

# Bacterial Nanocellulose Aerogel Membranes: Novel High-Porosity Materials for Membrane Distillation

Megan E. Leitch,<sup>†</sup> Chenkai Li,<sup>‡</sup> Olli Ikkala,<sup>§</sup> Meagan S. Mauter,<sup>\*,†,||</sup> and Gregory V. Lowry<sup>†</sup>

<sup>†</sup>Department of Civil and Environmental Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

<sup>‡</sup>Department of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

<sup>§</sup>Department of Applied Physics, Aalto University, P.O. Box 15100, FI-02150 Espoo, Finland

<sup>II</sup>Department of Engineering and Public Policy, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

**Supporting Information** 

**ABSTRACT:** We fabricated, characterized, and tested novel fibrous aerogel membranes in direct contact membrane distillation (MD) to elucidate the effects of a model high-porosity membrane material on MD performance. Unsupported bacterial nanocellulose aerogels exhibit higher porosity, thinner fibers, and lower bulk thermal conductivity than any previously reported MD materials. Modeling and experiments demonstrate that these material properties confer significantly higher intrinsic membrane permeability and thermal efficiency than symmetric PVDF phase inversion membranes with lower porosity. Development of macroporous fibrous membranes with aerogel-like porosity and thermal conductivity (>98% and <0.03 W m<sup>-1</sup> K<sup>-1</sup>, respectively) in thinner-film formats may further improve MD flux.



## INTRODUCTION AND BACKGROUND

Membrane distillation (MD) is a thermally driven separation process in which a solvent volatilizes from a warm feed solution, is transported through a lyophobic membrane, and condenses in a cool permeate stream. The weak dependence of vapor pressure on ionic strength makes this technology attractive for desalinating high-salinity feed streams [>100000 total dissolved solids (TDS)], including brines from carbon capture and storage operations,<sup>1</sup> reverse osmosis (RO) concentrate, and industrial wastewaters. Use of low grade heat as the energy input in MD may significantly reduce process energy intensity relative to other desalination technologies. Despite these process advantages, the commercial implementation of MD has been limited by the low permeability and high conductive heat loss of current MD membranes.<sup>2</sup>

Large pore diameter, low pore tortuosity, high porosity, low thermal conductivity, and optimized thickness of MD membrane materials are correlated with high vapor permeability and thermal efficiency, regardless of MD process conditions.<sup>2,3</sup> Optimized thickness refers to the balance between minimizing mass transfer resistance to flow of vapor while maximizing the thermal gradient. Past efforts to improve MD performance have focused almost entirely on varying pore diameter, tortuosity, and thickness.<sup>4–16</sup> There are very few experimental<sup>17,18</sup> or theoretical studies reporting MD performance of membrane materials with low thermal conductivity or high porosity (>90%).

One relevant class of materials is aerogels, which exhibit porosities of up to 99.9% and ambient-pressure thermal conductivities as low as 0.012 W m<sup>-1</sup> K<sup>-1</sup>.<sup>19–21</sup> These materials may be composed of silica or other metal oxides,<sup>22–25</sup> polymers,<sup>26</sup> hybrid organic/inorganic materials,<sup>27,28</sup> or nano-carbon<sup>29–31</sup> and are created by replacement of liquid with gas in a network produced by the sol–gel process. Unfortunately, traditional aerogels are difficult to process into uniform thin films, require a rigid support to compensate for their brittleness, tend to form small pores of only 10–20 nm,<sup>32,33</sup> and may be difficult to hydrophobize.

An alternative to traditional organic and polymeric aerogels is the fibrous nanocellulose aerogel. The high aspect ratio of nanocellulose fibers confers processability, flexibility, and tunable pore sizes ranging between 0.47 nm and 500  $\mu$ m.<sup>34,35</sup>

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Past work on nanocellulose aerogels has demonstrated that the cellulose source, processing, drying method, and surface functionalization can be adapted to achieve a wide range of structural and surface characteristics.<sup>36–38</sup>

The nanocellulose matrix material may originate from plant matter or may be produced as a biofilm by select aerobic mesophilic heterotrophs.<sup>37</sup> The characteristics of bacterial nanocellulose (BNC) vary depending on the subspecies of bacteria and growth conditions, but it most often comes in the form of a highly entangled web of highly crystalline cellulose-I nanofibers, bound together by hydrogen bonds where the fibers intersect. The fibers can be rod- or ribbon-shaped, are 5-100 nm in diameter, and are often >100  $\mu$ m in length.<sup>39-41</sup> When grown in static liquid media, pure cultures of Gluconacetobacter xylinus, Gluconacetobacter medellinensis, or other celluloseproducing species will form a uniform gel mat of  $\sim 1\%$  cellulose fibers and  $\sim$ 99% liquid at the air-medium interface.<sup>37</sup> The ultra-high-porosity fibrillar structure, the facile chemical surface modification of cellulose fibers, and their mechanical stability and flexibility in hydrogel form have motivated the use of BNC gels for applications in medicine, electronics, and tex-tiles.<sup>37,42-45</sup> Supercritical drying or lyophilization of the BNC matrix prevents collapse of the cellulose gel network and transforms nanocellulosic biofilms into a thin BNC aerogel (BNCA) membrane.<sup>36</sup>

This research introduces flexible, unsupported bacterial nanocellulose aerogels as a model material for investigating the influence of porosity and thermal conductivity on MD flux. We fabricate and characterize hydrophobic BNCAs for porosity, pore size, fiber diameter, thickness, and thermal conductivity prior to evaluating membrane flux in direct contact membrane distillation (DCMD) mode. We compare experimentally obtained intrinsic permeability and thermal efficiency against those of a lower-porosity commercial symmetric phaseinversion polyvinylidene fluoride (PVDF) membrane. Finally, we discuss commercially viable analogues to BNCA membranes that may form the basis for next-generation MD membrane materials.

## MATERIALS AND METHODS

**Fabrication of Hydrophobic BNCA Membranes.** We grow BNC gels from pure *G. medellinensis* cultures. Gels are cleaned and supercritically dried as described in the Supporting Information (SI-1). This process yields a hydrophilic nanocellulose aerogel that is hydrophobized via the "bottle-in-bottle" chemical vapor deposition method described in ref 46. BNCA reacts with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane vapor at 70 °C for 3 h, resulting in dense monolayer coverage of the cellulose fibers with hydrophobic silane.<sup>46</sup>

Characterization of BNCA and Benchmark Polymer Membranes. We use a Quanta 600 FEG scanning electron microscope to determine membrane morphology, thickness, and fiber diameter. Images are analyzed using ImageJ with the plug-in DiameterJ.<sup>47,48</sup> We calculate the membrane porosity ( $\varepsilon$ ) gravimetrically as described in SI-2. Pore size distribution is measured with a PMI CFP-1500-AE capillary flow porometer using Galwick commercial wetting fluid. To determine the effectiveness of silane hydrophobization, we obtain Fourier transform infrared (FTIR) spectra of hydrophilic and hydrophobic gels with a Thermo Nicolet Avatar 380 FTIR spectrometer and measure advancing contact angles of the hydrophobic gels using a Rame-hart contact angle goniometer as described in ref 49. The bulk thermal conductivity  $(k_m)$  of the membranes was calculated theoretically (eq 1).

$$k_{\rm m} = k_{\rm g}\varepsilon + k_{\rm pol}(1-\varepsilon) \tag{1}$$

where  $k_{\rm g}$  is the thermal conductivity of dry air in membrane pores (evaluated at the average temperature inside the membrane<sup>50</sup>) and  $k_{\rm pol}$  is the thermal conductivity of the pure polymer.

**DCMD Experiments.** We compare the flux performance of BCNAs to that of PVDF membranes (Millipore GVHP, 0.22  $\mu$ m nominal pore diameter) using a benchtop DCMD system. A schematic depicting the design of the benchtop unit is provided in SI-3. The experimental permeate temperature is held at 20 °C, while feed temperatures are chosen to simulate low-grade heat sources. In one set of experiments, membranes were tested with a 40 °C feed, representative of the heat rejected in the condenser streams of U.S. power plants.<sup>51</sup> Another set of membranes were tested with a 60 °C feed to simulate a higher-grade flue gas exhaust,<sup>51</sup> geothermal, or solar heat driving force. We subjected each membrane to DCMD conditions for 3–6 h such that the error in salt rejection calculations averaged <0.02%.

Membrane Morphology Change during DCMD. We infer structural and chemical stability of BNCA and PVDF membranes using theory, modeling, and experimental evidence. A complete discussion is provided in SI-4. We assess membrane compressibility under the  $\sim$ 6.2 kPa of transverse head pressure in the DCMD system by performing static tests on representative membrane samples and analyzing changes in cross-sectional thickness. We evaluate any changes in surface morphology via scanning electron microscopy (SEM) of membranes before and after DCMD, and we compliment this work with modeling to assess any potential implications of fiber aggregation on flux. We examine the chemical stability of the hydrophobic silane coating by performing contact angle measurements before and after exposure to high-temperature feed streams.

**Determination of Membrane Permeability and Thermal Performance.** To evaluate the intrinsic permeability  $(B_w\delta)$  and thermal performance of the tested membranes, we solve mass and heat transport equations (eqs 2–6), adapted from ref 2, simultaneously.

$$J_{\rm w} = B_{\rm w} \Delta p_{\rm w} \tag{2}$$

$$Q_{f} = Q_{m} = Q_{p} \tag{3}$$

$$Q_{f} = h_{f}(T_{f,b} - T_{f,m}) + J_{w}H_{w,f}$$
(4)

$$Q_{p} = h_{p}(T_{p,m} - T_{p,b}) + J_{w}H_{w,p}$$
(5)

$$Q_{\rm m} = \frac{k_{\rm m}}{\delta} (T_{\rm f,m} - T_{\rm p,m}) + J_{\rm w} H_{\rm w,vap}$$
<sup>(6)</sup>

As illustrated in Figure 1,  $J_w$  is the mass (vapor) flux through the membrane,  $B_w$  is the membrane permeability, and  $\Delta p_w$  is the difference in saturation vapor pressure between the feed and permeate side.  $Q_{fr} Q_{mr}$ , and  $Q_p$  are the combined convective and conductive heat flux through the feed boundary layer, the membrane, and the permeate boundary layer, respectively.  $T_{f,br}$ ,  $T_{f,mr}$ ,  $T_{p,mr}$ , and  $T_{p,b}$  are average in-cassette temperatures of the bulk feed stream, the feed-side membrane surface, the permeate-side membrane surface, and the bulk permeate stream, respectively. The boundary layer heat transfer Feed



Figure 1. Schematic of the membrane cross section in DCMD.

coefficients are  $h_{\rm f}$  and  $h_{\rm p}$ , and  $k_{\rm m}/\delta$  is the thermal conductivity of the membrane divided by its thickness. Enthalpies of the distillate convecting through the feed boundary layer, the membrane, and the permeate boundary layer are  $H_{\rm w,p}$   $H_{\rm w,vap}$ , and  $H_{\rm w,p}$ , respectively. In these equations,  $J_{\rm w}$ ,  $T_{\rm f,b}$ , and  $T_{\rm p,b}$  are measured directly during DCMD experiments and  $k_{\rm m}$  and  $\delta$  are found by characterizing each membrane. All other parameters are calculated using experimental data, as described in SI-5. Expressions for thermal efficiency ( $\eta$ ) and the average temperature polarization coefficient (TPC) are provided in eqs 7 and 8, respectively.

$$\eta = \frac{Q_{\rm m,vap}}{Q_{\rm m,total}} \tag{7}$$

$$TPC = \frac{T_{f,m} - T_{p,m}}{T_{f,b} - T_{p,b}}$$
(8)

The parameter  $Q_{m,vap}$  equals  $J_w H_{w,vap}$ , the heat flux through the membrane due to vapor convection; therefore,  $\eta$  is the ratio of "productive" heat to total heat transported in the MD process. Under identical DCMD system conditions, the TPC compares how effectively different membranes insulate the feed from the permeate stream and maintain the driving force along the length of a membrane module.

Finally, specific heat duty ( $\beta$ , i.e., the thermal energy used per mass of permeate produced) can be compared between the BNCA membranes and commercial PVDF membranes by taking the reciprocal of the ratio of their thermal efficiencies (eq 9).



**Figure 2.** Typical DCMD membrane samples: (A) BC biofilm growth in medium, (B) three cleaned BC gels in deionized water, (C) supercritically dried BNCA, (D) BNCA membrane surface at 10000× magnification, (E) BNCA cross section at 10000× magnification, (F) BNCA cross section at 250× magnification, (G) PVDF membrane surface at 10000× magnification, (H) PVDF cross section at 10000× magnification, and (I) PVDF cross section at 250× magnification.

# Table 1. Characterization of Polymer Benchmark and BNCA Membranes<sup>a</sup>

	PVDF	BNCA
thickness $(\mu m)^{a}$	$109 \pm 5$	$257 \pm 45$
thickness reduction, static compression $(\%)^a$	$8.9 \pm 4.1$	$13 \pm 3.7$
thickness reduction, surface fiber aggregation $(\%)^b$	not applicable	0-10
porosity <sup>c</sup> (%)	$62.2 \pm 3.1$	$98.0 \pm 0.5$
fiber diameter (nm)	not applicable	$32 \pm 15$
bubble point <sup>d</sup> (MPa)	0.033	0.266
maximum pore diameter <sup>d</sup> (nm)	1,390	171
average pore diameter <sup>d</sup> (nm)	244	115
SD pore diameter <sup>d</sup> (nm)	387	38
thermal conductivity <sup><math>e</math></sup> (W m <sup>-1</sup> K <sup>-1</sup> )	0.089	0.027
contact angle <sup>f</sup> (deg)	$147 \pm 2.8$	$156 \pm 5.5$

"Uncertainty represents variations between samples. There is significant variation in the BNCA membrane thickness from sample to sample. Similarly sized samples were used for each temperature experiment, which minimized intra-experiment variability. Errors are standard errors of the mean. "Scanning Electron Microscopy and transport modeling. "Gravimetric analysis." Capillary flow porometry, Galwick fluid. "Theoretical calculation." Contact angle goniometry.

$$\frac{\eta_{\text{GVHP}}}{\eta_{\text{BNCA}}} = \frac{Q_{\text{GVHP,vap}}Q_{\text{BNCA,total}}}{Q_{\text{BNCA,vap}}Q_{\text{GVHP,total}}} \\
= \frac{J_{\text{w,GVHP}}H_{\text{w,vap}}Q_{\text{BNCA,total}}}{J_{\text{w,BNCA}}H_{\text{w,vap}}Q_{\text{GVHP,total}}} \\
= \frac{\beta_{\text{BNCA}}}{\beta_{\text{GVHP}}} \tag{9}$$

## RESULTS AND DISCUSSION

Characteristics of Nanofibrous BNCA Membranes. BNCA membranes are formed from thin and uniform cellulose fibers with an isotropic orientation in the x-y plane (Figure 2). There is evidence of layering in the z-direction (Figure 2F), as well as slight cross-sectional asymmetry that is likely due to evaporative aggregation of surface fibers during biofilm growth and processing. This morphology is consistent with lyophilized and supercritically dried BNCA described elsewhere. 44,52-54 On average, the BCNA membranes are 2.3 times thicker than the commercial PVDF membrane (Figure 2F,I) and have a more open and interconnected pore network (Figure 2E,H). Gravimetric measurements confirm that BNCAs have a porosity (98.0%) much higher than that of the PVDF membrane (62.2%). The skeletal conductivities of PVDF and the cellulose polymer are comparable (0.17-0.25 and 0.054-0.13 W m<sup>-1</sup>  $\hat{K}^{-1}$ , respectively), <sup>55</sup> but the high porosity of the BNCA membrane results in a much lower effective bulk thermal conductivity. Table 1 summarizes quantitative characterization results.

FTIR spectra indicate the appearance of new infrared Si-OR stretching absorption bands at wavenumbers of 1145 and 897 cm<sup>-1</sup>, as well as  $CF_2-CF_2$  stretching absorption at 1238 and 1206 cm<sup>-1</sup> after silane functionalization of the BCNA membranes. FTIR spectra and advancing contact angle images are presented in Section SI-6 and Figures S10 and S11. Porometry data indicate that aerogels have an average pore diameter smaller than and a pore size distribution narrower than those of the commercial PVDF membranes (CFP data reported in SI-7).

Post-DCMD micrographs reveal aggregation of a thin layer of BNCA fibers on the feed side of the membrane, but experimental and modeling evidence suggests that this aggregation does not significantly affect membrane permeability or thermal efficiency (SI-4). Subsequent analysis of membrane permeability and thermal efficiency incorporates uncertainty related to *in situ* membrane thicknesses and surface morphology. Beyond this thin layer of fiber aggregation in the BNCA membranes, and approximately 10% compression in both BNCA and PVDF membranes due to DCMD head pressure, there is no evidence of significant structural or chemical change during membrane testing (Table 1 and SI-4).

High Intrinsic Permeability and Thermal Performance of BNCA Membranes. The metric of merit for symmetric membrane materials is intrinsic permeability, or the experimental permeability ( $B_w$ ) normalized by thickness ( $B_w\delta$ ) (Figure 3A). Figure 3B compares membrane thermal efficiencies, and Table 2 reports permeate flux, salt rejection, and TPC values. BNCA and PVDF flux are comparable because the BNCA membranes are substantially thicker. BNCA flux and salt rejection remained constant throughout each 3–6 h DCMD experiment, indicating stability of BNCA morphology and chemistry under the experimental conditions. Future work should explore the limits of BNCA durability under more extreme operating conditions, including performance in the presence of foulants and stability during chemical cleaning.

Intrinsic permeabilities of both BNCA and commercial PVDF membranes are higher than the theoretical permeability calculated with the Dusty Gas Model,<sup>56–58</sup> which assumes cylindrical nonconnected pores (see data presented in SI-8 and Figure S13). In membranes with pore size regimes between 1 and 100 times the mean free path of water vapor (14–1400 nm pore diameter at 50 °C), ordinary molecular diffusion (OMD) and Knudsen vapor diffusion are relevant transport mechanisms.<sup>57,59</sup> Greater pore interconnectivity, which produces an apparent increase in pore size, favors the OMD transport mechanism. We hypothesize that preferential OMD transport though interconnected pore space in fibrous aerogel materials is responsible for the 52% higher intrinsic permeability of BNCAs compared to that of the phase-inversion PVDF membrane.

The high void fraction of BNCA reduces conducted heat flux from the feed to the permeate stream, resulting in improved TPC (Table 2) and thermal efficiency ( $\eta$ ) (Figure 3A) compared to those of the PVDF membranes. The specific heat duty ( $\beta$ ) performance ratio is 2.47 for the 40 °C experiments, meaning the BNCA prototypes produced 2.47 times the freshwater permeate of the commercial benchmark membranes per kilojoule of heat energy. The ratio was 1.54 for



**Figure 3.** Experimentally measured intrinsic (thickness-normalized) membrane permeability (A) shows the enhanced morphological suitability of BC aerogel structure over commercial phase-inversion PVDF membranes. High thermal efficiency (B) observed for BNCA compared to the benchmark indicates high-porosity fibrous membranes could be advantageous under conditions where the quality or quantity of the thermal energy for desalination is limited, or where there is demand for very high recovery rates. For all experiments, the feed TDS equals 35 g/L NaCl, the permeate temperature is 20 °C, and feed and permeate velocities are 0.25 m/s. Error bars represent the standard error of the mean for multiple experiments.  $N \geq 8$  for all experimental results.

the 60  $^{\circ}$ C experiments. Because the thermal efficiency and specific heat duty of a membrane are largely independent of

membrane thickness,<sup>59</sup> these results can be ascribed to the high porosity and low thermal conductivity of the aerogel structure.

Increasing pore size, while maintaining high porosity, may further reduce the mass transport resistance of the fibrous aerogel materials. This can be accomplished by manipulating fiber diameter, as pore radius is directly proportional to fiber diameter when porosity is held constant.<sup>60</sup> One approach for achieving this material structure may be to adapt nanocellulose drying methods to induce partial aggregation of the 32 nm *G. medellinensis* fibers. Unfortunately, aggregation is not easily controlled, and earlier attempts have yielded a nonisotropic hierarchical structure.<sup>36</sup>

A simpler solution for increasing pore size while maintaining high porosity might be to mimic the BNCA structure using alternative materials and fabrication methods, for example, by electrospinning polymer membranes. Bacterial nanocellulose biofilms are a natural analogue to electrospun polymers, with similar isotropic fibrous structure yet tunable fiber diameter, between 15 nm and 7  $\mu$ m.<sup>61</sup> Though electrospun materials have been explored for use as MD membranes, <sup>3,8,12,62–64</sup> no published studies have maximized porosity (>93.3%)<sup>18</sup> of electrospun membranes in MD. Our research suggests it would be beneficial to minimize the bulk density of electrospun polymer membranes while optimizing fiber diameter/pore size to yield improved flux, thermal efficiency, and salt rejection performance in MD.

We have fabricated BNCA membranes with >98% porosity and shown them to be functional in MD. These experiments provide MD performance results for materials with porosity significantly higher than that of the benchmark PVDF membrane used in this study or those of other membranes tested in the literature. BNCA membranes exhibit substantial improvements in intrinsic permeability and thermal efficiency, suggesting that there is an opportunity to advance MD process viability through improved membrane design. Future membrane materials may benefit from mimicking the aerogel-like porosity and pore interconnectivity of BNCA but could further reduce mass transport resistance by increasing the pore size and optimizing the membrane thickness.

# ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00030.

Methods for fabricating BNCA membranes, characteristics and schematic of the benchtop DCMD system, a BNCA stability discussion, DCMD model equations and DGM explanation, detailed membrane characterization data, and experimental versus theoretical permeability of tested membranes (PDF)

Table 2. Comparison of Flux, Salt Rejection, and Temperature Polarization Coefficient (TPC) between Membrane Types<sup>4</sup>

	thickness $(\mu m)$	$T_{\rm f,b}$ (°C)	flux (kg $m^{-2} h^{-1}$ )	rejection (%)	TPC
PVDF	$109 \pm 5$	40	$5.79 \pm 0.27$	$99.53 \pm 0.08$	$0.500 \pm 0.004$
	$109 \pm 5$	60	$25.80 \pm 0.61$	$99.97 \pm 0.04$	$0.402 \pm 0.004$
BNCA	$218 \pm 30$	40	$8.42 \pm 0.21$	$99.87 \pm 0.05$	$0.711 \pm 0.012$
	$280 \pm 36$	60	$22.92 \pm 0.96$	$99.95 \pm 0.04$	$0.662 \pm 0.018$

"Error expressed as the standard error of the mean for multiple experiments. There is significant variation in the BNCA membrane thickness from sample to sample. Similarly sized samples were used for each temperature experiment, which minimized intra-experiment variability.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: mauter@cmu.edu. Phone: 412-268-5688.

#### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

 $B_{\rm w}$  = membrane permeability coefficient (kg m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>)  $H_{\rm w}$  = enthalpy of distillate being transported from feed to permeate streams (J/kg)

- h = boundary layer heat transfer coefficients (W/m<sup>2</sup>K)
- $J = \text{mass flux} (\text{kg m}^{-2} \text{ s}^{-1})$

 $k_{\rm m}$  = bulk membrane thermal conductivity (W/mK)

- $k_{\rm g}$  = pore gas thermal conductivity (W/m·K)
- $k_{\rm pol}$  = pure polymer thermal conductivity (W/m K)

 $\Delta p_{\rm w}$  = difference in saturation vapor pressure between feed and permeate sides of the membrane (Pa)

 $Q = heat flux (W/m^2)$ 

r = average pore radius (m)

T =temperature (K)

TPC = temperature polarization coefficient (dimensionless)  $x_s$  = mole fraction solute

subscripts a, w, vap, f, p, m, and b = air, water, vapor, feed, permeate, membrane, and bulk, respectively

- $\beta$  = specific heat duty (dimensionless)
- $\delta$  = membrane thickness (m)
- $\varepsilon$  = membrane porosity (dimensionless)
- $\eta$  = thermal efficiency (dimensionless)
- $\mu$  = dynamic fluid viscosity (kg m<sup>-1</sup> s<sup>-1</sup>)
- $\tau$  = tortuosity (dimensionless)

# REFERENCES

(1) Burant, A.; Lowry, G. V.; Karamalidis, A. K. *Environ. Sci. Technol.* 2013, 47, 37–54.

- (2) Khayet, M. Adv. Colloid Interface Sci. 2011, 164, 56-88.
- (3) Tijing, L. D.; Choi, J. S.; Lee, S.; Kim, S. H.; Shon, H. K. J. Membr. Sci. 2014, 453, 435–462.
- (4) Qtaishat, M.; Rana, D.; Khayet, M.; Matsuura, T. J. Membr. Sci. 2009, 327, 264–273.
- (5) Khayet, M.; Mengual, J. I.; Matsuura, T. J. Membr. Sci. 2005, 252, 101–113.
- (6) Qtaishat, M.; Khayet, M.; Matsuura, T. J. Membr. Sci. 2009, 341, 139-148.
- (7) Qtaishat, M.; Khayet, M.; Matsuura, T. J. Membr. Sci. 2009, 329, 193–200.
- (8) Wu, H. Y.; Wang, R.; Field, R. W. J. Membr. Sci. 2014, 470, 257–265.
- (9) Drioli, E.; Ali, a.; Simone, S.; Macedonio, F.; AL-Jlil, S. a.; Al Shabonah, F. S.; Al-Romaih, H. S.; Al-Harbi, O.; Figoli, a.; Criscuoli, a. *Sep. Purif. Technol.* **2013**, *115*, 27–38.

(10) Tijing, L. D.; Woo, Y. C.; Johir, M. A. H.; Choi, J.-S.; Shon, H. K. Chem. Eng. J. 2014, 256, 155–159.

- (11) Liao, Y.; Wang, R.; Tian, M.; Qiu, C.; Fane, A. G. J. Membr. Sci. **2013**, 425–426, 30–39.
- (12) Liao, Y.; Wang, R.; Fane, A. G. J. Membr. Sci. 2013, 440, 77–87.
  (13) Liao, Y.; Loh, C.-H.; Wang, R.; Fane, A. G. ACS Appl. Mater. Interfaces 2014, 6, 16035–16048.
- (14) Liao, Y.; Wang, R.; Fane, A. G. Environ. Sci. Technol. 2014, 48, 6335–6341.
- (15) Dumee, L.; Sears, K.; Schuetz, J.; Finn, N.; Duke, M.; Gray, S. Desalin. Water Treat. **2010**, *17*, 72–79.
- (16) Dumée, L.; Germain, V.; Sears, K.; Schütz, J.; Finn, N.; Duke, M.; Cerneaux, S.; Cornu, D.; Gray, S. *J. Membr. Sci.* **2011**, 376, 241–246.

(17) Li, Z.; Peng, Y.; Dong, Y.; Fan, H.; Chen, P.; Qiu, L.; Jiang, Q. *Appl. Surf. Sci.* **2014**, *317*, 338–349.

- (18) Essalhi, M.; Khayet, M. J. Membr. Sci. 2014, 454, 133-143.
- (19) Lu, X.; Arduini-Schuster, M. C.; Kuhn, J.; Nilsson, O.; Fricke, J.; Pekala, R. W. *Science* **1992**, *255*, 971–972.
- (20) Sun, H.; Xu, Z.; Gao, C. Adv. Mater. 2013, 25, 2554-2560.
- (21) Kugland, N. L.; Moody, J. D.; Kozioziemski, B. J.; Rubenchik, a. M.; Niemann, C. *Appl. Phys. Lett.* **2008**, *92*, 221913.
- (22) Gash, A. E.; Tillotson, T. M.; Satcher, J. H., Jr.; Hrubesh, L. W.; Simpson, R. L. J. Non-Cryst. Solids 2001, 285, 22-28.
- (23) Clapsaddle, B. J.; Sprehn, D. W.; Gash, A. E.; Satcher, J. H., Jr.; Simpson, R. L. J. Non-Cryst. Solids **2004**, 350, 173–181.
- (24) Teichner, S. J.; Nicolaon, G. a.; Vicarini, M. a.; Gardes, G. E. E. Adv. Colloid Interface Sci. **1976**, 5, 245–273.
- (25) Kistler, S. S. Nature 1931, 127, 741.
- (26) Pekala, R. W. J. Mater. Sci. 1989, 24, 3221-3227.
- (27) Nguyen, B. N.; Meador, M. A. B.; Medoro, A.; Arendt, V.; Randall, J.; Mccorkle, L.; Shonkwiler, B. ACS Appl. Mater. Interfaces 2010, 2, 1430–1443.
- (28) Randall, J. P.; Meador, M. A. B.; Jana, S. C. ACS Appl. Mater. Interfaces **2011**, *3*, 613–626.
- (29) Bryning, B. M. B.; Milkie, D. E.; Islam, M. F.; Hough, L. A.; Kikkawa, J. M.; Yodh, A. G. *Adv. Mater.* **2007**, *19*, 661–664.
- (30) Lin, Y.; Ehlert, G. J.; Bukowsky, C.; Sodano, H. A. ACS Appl. Mater. Interfaces 2011, 3, 2200–2203.
- (31) Kim, K. H.; Oh, Y.; Islam, M. F. Nat. Nanotechnol. 2012, 7, 562–566.
- (32) Soleimani Dorcheh, A. S.; Abbasi, M. J. Mater. Process. Technol. 2008, 199, 10–26.
- (33) Suh, D. J.; Park, T. Chem. Mater. 1996, 8, 509-513.
- (34) Lavoine, N.; Desloges, I.; Dufresne, A.; Bras, J. Carbohydr. Polym. 2012, 90, 735–764.
- (35) Zaborowska, M.; Bodin, A.; Bäckdahl, H.; Popp, J.; Goldstein, A.; Gatenholm, P. Acta Biomater. **2010**, *6*, 2540–2547.
- (36) Pääkkö, M.; Vapaavuori, J.; Silvennoinen, R.; Kosonen, H.; Ankerfors, M.; Lindström, T.; Berglund, L. a.; Ikkala, O. *Soft Matter* **2008**, *4*, 2492.
- (37) Klemm, D.; Kramer, F.; Moritz, S.; Lindström, T.; Ankerfors, M.; Gray, D.; Dorris, A. Angew. Chem., Int. Ed. 2011, 50, 5438-5466.
- (38) Wang, M.; Anoshkin, I. V.; Nasibulin, A. G.; Korhonen, J. T.; Seitsonen, J.; Pere, J.; Kauppinen, E. I.; Ras, R. H. a; Ikkala, O. *Adv.*
- Mater. 2013, 25, 2428–2432. (39) Haigler, C. H.; White, a R.; Brown, R. M.; Cooper, K. M. J. Cell
- Biol. 1982, 94, 64–69.
- (40) Zhang, K. Appl. Microbiol. Biotechnol. 2013, 97, 4353-4359.
- (41) Ross, P.; Mayer, R.; Benziman, M. Microbiol. Rev. **1991**, 55, 35–58.
- (42) Petersen, N.; Gatenholm, P. Appl. Microbiol. Biotechnol. 2011, 91, 1277-1286.
- (43) Iguchi, M.; Yamanaka, S.; Budhiono, A. J. Mater. Sci. 2000, 35, 261–270.
- (44) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. Chem. Soc. Rev. 2011, 40, 3941–3994.
- (45) Klemm, D.; Schumann, D.; Udhardt, U.; Marsch, S. Prog. Polym. Sci. 2001, 26, 1561–1603.
- (46) Jin, H.; Kettunen, M.; Laiho, A.; Pynnönen, H.; Paltakari, J.; Marmur, A.; Ikkala, O.; Ras, R. H. a. *Langmuir* **2011**, *27*, 1930–1934.

(48) Hotaling, N. A.; Bharti, K.; Kriel, H.; Simon, C. G. Biomaterials 2015, 61, 327-338.

(49) Korhonen, J. T.; Huhtamäki, T.; Ikkala, O.; Ras, R. H. a. Langmuir 2013, 29, 3858–3863.

(50) Kadoya, K.; Matsunaga, N.; Nagashima, A. J. Phys. Chem. Ref. Data 1985, 14, 947–970.

(51) Gingerich, D. B.; Mauter, M. S. Environ. Sci. Technol. 2015, 49, 8297-8306.

(52) Klemm, D.; Schumann, D.; Kramer, F.; Heßler, N.; Koth, D.; Sultanova, B. Nanocellulose materials–Different cellulose, different functionality. In *Macromolecular symposia*; WILEY-VCH Verlag, June 2009, 280 (1), 60–71 (DOI: 10.1002/masy.200950608).

(53) Liebner, F.; Haimer, E.; Wendland, M.; Neouze, M. A.; Schlufter, K.; Miethe, P.; Heinze, T.; Potthast, A.; Rosenau, T. *Macromol. Biosci.* **2010**, *10*, 349–352.

(54) Zeng, M.; Laromaine, A.; Roig, A. Cellulose 2014, 21, 4455–4469.

(55) Brandrup, J., Immergu, E. H., Abe, A., Bloch, D. R., Eds. *Polymer Handbook*, 89th ed.; Wiley: New York, 1999.

(56) Mason, E. A.; Malinauskas, A. P. Gas transport in porous media: the dusty-gas model; Elsevier: Amsterdam, 1983; Vol. 17.

(57) Lawson, K.; Lloyd, D. J. Membr. Sci. 1997, 124, 1-25.

(58) Khayet, M.; Matsuura, T. Membrane Distillation: Principles and Applications; Elsevier B.V.: Amsterdam, 2011.

(59) Field, R. W.; Wu, H. Y.; Wu, J. J. Ind. Eng. Chem. Res. 2013, 52, 8822-8828.

(60) Eichhorn, S. J.; Sampson, W. W. J. R. Soc., Interface 2005, 2, 309-318.

(61) Wang, C.; Cheng, Y. W.; Hsu, C. H.; Chien, H. S.; Tsou, S. Y. J. Polym. Res. 2011, 18, 111–123.

(62) Feng, L.; Zhang, Y.; Xi, J.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. *Langmuir* **2008**, *24*, 4114–4119.

(63) Essalhi, M.; Khayet, M. J. Membr. Sci. 2013, 433, 167-179.

(64) Li, X.; Wang, C.; Yang, Y.; Wang, X.; Zhu, M.; Hsiao, B. S. ACS Appl. Mater. Interfaces **2014**, *6*, 2423–2430.