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Membrane Based Pervaporation for Heating and Cooling

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Abstract

Recent advances have introduced ionic membranes that can provide high water permeability in heating, ventilation, and air conditioning (HVAC) applications. These materials can be useful in many applications to help provide more efficient building technologies and higher indoor air quality through devices such as ionic liquid heat pumps (ILHPs), ionic liquid desiccants (ILDs), and energy recovery ventilators (ERVs). Water transmission mechanisms behind the water transport is not well understood, since different ionic membranes provide transmission in different ways. Water transportation can be a function of ionomer structure via the building blocks of the backbone, or from the functional groups on the side chains or from subtle features in membrane design and composition. In this work, we studied the permeation properties of different advanced ionic membranes. Membranes that show high water selectivity, and permeabilities exceeding 2*10-5 g/(s*m^2*Pa) are presented. High performance membranes are identified for optimum applications for different HVAC systems.

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Keywords: Pervaporation; Membranes; Ionic Liquid Dessicants; Evaporative Cooling;

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1. Introduction

Building operation consumes more than 40 percent of the total energy used in the United States and building heating and cooling loads comprise the largest fraction [1]. Demand for cooling energy is exacerbated in hot and humid climates. High humidity poses a serious limitation to the design and operation of buildings, promoting mold and dust mites and often associated with increased disease transmission. Consequently, dehumidifying air in building ventilation systems is normally a requirement to mitigate the effects of high humidity, improve indoor thermal comfort, and meet indoor design conditions.

For over a century, the vapor-compression system (VCS) has been the de facto technology of choice in heating, ventilation, and air conditioning (HVAC), especially for dehumidification and cooling. Despite its success, research, policy, and economics all encourage change considering its many inherent shortcomings. From an energy standpoint, the inability of the VCS system to decouple latent and sensible loads leaves condensation, an energy intensive process, as the only means for dehumidification. The heart of the VCS system lies in the refrigerant, whose chemistry has evolved in response to policy and environmental concerns. From chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), banned under the Montreal Protocol in 1987, to hydrofluorocarbons (HFCs), such as R-134a with a global warming potential (GWP) 1430 times that of carbon dioxide (CO_2), environmental concerns associated with VCS can no longer be overlooked [2]. These concerns, coupled with potential excess greenhouse gas (GHG) emissions resulting from the inefficiencies inherent in the system, place research on future HVAC technologies at the cornerstone of any effort aimed at mitigating climate change.

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Researchers are pursuing alternatives to these conventional practices, especially for cooling and dehumidification. Advancements in artificial membranes enable new possibilities in this area. While traditionally used for industrial separations, such as reverse osmosis and gas separation, membranes provide a means to selectively transfer water vapor from one fluid to another [3], [4]. Polymeric, non-porous reinforced membranes are made from ionically functionalized polymer materials. These materials have ionically conductive groups embedded in the repeating unit of the polymer that aid in the transportation of water through the membrane. The methods for this mass transfer are being researched, and a few of the HVAC applications and transport methods are discussed in the following section.

2. Technology Description

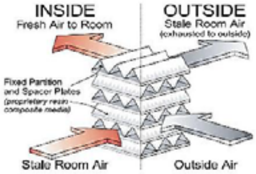


Fig. 1. Schematic of an ERV

In this paper, we explain the importance of pervaporation in heating, ventilation and air conditioning. The term ‘pervaporation’ is derived from a three-step process: (a) Sorption of permeating components at the feed side into a membrane, (b) Transport of components across a membrane by diffusion according to Fick’s law and (c) Evaporation or desorption at the permeate side into vapor phase. The driving force for transport of different components is provided by a chemical potential difference between the liquid feed/retentate and vapor permeate at each side of the membrane. The main advantage of a pervaporation technique versus conventional approaches in a heat and mass exchange application is its fundamental capacity to save energy and water. Pervaporation systems eliminate aerosols or air contamination by liquid water and therefore avoid any entrained contaminants evolved from dissolved solids in the feed water stream carried over to air streams. Pervaporation systems are modular, scalable, simple to operate and can be started up and shut down rapidly. The objective for these pervaporative systems and membranes are to reduce the total energy load for the systems. This is done by latent cooling i.e. reducing the relative humidity in the air to be treated. Energy recovery ventilators (ERV) and pervaporative cooling of water are also discussed.

Ionic liquids, as the name implies, are synthetic ionic salts that remain liquid under normal operating conditions. These fluids are mainly useful for their water desiccation properties, as they can adsorb or desorb water vapor to help control the relative humidity of the air in its container. With membranes, they are mainly utilized in flat sheet or shell and tube contactors that utilize fluid flows of air and desiccant in crossflow patterns. These systems can dehumidify gas streams with relatively high efficiency. Additionally, these contactors can be paired with a heat pump system to regenerate the desiccant so that the system can be operated in a loop. The synthetic ionic liquids can be engineered such that the waste heat from the heat pumps can be utilized to regenerate them.

ERVs will use an assembly of corrugated sheet membranes to allow heat and mass transfer between the outgoing exhaust air stream and incoming makeup air. A schematic of an ERV is shown in Fig. 1. In this figure “outside” makeup air is contacted with “inside” exhaust air and heat and moisture are exchanged. This passively conditions the air before entering the air-conditioner and reduces energy load of the HVAC system.

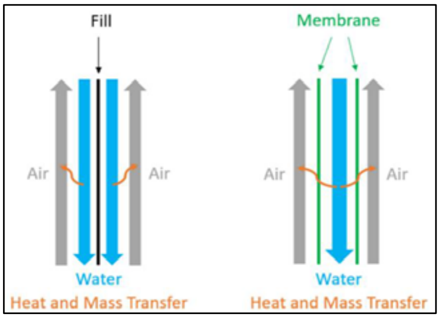
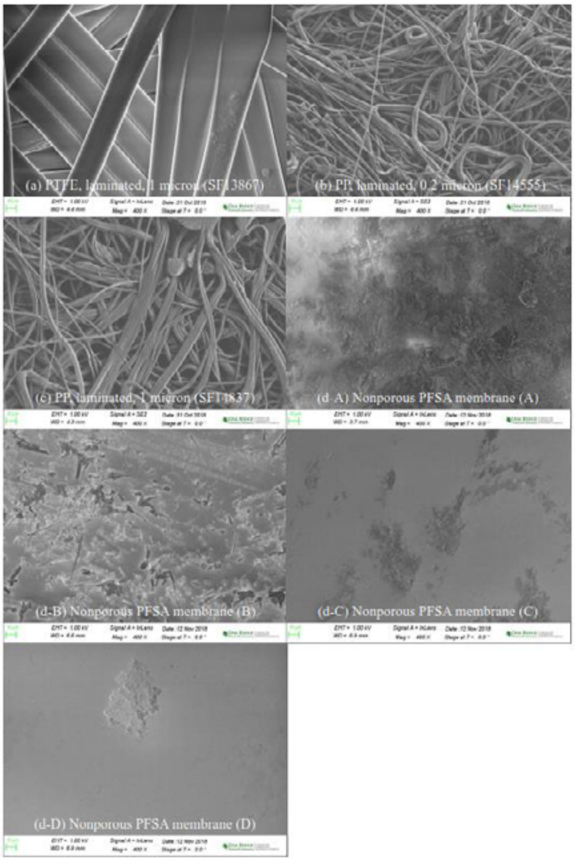


Fig. 2. Schematic of a cooling tower fill and our proposed membrane based evaporative condenser

Pervaporation can also be used as a substitute to evaporative cooling. Unlike conventional cooling tower fills (shown in the left side of Fig. 2), in which the cooling water and the ambient air are in direct contact, in the proposed concept, (shown in right side of Fig. 2) the membrane acts as a selective barrier between the two phases: the liquid-phase feed and the vapor-phase permeate. It allows the desired component(s) of the liquid feed to permeate (transfer) through it by vaporization. The driving force for the separation is the difference in the partial pressures of the components on the two sides and not the volatility difference of the components in the feed.

3. Experiment & Results



(a) PTFE, laminated, 1 micron (SF13867)

(b) PP, laminated, 0.2 micron (SF14555)

(c) PP, laminated, 1 micron (SF14837)

(d-A) Nonporous PFSA membrane (A)

(d-B) Nonporous PFSA membrane (B)

(d-C) Nonporous PFSA membrane (C)

(d-D) Nonporous PFSA membrane (D)

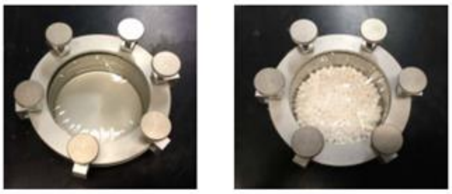
Fig. 3. Microstructures of membranes tested

In this section we discuss moisture vapor transmission results of four PFSA (perfluoronated sulfonic acid) nonporous membranes with different acidity and three commonly used porous membranes. The four PFSA nonporous membranes are the acid form of the perfluorinated sulfonic ionomer membrane (PFSA), which is an ion-conductive polymer, with an electrically neutral semi-crystalline polymer backbone (hydrophobic polytetrafluroethylene) and a randomly tethered sidechain with a pendant ionic group (hydrophilic), SO_3^-, that is associated with a specific counterion (e.g., $SO_3^- + H^+ \rightarrow SO_3H$). Two of porous membranes are unlaminated polypropylene membranes with the pore size of 0.2 µm (model number: SF14555) and 1.0 µm (model number: SF14837), respectively. They have a thickness of 150~250 µm and a porosity of 60% approximately. Another is a laminated PTFE membrane with the polypropylene (PP) support (model number: SF13867). It has a pore size of 1.0 µm, a thickness of 150~220 µm, and a porosity of 80~90% approximately [5], [6]. The test index, type, and properties of the investigated membranes are listed in Table 1. Moreover, the microstructures of the tested membranes are photographed using the transmission electron microcopy technology, as shown in Figure 5.

Table 1. Properties of the tested membranes.

Model Number	A	B	C	D	SF13867	SF14555	SF14837
Membrane Test Index	1	2	3	4	5	6	7
Dense/Porous	Non-Porous	Non-Porous	Non-Porous	Non-Porous	Porous	Porous	Porous
Wettability	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophobic	Hydrophobic	Hydrophobic
Pore size (μm)	N/A	N/A	N/A	N/A	1.0	0.2	1.0
Porosity (%)	N/A	N/A	N/A	N/A	80-90%	60%	60%
Thickness (μm)	~25	~25	~25	~25	150-220	150-250	150-250

The water vapor transmission rate (WVTR) of the membranes were measured with the wet cup and dry cup method described by ASTM E96 (ASTM 1995), as well as some modified methods such as upright wet cup fulfilled with water, reversed wet cup, and upright wet cup filled with liquid desiccant. The basic procedure of the test is sealing a tested membrane to the open mouth of a permeability cup which contains a certain amount of water or desiccant inside. During the test, the permeability cup is placed on the top of a scale in an air-conditioned chamber with controlled air temperature and humidity. Periodic weighing is documented by the data acquisition system to determine the rate of water vapor movement through the membrane from the cup inside to the controlled chamber or vice versa.



(a) Wet cup (with airgap) (b) Dry cup (with airgap)

(c) Wet cup (without airgap) (d) Reversed wet cup (without airgap)

Figure 4: Cup configurations: (a) wet cup with air gap, (b) dry cup using solid desiccant, (c) wet cup without air gap, and (d) reversed wet cup

The first method we used is wet cup method. The wet cup is shown in Figure 4(a), with distilled water inside, and an air gap existing between the membrane and distilled water. The second method is the dry cup method containing a certain amount of anhydrous calcium chloride ($CaCl_2$) as shown in Figure 4(b). The membrane and the solid desiccant do not contact with each other. The wet cup method is typically used to simulate regions of high humidity and the dry cup is more reflective of drier climates. The third method is the wet cup without air gap method. This method is very similar to the conventional wet cup method. The only difference is that the distilled water is filled in the permeability cup and the membrane is bonded and contacted with the water tightly without any air gap, as shown in Figure 4(c). The fourth one is the reversed wet-cup method. This method is also very similar to the wet cup method. The only difference is that the permeability cup is reversely placed in the chamber so that the distilled water inside the cup contacts with the membrane directly as shown in Figure 4(d). By inverting the cup, there is a greater pressure driving force across the membrane making the test more reflective of conditions with a signifigant pressure driving force.The last two methods we used are the liquid desiccant methods (not pictured), which use an aqueous solution of calcium chloride ($CaCl_2$) with a mass concentration of 40% with air gap (e) or without any air gap (f). The test conditions are listed in Table 2.

Table 2. Summary of test conditions

Cup method	B	A	C	D	E	F
Membrane Test Index	1-7	1-7	2,3,4	1-7	1-7	1-7
Air gap	Yes	Yes	No	No	Yes	No
$T_{chamber}$ (°C)	24.5	24.5	24.5	24.5	24.5	24.5
$RH_{chamber}$ (%)	80.8%	80.8%	80.8%	80.8%	80.8%	80.8%
$Pv_{chamber}$ (Pa)	2495	2495	2495	2495	2495	2495
Materials inside cup	$CaCl_2$	Distilled water	Distilled water	Distilled Water	$CaCl_2$ Solution	$CaCl_2$ Solution
Pv_{cup} (Pa)	0	3076	3076	3076	1260.5	1260.5
Pv_{diff} (Pa)	2495	581	581	581	1234.5	1234.5

With the above experimental apparatus, the water vapor permeance of the seven membranes were tested at several different conditions, including wet cup with air gap, wet cup without air gap, reversed wet cup and dry cup (using solid desiccant) with air gap. These experiments were used to generate weight change data, with respect to time. Figures 5 and 6 provide examples of the results of these experiments.

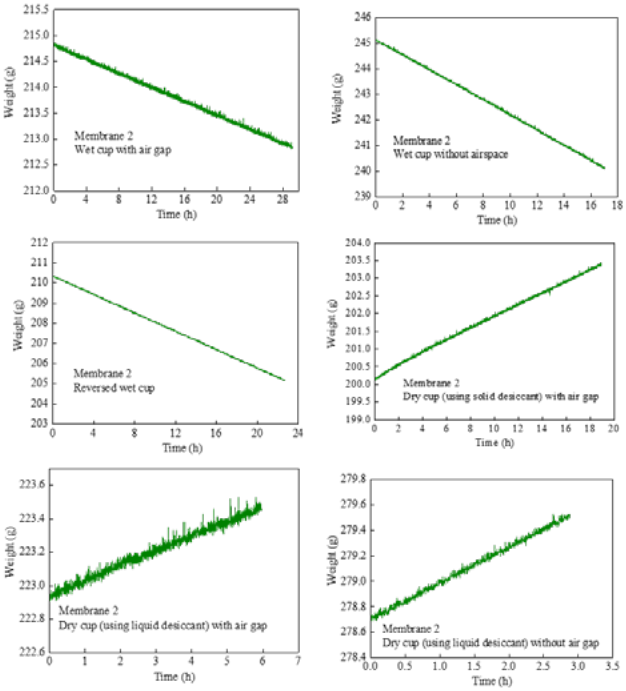


Fig. 5. Example weight change with time for a non-porous membrane (membrane 2)

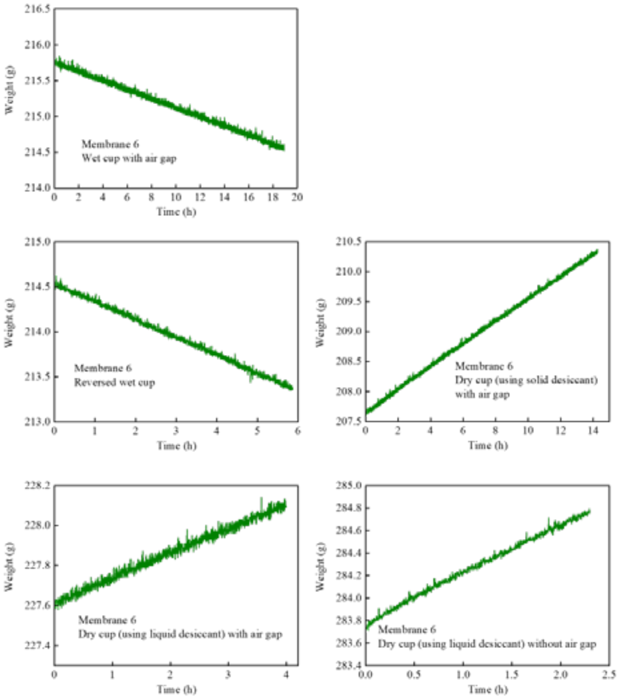


Fig. 6. Example weight change with time for a porous membrane (membrane 6)

The water vapor transmission rates of the membranes were derived for each membrane using figures similar to Figure 5 and 6. These rates were normalized to the surface area of the membrane and the pressure difference across the membrane (the driving force of permeation) to calculate the water vapor permeance, as reported in Table 3.

Table 3. Measured water vapor permeance of seven membranes (10^{-5} g/m^2-s-Pa)

Cup Test Method	Non-Porous Membrane				Porous Membrane		
	1	2	3	4	5	6	7
A	0.8474	1.080	1.118	1.118	0.9810	1.010	0.9684
C	N/A	4.689	4.465	4.396	N/A	N/A	N/A
D	3.150	3.638	3.482	3.654	3.155	3.168	3.133
B	0.5796	0.6138	0.7546	0.6589	0.8110	0.6993	0.7773
E	0.7899	0.6594	0.8163	0.8372	0.9047	0.9267	0.8412
F	2.696	2.090	2.944	2.767	2.824	3.259	3.267

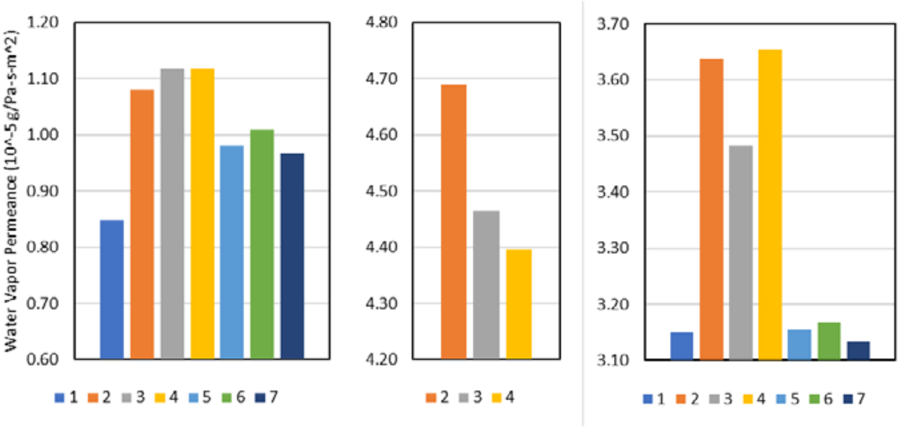


Fig. 7. Water vapor permeance of different membranes measured with (left to right) wet cup with air gap, wet cup without air gap, and reversed wet cup methods

The wet cup testing methods are the most reflective of the conditions seen in ERVs, evaporative cooling towers, and ILD modules. As seen in Fig. 7, Membrane 2 had on average the best performance during the wet cup tests. Membrane 4 was a close second, however, taking economic considerations into account, (Membrane 2 is commercially produced while Membrane 4 is currently only produced for R&D purposes), Membrane 2 was selected as the transport element in the experimental heating and cooling devices. While Cup Test Methods E and F could have provided insight into the interaction between the membranes and a liquid desiccant, the tests did not produce conclusive results. The results of Cup Test Method B, which is more commonly used with low permeation materials [7], was not analyzed further in this study.

4. Pervaporative HVAC Devices using Membrane 2

4.1. Ionic Liquid Desiccant based dehumidifier

A new membrane-based liquid desiccant air dehumidification (MLDAD) technology utilizes the membrane technology and ionic liquid desiccants (ILDs) to prevent carryover and corrosion in LDAD [8]. The semi-permeable membrane separates the air and liquid desiccant but allows a good mass transfer between them. Therefore, solution droplets cannot enter the air stream to corrode the metal ductwork and degrade the air quality. The ILDs are synthesized salts in the liquid phase. They are non-corrosive to metal and non-crystallizable so that the solution side corrosion issues can be avoided and the reliability of the MLDAD system can be improved. The performance of the dehumidifier at different conditions are as shown in Figures 8 through 10.

The high humidity upstream air was dehumidified by the MLDAD to the decreased humidity downstream. The analysis of these figures was only performed at steady-state, roughly 5 minutes after the test began and after the inlet (upstream) humidity stabilized. Startup conditions varied, depending on the air flow rate. The primary variable effecting the dehumidification power of the system was found to be the ambient (upstream) relative humidity. When comparing Figures 9 and 10, the high inlet humidity (94.0% RH, Figure 9) increased the absolute humidity drop across the module to over twice the absolute humidity drop under the inlet conditions of Figure 10. At low upstream absolute humidities and low airflow, as in Figure 8, the MLDAD module does not provide significant latent cooling – the average absolute humidity drop across the membrane is about 1 g/m^3.

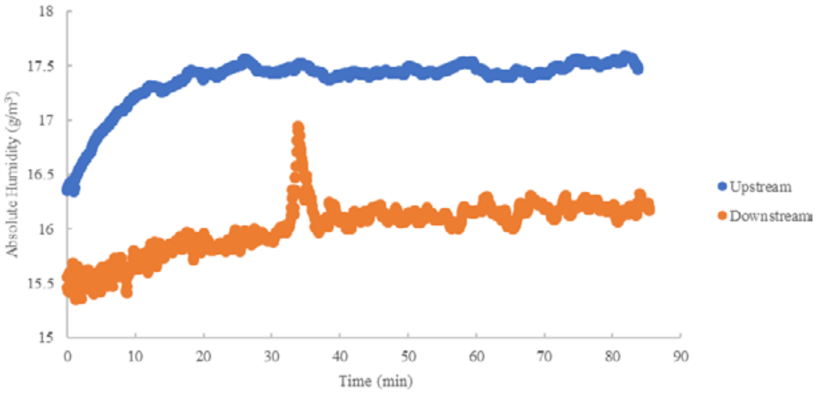


Fig. 8. Dehumidification of air at 0.28 m^3/min (10 CFM), average inlet (upstream) RH of 53.0% and an average outlet (downstream) of 50.0% RH (30.5°C). Note that the spike in AH between 30 and 40 min was caused by a leak in the system. This leak was resolved during the test and these data points were disregarded in the analysis.

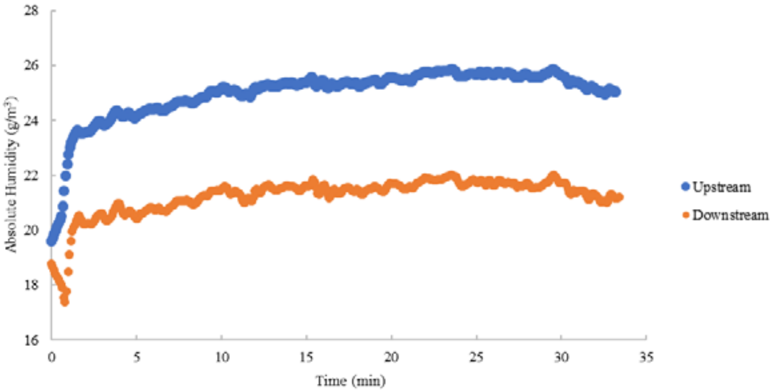


Fig. 9. Dehumidification of air at 0.85 m^3/min (30 CFM), average inlet (upstream) RH of 94.0% and an average outlet (downstream) RH of 78.5% (26.8°C)

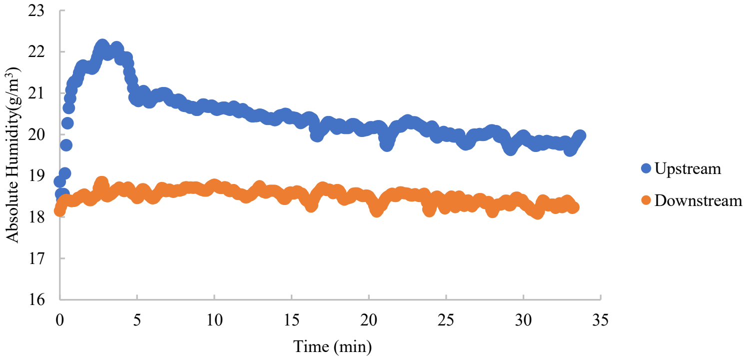


Fig. 10. Dehumidification of air at 0.85 m^3/min (30 CFM), average inlet (upstream) RH of 70.3% and an average outlet (downstream) RH of 63.3% (28.8°C)

4.2. Membrane based cooling towers

Pervaporative membrane tubes or flat sheets can also be used in manufacturing advanced evaporative cooling devices. These devices can be used to provide cooling to water downstream of the condenser side of chiller. They can also be used to cool large datacenters and other electronics cooling applications. In Figure 11, we show an evaporative cooling prototype made of pervaporative membranes. It is 40.6 cm (16”) in height, 30.5 cm (12”) in width and 15.2 cm (6”) in depth. The small scale evaporative cooling device made of pervaporative membranes was tested using inlet water at 35°C (95°F) and water flow rate between 9.5 and 37.9 LPM (2.5 and 10 GPM). Figure 12 compares the heat transfer capacity of pervaporative cooling device at different flow rates of water. The test data shows a significant enhancement of pervaporation cooling performance due to an increase in water flow rate; the heat rejection is nearly directly proportional to the flow rate. This shows that advanced pervaporative cooling towers are feasible and scalable, especially when coupled with energy efficient water pumps.

Figure 11. Membrane Evaporative Cooling Module

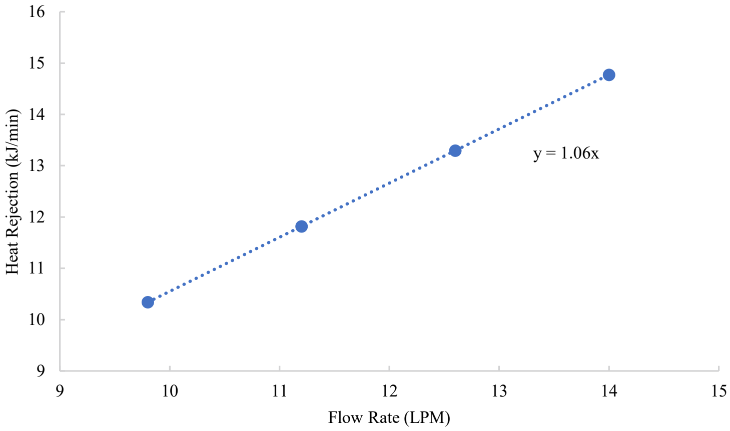


Figure 12. Heat rejection characteristics of membrane evaporative cooling module & linear fit where “y” is the heat rejection in kJ per min and “x” is the flow rate in liters of water per minute

5. Conclusions

Pervaporative membranes show strong potential for energy efficient heating and cooling. As presented in this paper, proof-of-concept laboratory protoypes have been developed for membrane based liquid desiccant air dehumidification and pervaporative membrane heating and cooling towers. The MLDAD system was able to provide dehumidification while preventing the potential for corrosion, seen in previous systems. Membrane based cooling towers were found to be a scalable source of evaporative cooling. However, as HVAC membrane technology is considerably young, when compared to traditional vapor compression air conditioning, there is still significant research and development to be made in the field. In order to be competive with conventional technology, the next steps to commercialization is cost and longevity research. However, the technologies described in this paper are at different stages and have their own research needs.

Specifically, measured performance is needed on commercial products for a range of inlet temperatures and humidities. In-the-field monitoring can also show how performance varies with inlet condition, and also how it deteriorates with time. Membrane liquid desiccant dehumidifiers require manufacturing methods that ensure leak-free modules, which can be checked with accelerated life testing of the conditioner and regenerator. Membrane prototypes for evaporative cooling and humidification have shown the feasibility of this process. It is also unclear whether membranes, with their added cost, will be preferred to wicked surfaces. Across all systems membrane fouling may present a problem. However, using lessons learned from the fouling issues in industrial membrane processes, the magnitude of this problem can be mitigated. The HVAC applications are also expected to see fewer contaminants than traditional industrial membrane processes, further decreasing the significance of this issue.

The outlook for these membrane devices is uncertain. Advances in membrane technology over the previous few decades have enabled these unique devices for HVAC applications, which could potentially lead to more energy efficient products. But more research and development are needed if these products are to compete against the inexpensive and established air conditioning technologies.

6. Nomenclature

Table 4. Acronyms and abbreviations, defined.

Term	Definition
AH	Absolute humidity (g/m^3)
CFC	Chlorofluorocarbons
CFM	Cubic feet per minute
ERV	Energy recovery ventilation
GHG	Greenhouse gas
GPM	Gallons per minute
GWP	Global warming potential
HCFC	Hydrochloroflurocarbon
HFC	Hydroflurocarbon
HVAC	Heating, ventilation, and Air Conditioning
ILD	Ionic liquid desiccant
ILHP	Ionic liquid heat pump
LDAD	Liquid desiccant air dehumidifier
LPM	Liters per minute
PFSA	Perfluorosulfonic acid
PP	Polypropylene
PTFE	Polytetrafluoroethylene
RH	Relative humidity
VCS	Vapor compression system
WVTR	Water vapor transmission rate

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References

[1] Abdel-Salam, M.R.H., Ge, G., Fauchoux, M., Besant, R., Simonson, C. (2014), State-of-the-art in liquid-to-air membrane energe exchangers (LAMEEs): A comprehensive review. *Renewable and sustainable Energy Reviews*, 39: 700-728. doi:10.1016/j.rser.2014.07.022

[2] “The Montreal Protocol on Substances that Depleate the Ozone Layer.” *United Nations Environment Programme* (1987).

[3] Lonsdale, H.K. The growth of membrane and technology, J. Membr. Sci. 10 (1982) 81

[4] Binning, R.C., Lee, R.J., Jenning, J.F., Martin, E.C. Separation of liquid mixtures by permeation, Ind. Eng. Chem. 53 (45) (1961) 6–50.

[5] Adachi, M., Navessin, T., Xie, Z., Frisken, B., Holdcroft, S. “Correlation of in situ and ex situ measurments of water permeation through Nafion NRE211 proton exchange membranes. *J. Electrochem. Soc.* (2009). 156 (6): 782-790.

[6] Kusoglu, A., Weber, A.Z. “New Insights into Perfluroninated Sulfonic Acid Ionomers” *Chem. Rev.* 2017, 117, 3, 987-1104. doi: https://doi.org/10.1021/acs.chemrev.6b00159

[7] ASTM D1653-13, Standard Test Methods for Water Vapor Transmission of Organic Coating Films, ASTM International, West Conshohocken, PA, 2013, www.astm.org. doi: 10.1520/D1653-13

[8] Abdelaziz, O.A., Qu, M., Sun, X., Bahar, B., Parmelee, W., Fackler, S., Sherrer, R., Zerby, J., Chouhan, A. “Developent of Separate Sensible and Latent Cooling System Using Electrochemical Compressor,” *12th IEA Heat Pump Conference* (2017).

[9] US Patents: 10,202,292 and Applications: 20190291054, 20190256384, 20190226703, 20180251616, 20180187906, 20180093905, 20170284685