fresh water supply is provided by means of desalination using thermal distillation (multi-stage flash or multi-effect distillation) or reverse osmosis [1]. Membrane distillation is often proposed as an alternative technology for these techniques [2,3]. However, the membrane distillation performance in terms of flux, energy consumption and cost is still inferior compared to the mature reverse osmosis systems [4]. Nevertheless, membrane distillation efforts are increasingly oriented towards treatment of concentrated solutions, which are not viable for reverse osmosis [5–7]. Currently hydrophobic microfiltration membranes are used in membrane distillation, although these membranes are not optimized for the MD process [8,9]. The specific requirements for membrane distillation membranes are described in the literature [3,10,11]. Most importantly, the membrane must consist of at least one layer that is not wetted by the liquid stream under the operational pressures used in the module. The minimum pressure required to wet a hydrophobic membrane is the liquid entry pressure (LEP), which depends both on the membrane characteristics and the feed composition:

$$LEP = \frac{-2B\gamma_l \cos(\theta)}{r_{max}}, \quad (1)$$

where γ_l is the surface tension (N/m) of the liquid, θ the contact angle (°), r_{max} the maximum pore size (μm) and B is a geometric factor. The pressure drop over a spiral wound module is experimentally

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Nomenclature

Abbreviations

DCMD	direct contact membrane distillation, [−]
MD	membrane distillation, [−]
PE	polyethylene, [−]
PES	polyethersulfone, [−]
PP	polypropylene, [−]
PTFE	polytetrafluoroethylene, [−]
PVDF	polyvinylidene fluoride, [−]

Symbols

A	membrane surface area, [m^2]
B	geometric factor, [−]
F	flow rate, [kg/s]
LEP	liquid entry pressure, [bar]
m	mass, [kg]
N	flux, [kg(/h.m^2)]
ρ_m	membrane density, [g/cm^3]
ρ_{pol}	polymer density, [g/cm^3]
r_{max}	maximum pore radius, [μm]
T_f	feed temperature, [°C]
T_{in}	temperature at channel inlet, [°C]
T_{out}	temperature at channel outlet, [°C]
T_p	permeate temperature, [°C]
v	flow velocity, [m/s]
V_m	membrane volume, [m^3]
V_{pores}	pore volume, [m^3]
γ	surface tension, [N/m]
δ	membrane thickness, [μm]
ΔH	enthalpy of vaporization, [J/(kg.°C)]
$\delta_{support}$	thickness of the support, [μm]
ε	porosity, [%]
Θ	water contact angle, [°]

determined by Winter et al. ranging from 0.2 to 0.7 bar [12]. However, to ensure proper membrane operation, the reduction of LEP over time due to fouling and scaling, the effect of surfactants/oil/detergents on LEP and the effect of temperature and salinity should be considered. Therefore, a LEP of at least 2.5 bar is recommended in membrane distillation [13]. To achieve sufficient LEP, membranes with maximum pore diameter between 0.1 and 1 μm with a contact angle above 90° are recommended for membrane distillation. Regarding the membrane structure, it is generally agreed that a high membrane porosity is one of the most important membrane parameters in membrane distillation for both flux and energy efficiency, regardless of the MD configuration [14–18]. Additionally, membranes with thickness between 30 up to 60 μm are recommended for DCMD, however recently it is shown that this optimal value depends on salinity. At high salinity, thicker membranes are preferred [19]. Table 1 shows the optimal membrane properties for membrane distillation and the variety of suitable characterization methods as proposed in the literature.

Table 2 shows the reported fluxes of flat sheet commercial membranes in the literature. This table shows a wide variety in process conditions, often with temperature differences of 50 to even 70 °C, which are irrelevant for large scale DCMD [29,30]. Moreover, the flow is often reported as the stirring rate (rpm) or flow rate (l/h), whereas the hydrodynamics in the channel depend also on the module dimensions, the pump type and calibration. To be able to make a fair comparison between studies using different pumps and module sizes, the flow velocity (m/s) should be reported together with the characteristic module dimension and fluid properties. From these values, the Reynolds number can be calculated, which is used to study the similarity between different flows. Additionally, there is a lack of data on the single pass thermal energy efficiency and salt retention of the membranes and hence, a recommendation on the choice of the membrane that should be used in direct contact membrane distillation is not available. Furthermore, a number of innovative synthesis methods have been recently proposed to improve the performance of the membrane [31–39]. However, it is impossible to compare and evaluate the performance of these membranes based on the published information. Often artificially high driving forces are applied using water as feed stream, resulting in unrealistic fluxes. To enable a fair evaluation and comparison of membrane distillation membranes, a standard characterization procedure and reference process conditions are required.

This article studies over 20 (semi-)commercial hydrophobic membranes synthesized through different methods, including the phase inversion technique, stretching and electrospinning. Not only the standard PTFE, PP and PVDF membranes are studied, but also PE and PES membranes are included. These membranes are not specifically developed for membrane distillation, although due to their hydrophobicity and microporous structure, they have the required specifications for the process. Different characterization techniques are compared and a standard method to characterize membrane distillation membranes is proposed to investigate the suitability of a membrane for membrane distillation. Moreover, a benchmark performance in DCMD is formulated at low and high salinity allowing evaluation of other commercial or newly synthesized membranes.

2. Materials and methods

2.1. Membranes

In Table 3, an overview is given of the membranes used in this study.

2.2. Characterization methods

The contact angle of the membranes is measured with an OCA 15EC Contact Angle System of Dataphysics (Filderstadt, Germany) using the

Table 1
Overview of the optimal membrane properties and characterization methods for membrane distillation.

Parameter	Symbol	Recommended	Characterization method
Contact angle	θ	>90° [11]	Static sessile drop method [20] Dynamic sessile drop [20]
Liquid entry pressure	LEP	>2.5 bar [13]	Liquid entry pressure measurement [21]
Porosity	ϵ	80–90% [11]	Gas permeation test (effective porosity) [22] Electron Microscopy (surface porosity) [23] Liquid Pycnometer (bulk porosity) [21]
Pore diameter	d_{av}, d_{max}	0.1–1 μm [11,13]	Gas permeation test (d_{av}) [22] Wet/dry flow method (pore distribution) [24] Mercury porosimetry (pore distribution) [24] Electron Microscopy (pore distribution) [23]
Thickness	δ	30–60 μm [25–27] 2–700 μm [19]	Digital micrometer [28]